Molecular dynamics of alkyl radicals grafted onto silica surface

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Correlation times for $\equiv$SiOC$^{\cdot}$X$_2$ radicals grafted onto activated silica surface were estimated to be $1.3 \cdot 10^{-8}$ s (X = H) and $2.5 \cdot 10^{-8}$ s (X = Me) at room temperature.

Key words: grafted radicals, correlation time.

The study of interactions of molecules and radicals with a solid surface by spectroscopic and radiospectroscopic techniques provides data on the transition energies, intensities, and shapes of the absorption bands which are useful for determination of the structure and potential field of a surface, the dynamics of molecules and radicals adsorbed or chemically bound to a surface, *etc.* This information is of interest for the development of solid state and intermolecular interaction theories and study of the surface states and molecular dynamics of para- and diamagnetic particles isolated on a surface as well as their behavior in the adsorption layers.

However, investigation of the molecular dynamics and molecular friction, which depend on intra- and intermolecular interactions and, to a large extent, are determined by the energies of these interactions, carried out in adsorption layers up to several nanometers, is a difficult task because such layers usually have negligible density. Interpretation of NMR data obtained by means of both stationary and time-resolved approaches is complicated by the line broadening induced by dipole-dipole interaction and the magnetic susceptibility contribution. Nonuniformity and porosity of adsorbent usually make this broadening inhomogeneous. Dielectric relaxation also does not provide a reliable tool for determination of molecular mobility in thin layers due to the contribution of the solid to the dielectric loss and its wide frequency distribution.

The ESR method is the most convenient for studying the dynamics of paramagnetic centers on solid surfaces and in adsorption layers, being simple and informative. Although stable nitroxyl radicals have already been used for investigating solid surfaces and adsorption strength and irregularity,[1] they are not useful for studying the molecular dynamics in layers with a thickness comparable to the size of the probe due to the lower spatial resolution along the depth of the thin layer. The ideal probe for the purpose of molecular dynamics analysis should be chemically attached to a surface, whereas its free end carrying the electronic spin should be placed in the potential field of a surface or in the thin adsorbate film. Providing that the free and attached ends are linked by a flexible bridge of fixed molecular length, such a probe is able to gain information on the molecular mobility at the a fixed distance from a surface. The flexibility of the molecular bridge implies that the restrictions on molecular mobility due to hindrance of internal rotation of the probe should not exceed the restrictions on molecular mobility due to interactions of the probe with the potential field of the surface or with the media. In other words, the external friction must be larger than or equal to the internal friction. This condition is crucial for successful probing.

Spin probes of this kind can be obtained on aerosil surface by attachment of organic molecules to three-coordinated silicon atoms $\equiv$Si$^{\cdot}$ or terminal oxygen atoms $\equiv$SiO$^{\cdot}$.[2] For instance, being attached to the former centers, formaldehyde and acetone form $\equiv$SiOC$^{\cdot}$H$_2$ (**1**) and $\equiv$SiOC$^{\cdot}$Me$_2$ (**2**) radicals chemically bound (grafted) to an aerosil surface.

Figure 1 shows the dependences of the line widths $\Delta H_{\max}$ ($\Delta H_{\max}$ is the distance between the points of maximum slope) of the ESR spectra of these radicals on the nuclear magnetic quantum number m_I. For radical **1** with two magnetically equivalent protons the three components of the ESR spectra correspond to the projections of total spin of the protons equal to $m_I = 0$ and ± 1. For radical **2** with six magnetically equivalent protons the m_I values are equal to 0, ± 1, ± 2, and ± 3. Figure 1 clearly shows that the width of the ESR lines depends on m_I, *i.e.*, on the projection of the total magnetic momentum of the nuclei (protons) onto the z axis.

It is known[3] that the width of ESR lines exhibits a remarkable dependence on the dynamics of spin relaxation of a radical. In the case where the electron spin is subjected to two fluctuating fields, one of which is induced by the anisotropic Zeeman interaction (by g-factor anisotropy), while the other is induced by the hyperfine interaction (HFI), the dependence of the

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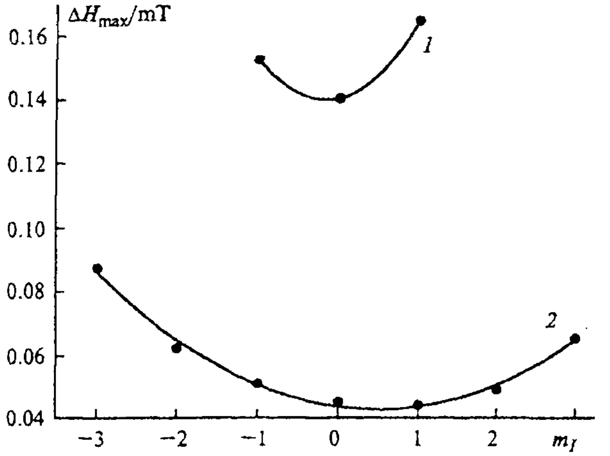

Fig. 1. Dependence of the line width (distance between the points of maximum slope) on the projection of the total spin of the protons onto z axis in the ESR spectra of grafted radicals $\equiv$SiOC$^\cdot$H$_2$ (*1*) and $\equiv$SiOC$^\cdot$Me$_2$ (*2*).

width of the hyperfine structure ESR lines $\Delta H_{\max}$ on m_I can be described as

$$\Delta H_{\max} = A + Bm_I + Cm_I^2,$$

where A, B, and C are constants which incorporate the structural parameters of a radical and its rotational correlation time.[4,5] That is, the ESR line broadening is a function of HFI and g-factor anisotropy as well as of the modulation frequencies of these interactions by molecular rotation.

The theory of spin relaxation has been described in a relatively simple manner and in sufficient detail in the monograph[3] (chapter 3). We will use below the equations of this theory to calculate the correlation time τ. (It should be pointed out that the equations are derived under the assumption of isotropic rotation of the paramagnetic particle. This model can be considered only as an approximation for estimating the correlation time of the radicals grafted to a surface*.) Equations III.61 from Ref. 3 are the key ingredients for calculation of τ. The difference in width between the low field ($m_I = +1$) and the high field ($m_I = -1$) components of the ESR spectra of the radical **1** δH = 0.011 mT (see Fig. 1) obeys the formula

$$\delta H = \Delta H_{\max}(m_I = +1) - \Delta H_{\max}(m_I = -1) =$$
$$= (16/3)[J_1^{\mathrm{DG}}(0) + J_2^{\mathrm{DG}}(0)] \cdot H,$$

which follows from equations III.61.[3] Here $J_1^{\mathrm{DG}}(0)$ and $J_2^{\mathrm{DG}}(0)$ are the spectral densities at the frequency of the resonant transitions of the H(1) and H(2) (see the scheme of molecular axes for the OCH$_2$ fragment of radical **1** on Fig. 2), and H is the intensity of the magnetic field ($H \approx 320$ mT). Using this equation, we determined the spectral densities of the cross-correlation functions for dipole anisotropic HFI and anisotropic g-factor for H(1) and H(2):

$$J_1^{\mathrm{DG}}(0) = J_1^{\mathrm{DG}}(0) \approx 3.2 \cdot 10^{-6}.$$

The values of spectral densities of the cross-correlation functions for dipole anisotropic HFI and anisotropic g-factor for H(1) and H(2) obey the following formula (see Eq. III.62 [3]):

$$J_i^{\mathrm{DG}}(0) = (1/10)\beta\gamma_e\gamma_i\tau \cdot \sum_{n=-2}^{2} \left|D_i^{(n)} g_i^{(n)}\right|, \qquad (1)$$

where i enumerates the protons (i = 1, 2), index (n) specifies the rank of Legendre spherical harmonics, β is the Bohr magneton, γ_e, γ_i are the hyromagnetic ratios for electron and nucleus, and τ is the characteristic time of rotational motion of a radical. The absolute value is taken in equation (1) because the value of spectral density of the cross-correlation function depends only on the dipole interaction energy between unpaired electron and nucleus. Coefficients $D_i^{(n)}$, which determine the dipole interaction between unpaired electron and nucleus, can be represented as the sum

$$D_i^{(n)} = D_{i,1}^{(n)} + D_{i,\mathrm{nonl}}^{(n)},$$

where the first term corresponds to the local contribution (from the π-electron spin density on a given nucleus), while the second term corresponds to the nonlocal contribution (from the spin density on neighboring nuclei). The first term vanishes for the protons, whereas the second term is equal to $\rho D_i^{(m)}$, where ρ is the spin density of π-electron on the C atom of the methylene group of radical **1**, $\rho \approx 1$. In Eqs. (1)

$$\left.\begin{aligned}
&g^{(0)} = 6^{-1/2}(2g_{zz} - g_{xx} - g_{yy}),\\
&g^{(\pm1)} = 0,\\
&g^{(\pm2)} = (1/2)(g_{xx} - g_{yy}),\\
&D_1^{(0)} = D_2^{(0)} = -(1/2)(3/2)^{1/2}T_{zz},\\
&D_1^{(\pm1)} = D_2^{(\pm1)} = 0,\\
&D_1^{(\pm2)} = -(1/4)(T_{xx} - T_{yy}),\\
&D_2^{(\pm2)} = D_1^{(\pm2)} = \exp(\mp 2i\alpha),
\end{aligned}\right\} \qquad (2)$$

where g_{zz}, g_{xx}, g_{yy}, T_{zz}, T_{xx}, T_{yy} are the principal values of the g-tensor and the anisotropic parts of the HFI tensor in the molecular coordinate frame (see Fig. 2), α is the angle between the C—H(2) bond and the principal axis of HFI and g tensors directed along the C—H(1) bond; $\alpha \approx 120°$ (for the HOOCC$^\cdot$H$_2$ radical α = 116±5°).[7]

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* The influence of the character and velocity of molecular motion and orientation of paramagnetic probe in isotropic or anisotropic medium on the line width of the ESR spectra is analyzed in detail for nitroxyl radicals in a monograph.[6]

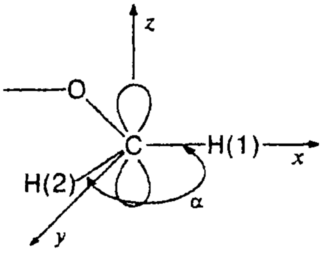

Fig. 2. Scheme of the molecular axes of OCH_2 fragment of radical **1**.

We assume that to a good accuracy the g-tensor of $\equiv SiOC^{\cdot}H_2$ and $\equiv SiOC^{\cdot}Me_2$ radicals chemically bound to the silica surface can be taken as axially symmetric, *i.e.*, $g_{xx} = g_{yy} = g_{\perp}$ and $g_{zz} = g_{\parallel}$. Under this approximation Eqs. (2) can be represented as

$$\left.\begin{aligned}
&g^{(0)} = 6^{-1/2}\cdot 2(g_{\parallel} - g_{\perp}),\\
&g^{(\pm1)} = g^{(\pm2)} = 0,\\
&D_1^{(0)} = D_2^{(0)} = -(1/2)(3/2)^{1/2}T_{zz},\\
&D_1^{(\pm1)} = D_2^{(\pm1)} = 0,\\
&D_1^{(\pm2)} = -(1/4)(T_{xx} - T_{yy}),\\
&D_2^{(\pm2)} = D_1^{(\pm2)} = \exp(\mp 2i\alpha),
\end{aligned}\right\} \qquad (3)$$

whereas the Eqs. (1) as*

$$J_i^{DG}(0) = (1/20)\cdot\tau\cdot(g_{\parallel} - g_{\perp})\cdot T_{zz}. \qquad (4)$$

It is known[7] that if the radical contains two α-protons, they have distinct although not very different HFI tensors. For instance, for the $HOOCC^{\cdot}H_2$ radical stabilized in the single crystal of malonic acid, whose structure is close to that of the $\equiv SiOC^{\cdot}H_2$ radical, the principal values of the HFI tensors were determined experimentally as -55, −30, and −91 MHz for one proton and as −59, −37, and −92 MHz for the other. The calculation of anisotropic contributions A_{zz}, A_{xx}, A_{yy} to the components of the HFI tensors yields the values of +4, +29, and −32 MHz, respectively, for one proton and +4, +26, and −29 MHz for the other. These data allow one to accept the assumption of axial symmetry of tensors with components A_{zz}, A_{xx}, A_{yy}.

Simulating the spectrum of radical **1****, we determined the anisotropic parts of g and HFI tensors which are not compensated by the radical rotations under our experimental conditions (at room temperature): $(g_{\parallel} - g_{\perp}) \approx 0.0016$ and $T'_{zz} \approx 1.0$ MHz. For calculating τ it is necessary to use the anisotropic part of the z-component of the HFI tensor compensated by rotation, *i.e.*, the value $T_{zz} = A_{zz} - T'_{zz} = 3$ MHz. Providing that $J_1^{DG}(0) = 3.2\cdot10^{-6}$ (see above) and $\rho \approx 1$, one arrives at $\tau \approx 1.3\cdot10^{-8}$ s (frequency $\nu \approx 7.7\cdot10^{7}$ s^{-1}).

Analogous calculations were also carried out for radical **2**, for which the value of spectral density of the cross-correlation functions $J^{DG}(0)$ amounts to $-2.1\cdot10^{-6}$. Comparing the experimental ESR spectrum of radical **2** with the calculated spectrum within the assumption of axial symmetry of the HFI and g-tensors, we determined $T'_{zz} \approx 0.47$ MHz and $(g_{\parallel} - g_{\perp}) \approx -0.0003$. Analysis of the ESR spectrum of the $MeC^{\cdot}H(COOH)$ radical stabilized in a single crystal of alanine[7] gave the principal values of the HFI tensor for the rotating protons of the Me group symmetric with respect to rotations along the C—C bond as ~76 and ~67 MHz. These data make it possible to estimate the anisotropic part of the z-component of the HFI tensor: $A_{zz} = A_{\parallel} \approx 6$ MHz. As a result, the value $T_{zz} = A_{zz} - T'_{zz}$, which is needed for calculating τ, amounts to *ca.* 5.5 MHz. The value τ for radical **2** calculated from these data appeared to be equal to $2.5\cdot10^{-8}$ s (frequency $\nu \approx 4.0\cdot10^{7}$ s^{-1}).

It should be noted that the δH value in the ESR spectrum of radical **2** is proportional to the $|m_l - m_{-l}|$ difference (Fig. 3), as should be expected from equations III.61.[3]

Assuming that the preexponential factor in the equation $\nu = \nu_0\exp(-\Delta E/RT)$ is equal to 10^{13} s^{-1}, the activation energy for rotational motion at $T = 300$ K ΔE can be estimated as ~30 kJ · mol^{-1} for radical **1** and as ~31 kJ · mol^{-1} for the radical **2**. It is likely that the values thus obtained are overestimated because $\nu_0 < 10^{13}$ s^{-1}. Corrected values can be calculated from the temperature dependence of the correlation times for the radicals under study.

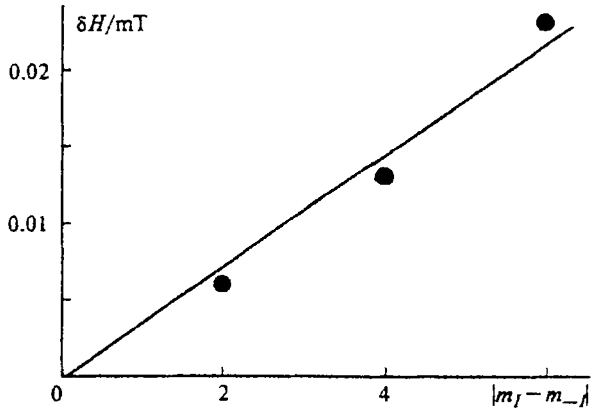

Fig. 3. Dependence of the difference in the line width on the difference of the z-projections of the total spin of the protons for corresponding lines in ESR spectrum of the radical **2**.

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* If the value T_{zz} in relation (4) is expressed in frequency units, the normalizing constants β, γ_e, and γ_i are not necessary.

** The program employed for the present calculations made it possible to calculate the allowed transitions within the first-order perturbation theory under the assumptions of axial symmetry of HFI and g-tensors and Lorentzian line shape.

We are not acquainted with other works on the dynamics of carbon-centered radicals adsorbed or grafted onto the silica surface. There is information on the rotational mobilities of nitroxyl radicals adsorbed on aerosil surface or grafted onto silica surface. The correlation time for adsorbed 2,2,6,6-tetramethylpiperidine-1-oxyl was estimated as $\sim 6 \cdot 10^{-9}$ s at 20 °C,[1] whereas for grafted nitroxyl radicals the correlation times vary from $1.6 \cdot 10^{-8}$ to $3.2 \cdot 10^{-8}$ s at 20 °C depending on the structure of the bridge between the paramagnetic center and the surface. The activation energies for rotational motion are equal to 18—24 kJ · mol^{-1}.[8] The results of experimental ESR study on the mobility of $\sim CH_2—O—C^{\cdot}H_2$ radical in the polyoxymethylene have been presented in Ref. 9. Within the 180—240 K temperature range the correlation times vary from $\sim 4.4 \cdot 10^{-9}$ to $\sim 1.6 \cdot 10^{-9}$ s, while the activation energy for rotational motion and rotational correlation time estimated by us at ~20 °C amount of ~5.6 kJ · mol^{-1} and $\sim 1.8 \cdot 10^{-10}$ s, respectively.

Our results show that interaction of the grafted radicals with aerosil surface leads to the hindrance of their rotational motions. According to the concept proposed at the beginning of the paper, the next step should be to study how the polymolecular adsorption layers affect the molecular dynamics of grafted radicals.

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