

EPR SPECTROSCOPY INTERFACED WITH DFT CALCULATIONS – A POWERFUL APPROACH TO STUDY PARAMAGNETIC SPECIES IN HETEROGENEOUS ENVIRONMENTS

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Molecular modeling and computational spectroscopy is a combination of robust simulation of complex electron paramagnetic resonance (EPR) spectra with density functional theory (DFT) calculations of the magnetic parameters. This approach was used for guiding interpretation of the experimental EPR data of large systems containing transition-metal ions, characterized by irregular geometry, profound speciation and low symmetry features. As a result a quantitative connection between the molecular structure of the investigated paramagnets and their spectroscopic fingerprints, unavailable through classic semiempirical analysis, was obtained. Various levels of treatment of the relativistic effects and selection of proper exchange-correlation functionals were also discussed and illustrated with selected examples coming from our laboratory.

INTRODUCTION

Chemical properties and reactivity of nanoporous oxides or zeolites are intrinsically connected with their reduced size and dimensionality, pronounced surface area or presence of structural and morphological defects. The resultant inherent heterogeneity of the exposed surface sites gives rise to low symmetry phenomena and obvious speciation of the paramagnetic surface species, leading to complicated multi-component powder electron paramagnetic resonance (EPR) spectra (Sojka, 1995). These factors severely restrain recognition of the individual spectral features, which is especially pertinent for electron paramagnetic resonance, since the data coded in the spectra are often unevenly distributed over broad spectral range. As a consequence, a great deal of significant chemical information about the investigated system can only be recovered with the help of advanced computer analysis of the EPR spectra, supported by quantum chemical calculations of their parameters (Pietrzyk, Piskorz, Sojka & Broclawik, 2003; Pietrzyk, Sojka, Dzwigaj & Che, 2007a).

Principal types of surfaces and interfaces that are of our scientific interest are based on porous silica-alumina and calcia-alumina materials such as zeolites, pillared clays, mayenite, and nanostructured oxides. They may be readily rendered chemically and magnetically active by introduction of transition-metal guest ions to produce paramagnetic surface and cage complexes (Klier, 1988). A number of important catalytic processes occur with involvement of such centers. Electron transfer from

ligand to metal or from metal to ligand, spin pairing and spin crossing events, accompanying coordination and transformation of the reactants, may drastically alter magnetic states and reactivity of active sites constituted by the transition-metal ions (Pietrzyk & Sojka, 2007b).

Molecular modeling within density functional theory (DFT) and computational spectroscopy of heterogeneous systems is a rapidly developing field. Widely available and easy-to-use quantum chemical packages (DMol³, Gaussian, ADF, WIEN95, ORCA, deMon) have made such calculations accessible to researchers without profound theoretical background. However, in spite of the recent progress, quantum mechanical calculations can only be carried out for hundreds of atoms, and judicious approximations are often required to achieve sensible results. Therefore the calculated spectral parameters must be carefully compared with experimental values. Such approach leads to fruitful feedback, where experiments are used for validation computational data, and calculations are used for explaining experimental results.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

DFT modeling for constrained geometry optimization of the investigated systems was carried out with DMol³ (Delley, 1990) and Gaussian03 (Frisch, 2004) software. Spectroscopic calculations were carried out with ORCA program (Neese, 2007) based on the concept of spin-

orbit mean-field (SOMF) (Neese, 2001) as well as ADF program (de Velde, Bickelhaupt, van Gisbergen, Fonseca Guerra, Baerends, Snijders & Ziegler, 2001). All CW-EPR spectra were recorded at liquid nitrogen and room temperatures on a Bruker ELEXSYS-500 spectrometer working at X-band with 100 kHz modulation. For computer simulation of the powder spectra the EPRsim32 program developed in our laboratory was used (Spalek, Pietrzyk & Sojka, 2005).

THEORETICAL BACKGROUND

There are two reasons why DFT is superior for calculations of large systems over post Hartree-Fock methods. It includes exchange-correlation effects explicitly and scales favorably with the size of the system, which is important while dealing with large transition-metal ion containing systems. However, because of absence of the universal functional, approximate exchange-correlation potentials should be carefully selected. The hierarchy of the functionals includes simplest local density approximation (LDA), where the exchange-correlation effects are taken as being proportional to the local electron density, gradient-corrected functionals (GGA), and hybrid functionals containing admixture of the Hartree-Fock exact exchange. The selection of an appropriate functional is a delicate problem as we need to account adequately for the spin polarization effects, but exaggerated exchange may lead to artifacts of spin contamination. Another crucial issue is connected with the choice of the basis set. For satisfactory reproduction of hyperfine coupling constants (HFCC) one needs to calculate precisely spatial distribution of the spin density, which usually requires application of large basis sets, augmented by polarization functions. Within the standard spin density formulation (vide infra), the isotropic HFCC depend on the local quality of the wavefunction at the given nucleus, suggesting that Slater-type orbitals (STO) should be preferred as they better fulfill the correct cusp condition. However, the majority of studies employ Gaussian-type orbitals, which are easier for computation, as the cusp problem can also be satisfactorily addressed in this case.

In the spin-Hamiltonian formalism the \mathbf{g} tensor parameterizes the interaction between the effective spin \mathbf{S} of a paramagnet and the external magnetic field \mathbf{B} . The resultant electronic Zeeman term H^Z may be written as (in atomic units)

$$H^Z = (1/2c)\mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}. \quad (1)$$

Conventionally, the \mathbf{g} tensor can be factorized into scalar free electron (g_e) and a 3×3 matrix part $\Delta\mathbf{g}$, containing spin-orbit coupling and other relevant contributions:

$$\mathbf{g} = g_e \mathbf{1}_3 + \Delta\mathbf{g}, \quad (2)$$

where $g_e = 2.00232$ is the free electron value, and $\mathbf{1}_3$ is the unit matrix. Such form conveys the fact that $\Delta\mathbf{g}$ reflects spatially dependent shifts induced by various magnetic perturbations in bound atomic and molecular environments relative to the free electron reference.

There are several types of \mathbf{g} tensor calculation schemes that are implemented in the available quantum chemical software. Within the zeroth-order regular approximation (ZORA) to the Dirac equation, by using an auxiliary function $K = [1 - V/2c^2]^{-1}$ the Zeeman Hamiltonian H^Z can be written as: $H^Z = g_e/2c[K/2 \boldsymbol{\sigma} \cdot \mathbf{B} + K/4 \mathbf{B} \cdot \mathbf{L} + \mathbf{B} \cdot \mathbf{L} K/4 + \boldsymbol{\sigma} \cdot (\nabla K/2 \times \mathbf{A})]$, with $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, $\boldsymbol{\sigma}$ stands for the Pauli spin matrices, and c for the velocity of light. The first term represents the electron spin Zeeman term, the next two terms form the orbital Zeeman interaction, and the last term is the spin-orbit gauge correction. In the two-component ZORA approach, where the Kramers doublet (Φ_1 and Φ_2) completely determines magnetic properties of a system, the \mathbf{g} tensor can be obtained as a first order property from the following matrix elements (van Lenthe, Baerends & Snijders, 1993):

$$g_{xx} = 4c \operatorname{Re} \Phi_{12}^k = 4c \operatorname{Re} \Phi_{21}^k, \quad (3)$$

$$g_{yy} = -4c \operatorname{Im} \Phi_{12}^k = 4c \operatorname{Im} \Phi_{21}^k, \quad (4)$$

$$g_{zz} = 4c \operatorname{Re} \Phi_{11}^k = 4c \operatorname{Re} \Phi_{22}^k, \quad (5)$$

$$\Phi_{ij}^k = \langle \Phi_i | \partial H^Z / \partial B_k | \Phi_j \rangle. \quad (6)$$

The alternative one-component method for the \mathbf{g} tensor calculations used herein is due to Schreckenbach and Ziegler (Schreckenbach & Ziegler, 1997). In this formulation of the \mathbf{g} tensor, scalar relativistic effects are included in the quasi-relativistic framework within the first-order Pauli Hamiltonian: $H^{\text{Pauli}} = V + p^2/2 - p^4/(8c^2) + \nabla^2 V/(8c^2) + 1/2 \boldsymbol{\sigma} \cdot \mathbf{B} + 1/(4c^2) \boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p})$. The resultant \mathbf{g} tensor can be then expressed in terms of several contributions:

$$\Delta\mathbf{g}_{st} = \Delta\mathbf{g}_{st}^{\text{rel}} + \Delta\mathbf{g}_{st}^{\text{d}} + \Delta\mathbf{g}_{st}^{\text{p}}, \quad (7)$$

where $\Delta\mathbf{g}_{st}^{\text{rel}}$ combines scalar relativistic corrections to $\Delta\mathbf{g}$, while the terms $\Delta\mathbf{g}_{st}^{\text{d}}$ and $\Delta\mathbf{g}_{st}^{\text{p}}$ stand for dia- and paramagnetic contributions, respectively (Schreckenbach *et al.*, 1997).

High-accuracy results can be obtained using recently implemented SOMF scheme (Neese, 2001). Within this approximation, the \mathbf{g} tensor can be calculated as a second derivative of the energy (Neese, 2005). At the SCF level the $\Delta\mathbf{g}_{ij}$ shifts are described by mass-velocity, diamagnetic gauge-correction,

$$\Delta\mathbf{g}_{ij}^{\text{mv}} = -\frac{\alpha^2}{S} \sum_{kl} P_{kl}^{\sigma-\rho} \langle \phi_k | \hat{T} | \phi_l \rangle,$$

$\Delta g_{ij}^d = \frac{1}{2S} \sum_{kl} P_{kl}^{\alpha-\beta} \langle \varphi_k | \sum_A \xi(\vec{r}_A) [\vec{r}_A \vec{r}_O - \vec{r}_{A,r} \vec{r}_{O,s}] | \varphi_l \rangle$, and paramagnetic

spin-orbit coupling term $\Delta g_{ij}^p = \sum_{k,l} \frac{\partial P_{kl}^{\alpha-\beta}}{\partial B_i} \langle \varphi_k | \hat{h}_j^{SO} | \varphi_l \rangle$,

where S stands for total electron spin, α is the fine structure constant, $P^{\alpha-\beta}$ represents spin density matrix, $\xi(r_A)$ is an approximate radial operator, h^{SO} stands for the spatial part of the effective one-electron spin-orbit operator, with $\hat{H}_{SOC} \cong \sum_i \hat{h}_i^{SO} \hat{s}_i$. The derivative of the

spin density matrix is calculated from the coupled-perturbed Kohn-Sham theory with respect to the magnetic field perturbation (B_i). In this treatment of the g tensor, in addition to one-electron term, a two-electron term is included explicitly. The latter one comprises a Coulomb part treated at the resolution of the identity approximation, an exchange part involving both spin-own and spin-other-orbit interactions, and a correlation term that in practice contributes negligibly to SOC.

The hyperfine coupling tensor A^n is usually factorized into isotropic (a_{iso}^n) and anisotropic (T^n) components:

$$A^n = a_{iso}^n \mathbf{1}_3 + T^n. \quad (8)$$

The isotropic constant (Fermi contact term) is directly proportional to the spin density $\rho^{\alpha-\beta}(r_n)$ at the corresponding nucleus n and is given by:

$$a_{iso}^n = \frac{4\pi}{3} \beta_e \beta_n g_e g_n \langle S_z \rangle^{-1} \sum_{\mu,\nu} P_{\mu\nu}^{\alpha-\beta} \langle \varphi_\mu(r_{kn}) | \delta(r_{kn}) | \varphi_\nu(r_{kn}) \rangle \quad (9)$$

Two principal mechanisms, which contribute to the a_{iso} value in opposite ways, include direct delocalization of the spin density onto s -type orbitals and spin polarization. When a significant involvement of the metal s -orbital character in a SOMO is expected, which leads to dominance of the direct contribution to the spin density, than reasonable agreement between the theoretical and experimental values of a_{iso} is usually found (Munzarova, Kaupp, 1999). However, the situation becomes more complicated when the spin polarization is dominant. In such cases, the use of large basis sets, often fully uncontracted or loosely contracted, which accurately describe the spin density at the given nucleus, is essential for the correct prediction of the HFCC values. The anisotropic part, T^n , of the hyperfine tensor reflects the asymmetry of the spin density about each nucleus of interest. The coupling between the unpaired electron and nuclear spins is of a dipole-dipole nature. To the first order, it can be calculated from the following equation (Malkin, Malkina, Eriksson & Salahub, 1995):

$$T_{ij}^n = \frac{1}{2} \beta_e \beta_n g_e g_n \langle S_z \rangle^{-1} \sum_{\mu,\nu} P_{\mu\nu}^{\alpha-\beta} \langle \varphi_\mu(r_{kn}) | r_{kn}^5 (r_{kn}^2 \delta_{ij} - 3r_{kn,i} r_{kn,j}) | \varphi_\nu(r_{kn}) \rangle \quad (10)$$

It has been reported that calculations of the anisotropic hyperfine constants are rather insensitive to the applied method because this interaction depends on the whole spatial distribution of the spin density, as opposed to the spin density at the nucleus that gauges the isotropic component. Yet such statements should be taken with some caution.

RESULTS AND DISCUSSION

In a *computational EPR spectroscopy* we combine a hybrid genetic algorithm for robust and efficient simulation of complex experimental EPR spectra with DFT calculations of the magnetic parameters. Available experimental EPR parameters may be therefore directly compared with the corresponding calculated values, providing a quantitative connection between the molecular structure of investigated paramagnets and their spectroscopic signatures. This approach was used for guiding interpretation of the EPR data of large non-molecular systems containing transition-metals. Owing to recent progress in the relativistic DFT methods nearly quantitative reproduction of g , A , and D tensors is now possible at reasonable computing costs. Once the spin-Hamiltonian tensors are successfully reproduced, the DFT calculations open the access to vast additional information unavailable from powder experiments, such as molecular interpretation of their nature or about orientation of the principal magnetic axes. This approach was used for monitoring changes in the electron and spin states taking place during the interaction of small molecules with surface complexes of transition metals. Selected examples will demonstrate potential of the computational EPR approach in enhancing interpretation of complex EPR data of heterogeneous systems in low symmetry environments. Computational EPR spectroscopy was also used by us for investigation of changes in the electron and spin states, taking place during the interaction of small molecules, like NO, CO or O₂, with surface complexes of transition metals of various electron configuration (Cu, Co, Ni, Fe, Mo) encaged in zeolites (Pietrzyk *et al.*, 2007a, 2007b).

Monocarbonyl {Ni^I(CO)}⁹ complexes – g tensor calculation and molecular interpretation

To evaluate the impact of electron correlation and exchange interactions on theoretical prediction of g tensor we carried out calculations with unrestricted (UN) ZORA, scalar Pauli, and SOMF Hamiltonians using the experimental EPR parameters of nickel(I) complexes of

known structure and as the computation targets.

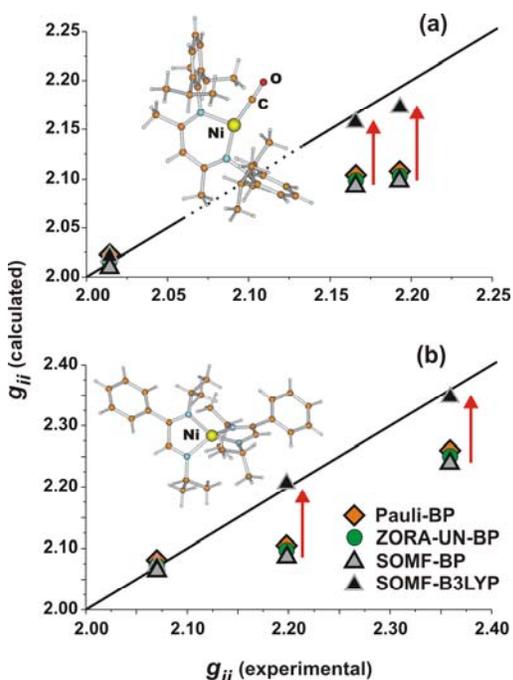


Fig. 1. Influence of exchange-correlation functional and the level of relativity treatment on the calculated g tensor for (a) $L^{Mc}NiCO$ and (b) $[Ni(L^1)_2]^+$ bioinorganic complexes.

For this purpose two exemplary complexes were selected: (1) three-coordinate diketimine-nickel(I) complex with a carbonyl ligand, $[L^{Mc}NiCO]$ ($L = \beta$ -diketimate ligand), (Eckert, Dinescu, Cundari & Holland, 2005) and (2) four-coordinate bis- α -diimine-nickel(I) complex $[Ni(L^1)_2]^+$ ($L^1 = 2$ -phenyl-1,4-bis(isopropyl)-1,4-diazabutadiene) (Muresan, Chlopek, Weyhermüller, Neese & Wieghardt, 2007). Our results (Fig. 1) indicate that the level of theoretical treatment of the spin-orbit interaction has a minor influence on the g tensor for the investigated Ni^I complexes. The ZORA-UN-BP and SOMF-BP calculations gave practically the same results. The major influence on the calculated g tensor has the choice of exchange-correlation functional. The calculations using the SOMF-B3LYP scheme were undoubtedly superior to those of SOMF-BP, showing the importance of the exact HF exchange. The results obtained for various GGA functionals were essentially insensitive to the individual functional. From the inspection of Fig. 1 it is clear that for the computation of the g tensor of the complexes of Ni^I the SOMF-B3LYP scheme can reproduce the experimental results in a quantitative way. It has been shown recently that this scheme may also be used for resolving the conformational Y vs. T dichotomy of the tricoordinated

Ni^I CO complexes in zeolitic, organometallic, and enzymatic systems (Pietrzyk, Podolska & Sojka, 2009).

Additional useful information concerning the molecular nature of the g tensor can be obtained from the scalar relativistic calculations using the Pauli Hamiltonian. It allows for partitioning of the g tensor into the relativistic, diamagnetic, and paramagnetic components, providing an in-depth insight into its electronic nature via diagrams of the magnetic orbitals. The latter reveal magnetic transitions of the most important contributions to the g shifts (Schreckenbach *et al.*, 1997). Such approach is illustrated for Ni^I CO complex with aqua ligands that can mimic surface ligands of oxide surfaces (Fig. 2). Principal orbital contributions provide molecular rational for the $g_{xx} > g_{yy} \gg g_{zz}$ sequence, which was experimentally observed in case of the silica-supported nickel(I) monocarbonyls (Bonnevot, Olivier & Che, 1983).

Mononitrosyl $\{Cu^I(NO)\}^{11}$ complexes – hyperfine tensor and assessment of spin polarization

In a classic approach the isotropic hyperfine coupling constant (HFCC) is factorized into Fermi contact, spin polarization, and pseudocontact terms. Unfortunately, the separation of those contributions is difficult because the values of the polarization constants, Q_d , are hard to be reliably assessed from the reference experimental data. Yet, this problem can be resolved readily by using the spin-restricted and spin-unrestricted calculation schemes (Munzarova *et al.*, 1999). The $\{Cu^I NO\}^{11}/ZSM-5$ complex, produced by adsorption of NO on $Cu^I ZSM-5$ can be used as an example (Sojka, Che & Giamello, 1997). The copper a_{iso} value for this complex was calculated with B3LYP and BPW91 functionals. The best results were obtained with the BPW91 ($a_{iso}^{Cu} = 158.7 \times 10^{-4} \text{ cm}^{-1}$) in conjunction with a flexible basis set 6-311G(*df*), which led to a formidable agreement with the $a_{iso}^{Cu} = 158.5 \times 10^{-4} \text{ cm}^{-1}$ value derived from the EPR data. As already mentioned, the contribution of the polarization effect may be evaluated by comparing the a_{iso}^{Cu} values obtained from the restricted-open shell (RO) and spin unrestricted (U) calculation schemes: $a_{iso}^{pol} = a_{iso}(RO) - a_{iso}(U)$. The resultant value of $a_{iso}^{pol} = 22 \times 10^{-4} \text{ cm}^{-1}$ for the BPW91 functional indicates that the polarization term contributes in 13% to the total isotropic coupling. A crude semi-empirical estimate of the a_{iso}^{pol} value yields $15 \times 10^{-4} \text{ cm}^{-1}$, which is reasonably close to DFT calculated value, taking into account large uncertainty in estimation of the polarization constant Q_d .

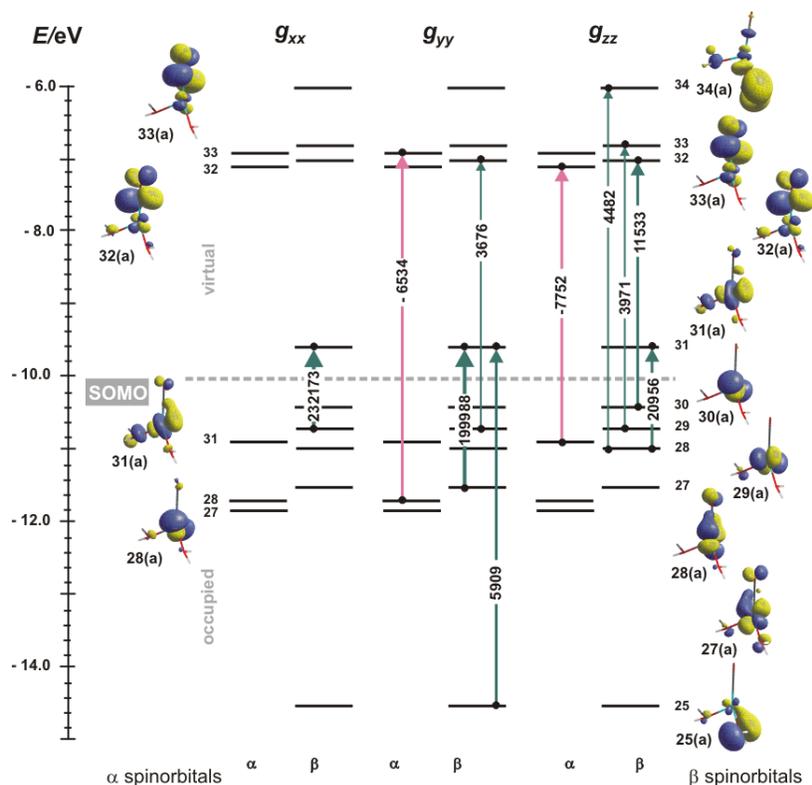


Fig. 2. Kohn-Sham orbital diagram for the most important paramagnetic contributions to the g tensor components of $[\text{Ni}^{\text{I}}\text{CO}(\text{H}_2\text{O})_2]^+$ complex based on the spin-unrestricted BP/TZP scalar relativistic calculations with Pauli Hamiltonian. The magnetic field-induced couplings are indicated with arrows, and the corresponding contributions ($>10\%$) are given in ppm.

Structure sensitivity of HFCC for $\bullet\text{CH}_2\text{OH}$ radical

Because of its dual nature involving delocalization of the unpaired electron density on ns orbitals and the spin polarization, the isotropic coupling parameters are very sensitive to the changes in geometry of the investigated paramagnet. To illustrate the structural sensitivity of the a_{iso} values by means of DFT calculations we have chosen a hydroxymethyl radical as a model (Sojka & Pietrzyk, 2006). A dihedral ($\theta_{\text{H-C-O-H}}$) distortion angle describing rotation of the OH group around the C–O bond and a bending angle ($\delta_{\text{H-C-H}}$) that measures the deformation of the CH_2 group, caused by the interaction with the environment (surface), were used as sensitive structural variables.

The response of the $a_{\text{iso}}(^{13}\text{C})$ values to angular distortion (variation of the bending $\delta_{\text{H-C-H}}$ and dihedral $\theta_{\text{H-C-O-H}}$ angles) of the free $\bullet\text{CH}_2\text{OH}$ radical are shown on the 3D plot in Fig. 3. It is clear that ^{13}C hyperfine coupling is very sensitive to bending deformation, whereas the sensitivity to torsional distortion is less pronounced. Two clear local minima can be distinguished in the plot. The first one at $\theta_{\text{H-C-O-H}} = -95^\circ$ corresponds to a nearly C_s symmetry of the $\bullet\text{CH}_2\text{OH}$ radical, with the mirror plane defined by the C–O–H atoms.

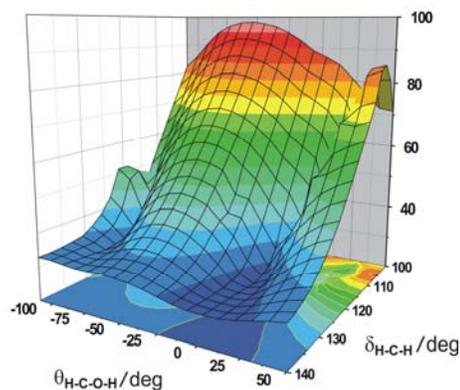


Fig. 3. Variation of ^{13}C a_{iso} (in gauss) calculated for isolated hydroxymethyl radical upon angular deformation of CH_2 group and rotation along H–C–O–H dihedral angle (adapted from Sojka *et al.*, 2006).

In such a case, the in-plane orbitals of the OH group are directly admixed to the SOMO, giving rise to an increase of the $a_{\text{iso}}(^1\text{H}(\text{O}))$ value up to 4.12 mT, at the expense of the carbon $2s$ contribution. A deeper minimum at $\theta_{\text{H-C-O-H}} = 0^\circ$ was associated with a slightly non-planar structure of the radical. For perfectly planar $\text{CH}_2\text{–O}$ group a negative value of $a_{\text{iso}}(^{13}\text{C})$ is expected, whereas the non-planarity allows for carbon $2s$

admixture to the SOMO, giving rise to a positive HFCC value. Since bending is the smallest for $\theta_{\text{H-C-O-H}} = 0^\circ$, this contribution is reduced and consequently $a_{\text{iso}}(^{13}\text{C})$ exhibits its lowest value. The changes induced by the variation of the $\delta_{\text{H-C-H}}$ angle are more uniform. They can easily be accounted for by rehybridization of the carbon atom. The observed decrease of the H-C-H angle results in pyramidization of the carbon and reduced involvement of the carbon 2s orbital in the SOMO.

The structural sensitivity of $a_{\text{iso}}(^1\text{H})$ for both methyl protons (Fig. 4) shows clearly different response to the $\theta_{\text{H-C-O-H}}$ angle, whereas the sensitivity to changes in the $\delta_{\text{H-C-H}}$ were more important and similar in magnitude. Due to polarization of the C-H bond, the methylene proton HFCC values essentially reflect the variation of the spin density at the carbon atom with $\delta_{\text{H-C-H}}$. The latter is manifested by the $a_{\text{iso}}(^{13}\text{C})$ coupling constant. Since $a_{\text{iso}}(^1\text{H}_{\text{trans}})$ is distinctly more affected by changes of the $\theta_{\text{H-C-O-H}}$ than the $a_{\text{iso}}(^1\text{H}_{\text{cis}})$ coupling, such deformation will increase the non-equivalence of both protons. Thus, it can be used as a sensitive diagnostic probe of the torsional deformation of the hydroxymethyl radical, caused by its interaction with its nearest environment.

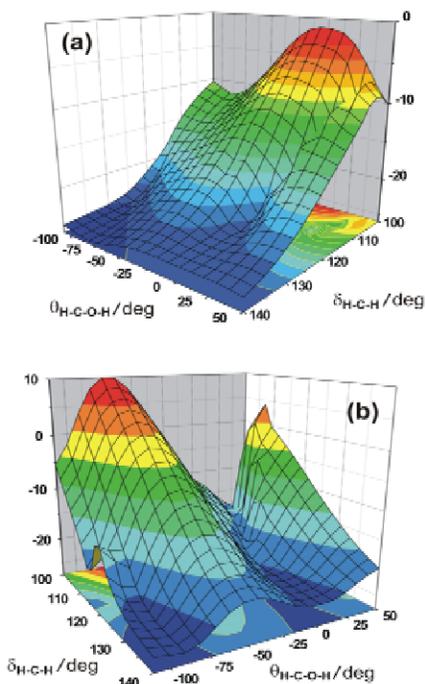


Fig. 4. Variation of (a) $^1\text{H}_{\text{trans}}$ a_{iso} and (b) $^1\text{H}_{\text{cis}}$ a_{iso} (in gauss) of isolated hydroxymethyl radical upon angular deformation of CH_2 group and rotation along H-C-O-H dihedral angle (adapted from Sojka *et al.*, 2006)

CONCLUSIONS

Molecular modeling combined with computational EPR spectroscopy is a powerful method for advanced interpretation of the molecular nature of the spin Hamiltonian parameters of the examined paramagnetic species. It allows not only predicting the main components of the \mathbf{g} or \mathbf{A} tensors, but provides also information about orientation of the principal axes, spin polarization or structural sensitivity of the magnetic parameters for various paramagnetic systems in low symmetry surroundings.

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