Molecular dynamics of ≡SiOC$^{\bullet}$O radicals "grafted" onto the Aerosil surface in adsorption layers of carbon dioxide

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As the formation of adsorption layers of carbon dioxide on the Aerosil surface proceeds, the character of rotational mobility of grafted radicals ≡SiOC$^{\bullet}$O changes from the anisotropic Brownian motion *in vacuo* to Brownian motion in a potential of 1.7—1.9 kcal mol^{-1}. The ≡SiOC$^{\bullet}$O radicals were proposed for use as probes to study the dynamic characteristics of adsorbates on the Aerosil surface.

Key words: grafted radicals, rotational diffusion, adsorption layers, silica, carbon dioxide.

Methods of paramagnetic probes and labels grafted onto the adsorbent surface are used to study adsorption processes on solid surfaces and the behavior of molecules in the adsorbed state.[1—3] Nitroxyl radicals of the piperidine, imidazoline, and imidazolidine series are most often used as paramagnetic probes, and silica serves as a "model" solid surface. The observed decrease in rotational and translational mobilities of labels and probes compared to their mobility in solution is caused, primarily, by chemical interactions, for example, formation of hydrogen bonds between nitroxyl radicals and silanol groups on the surface. The concentration of the silanol groups on the silica surface is[4] ~0.05 Å^{-2}. Hydrogen bonds can form after the chemical modification of silica[3] but the surface covered with modifier molecules changes its nature. It was attempted[2] to use data on the mobility of probes and labels for determination of kinetic (correlation times) and thermodynamic (enthalpies, entropies) characteristics. However, the results that emerged reflect, to a greater extent, chemical interactions and cannot be used for description of the behavior of molecules on the surface under conditions of physical adsorption.

An insight into the dynamics of grafted radicals obtained by silica activation caused by physical treatments (heating, photoirradiation)[5] can provide more objective information on the behavior of adsorbed molecules on the support surface. First of all, the thermal activation of the surface results in a decrease in the concentration of silanol groups by almost an order of magnitude (to ~0.007 Å^{-2}),[4] while the concentration of surface defects is lower than 0.0001 Å^{-2}.

The dynamics of radicals ≡SiOC$^{\bullet}$X$_2$ (X = H, D, F) and ≡SiOC$^{\bullet}$O grafted onto the Aerosil surface *in vacuo* was studied in several works.[6,7] Temperature dependences of the characteristic times of their rotational motion and rotation barrier of radical fragments about different bonds were also determined. These radicals differ from probes and labels[1—3]: their paramagnetic center is located near (≤5 Å) the solid surface. It is precisely the radicals of this type which were assumed[8] to serve as paramagnetic probes in studying regularities of the dynamics of processes that occur in adsorption layers.

In this work, we used radicals ≡SiOC$^{\bullet}$O grafted onto the Aerosil surface as paramagnetic probes is an attempt to elucidate whether their dynamic characteristics would change upon physical adsorption of carbon dioxide (which is inert toward this radical) on this surface.

Experimental

Radicals ≡SiOC$^{\bullet}$O were obtained by the photochemical activation of the Aerosil surface[5] with a specific surface area of ~100 m^2 g^{-1} in CO (pressure ~1—2 N m^{-2}) followed by evacuation of the sample. When experiments were carried out in the presence of CO$_2$, its pressure in a tube at room temperature being ~66500 N m^{-2}.

ESR spectra in the X-range were recorded on a Varian E-3 radiospectrometer at different temperatures in a Dewar tube placed into a radiospectrometer cavity. The temperature was maintained with an accuracy of ±1 °C using an E-4557-9 attachment (Varian).

To determine the main values of the g tensor of the ≡SiOC$^{\bullet}$O radicals from the experimental spectra recorded at 77 K (at this temperature, motions averaging the g tensor anisotropy are assumed to be absent), effective g factors of the third and fourth HFS components of diamagnetically dilute Mn^{2+} ions in MgO ($g_3 = 2.0328\pm0.0001$, $g_4 = 1.9812\pm0.0001$ and the value between them being 86.76±0.05 G at 20 °C; data from the All-Union Research Institute of Physicotechnical and Radio Engineering

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Measurements) and the known[9] value $g_\perp = 2.00055$ for the ≡Si$^\bullet$ radical were used as reference points. When the experimental ESR spectra of the ≡SiOC$^\bullet$O radical *in vacuo* and in the presence of CO_2 at 77 K are compared with the spectrum calculated in the "rigid limit," *i.e.*, in the absence of motions averaging the Zeeman interaction anisotropy, it is seen that the difference in components of the g tensor was ≤ 0.0001 for the following absolute values: $g_{xx} = 2.0028$, $g_{yy} = 2.0020$, and $g_{zz} = 1.9983$. The tensor components of the Lorentzian and Gaussian line widths used in simulation differed, being *in vacuo* 0, 0.13, 0.38 and 1.14, 0.67, 0 G, respectively, and in the presence of CO_2 0, 0.27, 0.52 and 1.32, 0.45, 0 G, respectively.

Components of the rotational diffusion tensor (R tensor) were determined by the comparison of the experimental ESR spectra recorded in a temperature range of ~120—250 K and simulated spectra. ESR spectra were simulated using a program[10] assuming anisotropic Brownian motion and in the framework of the MOMD (microscopic order—macroscopic disorder) model. Optimum parameters for describing the experimental ESR spectra were determined by the nonlinear least-squares method. Deviations of the simulated ESR spectrum from the experimental spectrum were minimized using an adaptive procedure.[11] The simulation was considered satisfactory if positions of extremes of the simulated and experimental spectra coincided and the sum of squared deviations of the simulated spectrum from the experimental one referred to the number of points of the simulated spectrum approximately corresponded to the sum of squared deviations caused by noise of the experimental spectrum. As a result, the simulation gave a set of varied parameters corresponding to a minimum in the n-dimensional surface (n is the number of varied parameters). The $\pm\Delta$ value, which is obtained by the use of the covariance matrices mentioned hereinafter, was assessed from the halfwidth of the cross-section line of the multidimensional surface in a region of the minimum by the chosen parameter.

Analysis of the data obtained by the simulation of spectra with three different variable rotational diffusion tensors suggests that the spectra can be simulated under the assumption of axial symmetry of the R tensor. Therefore, variables in the simulation of the spectra were only the values characterizing the dynamic behavior of species, *viz.*, components $R_{||}$ and $R_\perp$ of the axially symmetric rotational diffusion tensor, and parameters characterizing the shape of an individual spectral line. When simulating the spectra in terms of the MOMD model, rotation barrier values were additionally varied. The angle determining the mutual orientation of the tensors g and R (angle between the z components of the tensors), according to earlier obtained results,[7] was considered constant and equal to 17°. The procedure of ESR spectra simulation in the "rigid limit" and in a region of slow motions of radicals has been described in detail previously.[12]

Results and Discussion

The study of the dynamics of the ≡SiOC$^\bullet$O radicals grafted onto the activated Aerosil surface gave quantitative characteristics of rotational diffusion of the radicals *in vacuo*.[7] In this work, we studied the temperature dependence of the dynamic behavior of the ≡SiOC$^\bullet$O radicals under different conditions: *in vacuo* and in carbon dioxide.

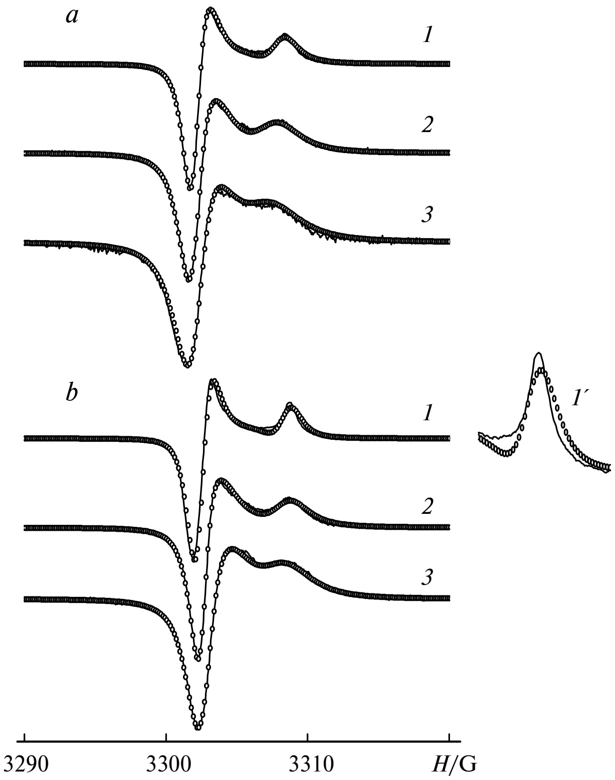

Fig. 1. ESR spectra of radicals ≡SiOC$^\bullet$O recorded in the absence (*a*) and presence (*b*) of carbon dioxide at temperatures 130 (*1*), 205 (*2*), and 270 K (*3*). Points are simulation of the spectra assuming anisotropic Brownian motion of the radicals. Simulation of the spectral z component at 130 K is shown in insert (*b*, *1′*) in an amplified scale.

The experimental ESR spectra of the ≡SiOC$^\bullet$O radicals and results of their simulation assuming anisotropic Brownian motion of paramagnetic species are presented in Fig. 1. A fairly good coincidence of the experimental and simulated ESR spectra is observed in the absence of carbon dioxide in almost the whole studied temperature range, whereas this coincidence is only satisfactory for the spectrum observed in carbon dioxide at temperatures below 200 K. This is seen most clearly for the z component of the ESR spectrum of the ≡SiOC$^\bullet$O radicals presented in Fig. 1, *b* (curve *1′*).

The plots of the components of the rotational diffusion tensor of the ≡SiOC$^\bullet$O radicals $R_{||}$ and $R_\perp$ in the coordinates $\ln R_i$ *vs.* T^{-1} are presented in Fig. 2. The results obtained in the absence of carbon dioxide (plots *1* and *2* for $R_{||}$ and $R_\perp$) correspond to the earlier data.[7] The Δ values in determining $\ln R_i$ do not exceed 0.3. The introduction of carbon dioxide changes the character of the plots for $R_{||}$ and $R_\perp$ (curves *3* and *4*), and the minimum difference in the $\ln R_\perp$ values observed in the absence and

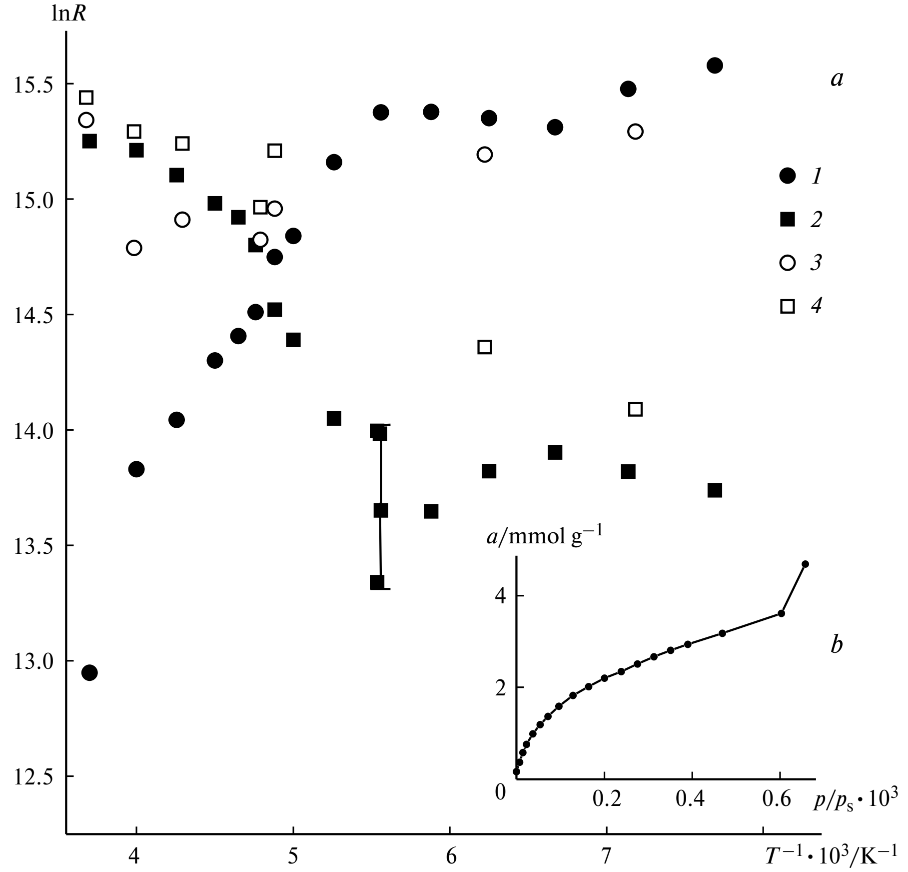

Fig. 2. *a*. Dependence of the components of the rotational diffusion tensor of radicals ≡SiOC$^•$O in the absence (*1*, *2*) and presence (*3*, *4*) of carbon dioxide on the inverse temperature obtained by the simulation of the ESR spectra assuming anisotropic Brownian motion: $R_{||}$ (*1*, *3*) and $R_{\perp}$ (*2*, *4*); *b*. Adsorption isotherm of carbon dioxide on silica at 195 K (p is the pressure of carbon dioxide above the sample, p_s = 105480 N m^{-2} is the pressure of saturated carbon dioxide vapor).

presence of CO_2 (curves *2* and *4*) is more than unity, *i.e.*, exceeds Δ.

Qualitatively different temperature dependences of the components of rotational diffusion tensors obtained by the simulation of the ESR spectra of the ≡SiOC$^•$O radicals in the absence and presence of carbon dioxide and the lack of good agreement of the simulated and experimental spectra for the latter system suggested that for experiments in carbon dioxide the dynamics of grafted radicals cannot longer be described by the model of anisotropic Brownian motion. The character of motions responsible for the parallel and perpendicular components of the rotational diffusion tensor has been proposed previously.[7] The parallel component was attributed to deformational changes in the Si—O—C angle (and, perhaps, torsional vibrations about the O—C$^•$ bond) in the radical, which occur without surmounting the activation barrier with an amplitude depending on the thermal motion energy. The perpendicular component was associated with the rotation of a radical fragment about the Si—O bond occurring with an activation barrier.

To make assumptions on a possible character of motion of a grafted radical when an amount of the adsorbate ensures the formation of adsorption mono- or polymolecular layers, we obtained the adsorption isotherm of carbon dioxide at 195 K on the Aerosil used in the above experiments (see insert *b* in Fig. 2). These measurements made it possible to determine the pressure interval in the gas phase for carbon dioxide needed for the formation of a mono- or multilayer coverage on the surface of the Aerosil sample at temperatures used in our experiments. Physical adsorption of carbon dioxide molecules on the Aerosil surface is caused by relatively weak van der Waals interactions. In this case, adsorbate molecules are fairly mobile, and their motion should not, most likely, induce the appearance of "rigid" potential barriers that dramatically change the dynamic characteristics of grafted radicals. We believe that for the surface with multilayer coverage by the adsorbate the dynamics of radicals grafted onto the surface should be described better in the framework of the model of paramagnetic species motion in some potential, whose effective value is specified by the

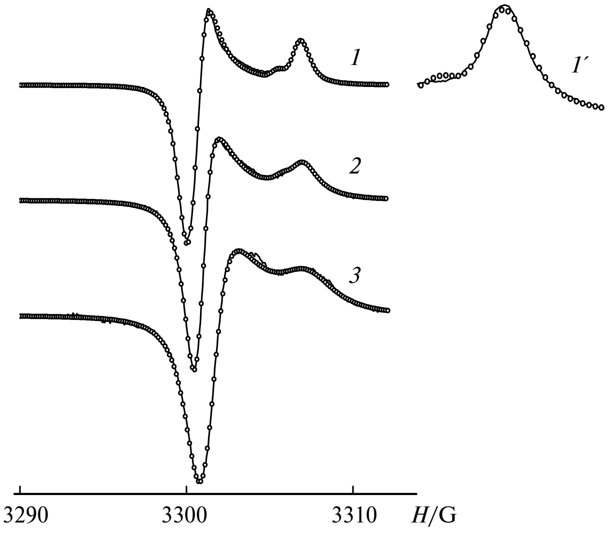

Fig. 3. ESR spectra of radicals $\equiv SiOC^{\bullet}O$ recorded in the presence of carbon dioxide at temperatures 130 (*1*), 205 (*2*), and 270 K (*3*). Points are simulation of the spectra in terms of the MOMD model. Simulation of the spectral *z* component at 130 K is shown in insert (*1′*) in an amplified scale.

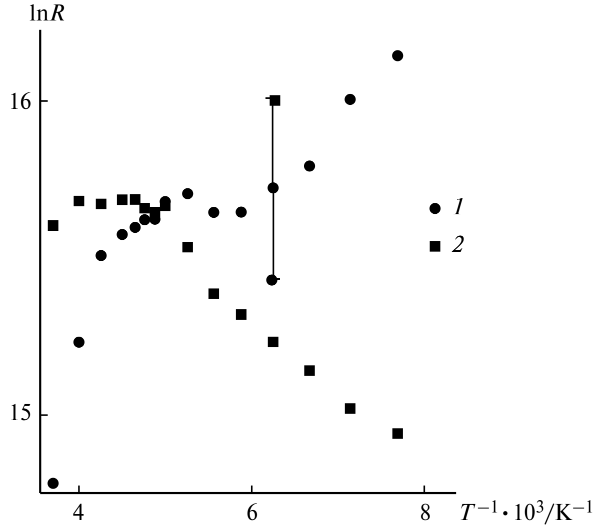

Fig. 4. Dependence of the components of the rotational diffusion tensor of the $\equiv SiOC^{\bullet}O$ radicals in the presence of carbon dioxide on the inverse temperature obtained by the simulation of the ESR spectra in terms of the MOMD model: $R_{||}$ (*1*) and $R_{\perp}$ (*2*).

adsorbed molecules of carbon dioxide. The MOMD model[10] predicts the algorithm for description of this motion.

As can be seen from comparison of the experimental and simulated ESR spectra (Fig. 3), the use of the MOMD model instead of the model of anisotropic Brownian motion leads to a better agreement at least in the region of the *z* component (*cf.* Fig. 1, *b* (curve *1′*) and Fig. 3 (curve *1′*)). The plots of the components of rotational diffusion tensor $R_{||}$ and $R_{\perp}$ in the coordinates $\ln R_i$—T^{-1}, obtained by processing of the ESR spectra of the $\equiv SiOC^{\bullet}O$ radicals obtained in carbon dioxide at different temperatures using the MOMD model, are presented in Fig. 4. The $R_{\perp}$ parameter decreases with a temperature decrease, while the response of $R_{||}$ to a temperature change in the system under study seems unusual. When the temperature decreases from room temperature to ~180—190 K, $R_{||}$ increases by ~3.3 times, reaching a limiting value in the temperature interval in which the formation of the adsorbate monolayer is completed. The further temperature decrease increases $R_{||}$. This can be related, most likely, to the formation of a multilayer adsorbate coverage on the surface and a decrease in the mobility of adsorbed molecules.

This character of the dependence of $R_{\perp}$ and $R_{||}$ on the inverse temperature in the presence of carbon dioxide can be explained by the fact that the amount of carbon dioxide adsorbed on the surface increases with a temperature decrease. This decreases the intensity of motions having an activation energy, *i.e.*, $R_{\perp}$ decreases. A simultaneous increase in the amount of adsorbed carbon dioxide shortens the amplitude of the bending vibration of the Si—O—C bond angle, which increases the frequency of vibrations and $R_{||}$ value. It can be assumed that the sharpest changes will be observed in the temperature range where the formation of the monolayer adsorbate is completed and multilayer adsorption commences. The effective potential calculated from the data on the simulation of the experimental spectra in the framework of the MOMD model is 1.7—1.9 kcal mol^{-1}.

The description of the experimental ESR spectra recorded at different temperatures in the framework of the MOMD model is better than that assuming anisotropic Brownian motion of radicals. In our case, the ESR spectrum is simple enough and contains an information only on the Zeeman interaction anisotropy. For temperatures higher than 100 K, the thermal motion of a radical provides such a partial averaging of the *g* tensor anisotropy that with high reliability can be considered axially symmetric. Note that an additional component is distinctly manifested in the spectra simulated by the MOMD model (see Fig. 3, curve *1′*). This component is not observed when simulating under assumption of anisotropic Brownian motion of radicals (see Fig. 1, *b*, curve *1′*). Since the MOMD model assumes both motions of radicals inside some regions of the space, restricted by potential barriers, and transitions of radicals through these barriers, the appearance of the additional component can be ascribed to the presence of two types of radicals on the surface. Radicals of one type can surmount potential barriers, and the second type radicals cannot surmount them at a given temperature. This separation, being based on analysis of the simulated ESR spectrum only, is rather conventional, because the correlation times for these two groups of radicals (obtained from the positions of maxima of the parallel components[7]) are close: the ratio of the correlation times for these groups is close to two.

The shape of a real line in the ESR spectrum cannot be described, as a rule, by only Lorentzian or Gaussian line shape.[13] The resonance absorption line has a Lorentzian shape. This shape is explained by different interactions that uniformly broaden the resonance absorption line. The factors inducing the nonuniform broadening of the resonance absorption line produce the Gaussian line shape. For a better description of the experimental spectrum by simulation, we varied the tensor components of the Lorentzian line width with the isotropic contribution of the Gaussian line. The simulation showed that the line corresponding to the x component of the g tensor is described by the Gaussian shape (the width of the Lorentzian line shape is smaller than the root-mean-square error of determination of the line width of the x component), and the y and z components are described by the convolution of the Lorentzian and Gaussian line shapes.

The temperature plots of the tensor components of the width of the Lorentzian and Gaussian line shapes obtained by experimental spectra simulation are presented in Fig. 5. It can be seen that the temperature increase from ~130 to ~270 K results in a monotonic increase in the width of the Lorentzian lines of the y and z components from ~0.5 to ~1.5 G. Evidently, the reason for this change in the line widths is an increase in the intensity of thermal motion of "grafted" radicals; the kinetic effects of this kind are well known.[14] When the temperature increases from ~130 to ~270 K, the width of the Gaussian line shape changes from ~0.8 to ~1.1 G, passing through a minimum value of ~0.3 G at 180 K. The multilayer type of adsorption is observed under the carbon dioxide pressures used (~66500 N m^{-2}) at ~180 K on the silica surface. It can be assumed that the line width increases with the temperature decrease from ~180 to ~130 K due to a decrease in the frequency of radical rotation about the Si—O bond, and the Gaussian line shape is envelope for many Lorentzian lines, each of which corresponds to radicals with a certain orientation of the g tensor relatively to the direction of the external magnetic field. Now we cannot substantiate any assumption about reasons for increasing the line width with the temperature increase from ~180 to ~270 K.

Thus, the ESR spectra of the grafted $\equiv$SiOC$^{\bullet}$O radicals change with the formation of adsorption layers on the Aerosil surface in a different way, compared to changes *in vacuo*. These changes related to the character of rotational mobility of grafted radicals can be interpreted as a transition from the anisotropic Brownian motion to Brownian motion in some potential. The results obtained show that grafted radicals can be used as probes for studying the dynamic characteristics of adsorbates of different nature on the Aerosil surface.

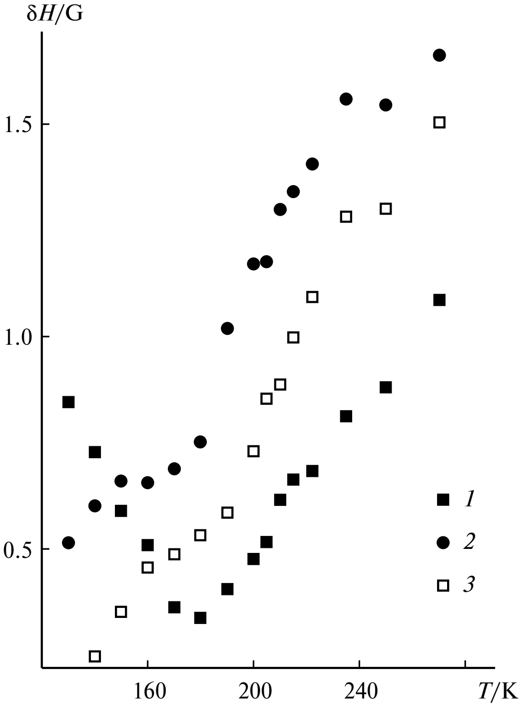

Fig. 5. Dependences of the tensor components of the line shape of radicals $\equiv$SiOC$^{\bullet}$O in the presence of carbon dioxide on the temperature obtained by the simulation of the experimental ESR spectra in terms of the MOMD model: halfwidth of the isotropic Gaussian line shape (*1*) and y (*2*) and z components (*3*) of the tensor of the Lorentzian line shape.

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