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TWO-SPIN PROBE INVESTIGATION OF MOLECULAR MOBILITY. A SIX-COORDINATE SILICON BIRADICAL

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The study of molecular mobility in viscous media by EPR is usually based on analysis of the change in shape of spectra of stable paramagnetic centers having sufficient magnetic anisotropy, due to the decrease in the correlation time for rotational molecular motion. Stable nitroxide radicals are widely used for this purpose as spin probes and labels [1]. However, the spectra of these radicals in the slow-motion domain have a complex shape which makes their analysis difficult and even impossible when the molecular motion of the system is nonuniform — for example, due to nonhomogeneity in a region of phase and structural transitions of the matrix.

It was shown earlier [2] that it is convenient to carry out an investigation of similar complicated situations with two-spin probes. In this case it is essential that the relaxation changes in the forbidden $\Delta M_s = 2$ transition lines, as shown in theoretical work [3], are sufficiently simple and easy to analyze. Consideration of the changes in the forbidden transition lines of triplet centers as given in [2] allowed establishment of the presence of dynamic nonhomogeneity in viscous matrices. In this work the drop in density of the forbidden transition lines was explained by the significant broadening of the spectrum of birradicals found in regions of increased molecular mobility. However, up to the present time the initial stage of the broadening of the forbidden-transition component has not been successfully observed, when this broadening is already noticeable but still insufficiently great and does not lead to complete disappearance of the spectrum.

In our work at temperatures from -140 to -60° C in a toluene matrix we observed a relaxation change in the forbidden-transition line shape (Fig. 1) of biradical III, formed by reaction of 3,6-di-t-butylorthoquinone (I) with silicon tetra-t-butylpyrocatechol (II) [4]:



The relaxation may be caused by rotation of the biradical as a whole, ligand exchange, and even as a consequence of reorientation of the axis of the fine-structure tensor due to intra-

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Fig. 1. The temperature dependence of the forbidden $\Delta M_s = 2$ transition EPR lines in a 10^{-2} M solution of silicon 3,6-di-t-butyl-bis-pyrocatecholate biradicals in toluene. The dotted line represents a Lorentz-ian line with the extrema coinciding with the experimental spectrum.

Fig. 2. Temperature dependence of the motional correlation time for biradicals in a toluene matrix in a two-component distribution. The height of the flags shows the fraction of (a) narrow and (b) broad components.

molecular hopping of the unpaired electrons. The latter two possibilities were excluded, since replacement of one of the symmetrical ligands by a nonequivalent one (eliminating intramolecular reorientation) and also a change in the biradical concentration did not change the characteristic features of the relaxation-broadening inhomogeneity discussed below. Furthermore, we have preliminary NMR data for these systems which indicate that the intermolecular ligand exchange frequency is $\sim 10^2$ sec⁻¹ at room temperature and above.

According to [2], the change in the forbidden-transition line shape is reduced to an increase in the width of the Lorentzian contribution to the lines which is proportional to the frequency of the rotational motion. Analysis of the broadened-line shapes showed that they may not be explained within the scope of this model (convolution of the initial unbroadened spectrum with the Lorentzian lines of the corresponding width). The intensity of the broadened spectra on the wings of the line decreases significantly more slowly than for a purely Lorentzian line (Fig. 1), which is evidence for the fact that the spectrum is the sum of lines of different widths.

As is well known, the problem of decomposition of a sum of Lorentzian lines into components does not have a unique solution. For a qualitative analysis of the system we generated the decomposition of the experimental spectra assuming that each of them is the sum of two lines with Lorentzian contributions of different widths. Even though such a decomposition is not uniquely possible, it determined the result in a unique manner. The analysis was carried out according to the equation

$$\frac{F(z)}{F(1)} = \frac{16z}{9\left(1 + \frac{16a}{9b^4}\right)} \left[\frac{1}{\left(1 + \frac{z^2}{3}\right)^2} + \frac{a}{\left(b^2 + \frac{z^2}{3}\right)^2} \right],\tag{1}$$

where $z = (H - H_0)/(H_{max} - H_0)$; H_0 is the center of the spectrum, and H_{max} is the position of the extremum of the spectrum. The scaling parameters a and b are found from anamorphosis of the experimental spectra in the coordinates $[zF(1)/F(z)]^{1/2} - z^2/3$. The relative widths of the spectra are determined by the magnitude of the parameter b > 1, the relative intensities by the ratio a/b. The line broadening is found by excluding the contribution of the unbroadened line, recorded at -140° C, from the widths of the components obtained. Since this line has a Gaussian shape, the broadening is determined according to the equation [5]

$$\Delta H = \Delta H_0 [1 - (\Delta H / \Delta H_0)^2].$$
⁽²⁾

The rotational correlation times corresponding to the broadening are obtained from the relationship $\tau_c = (\gamma \Delta H)^{-1}$.

Results of the analysis performed are presented in Fig. 2. In the temperature interval -90° to -60° C the correlation time for the narrow component changes from 10^{-7} to $1.6 \cdot 10^{-8}$ sec, while the temperature dependence is described well by the Arrhenius law with parameters $E = 21 \pm 2 \text{ kJ/mole}$ and $\tau_0 = 10^{-13} \text{ sec.}$ The correlation time for the broad component changes from 1.8 · 10⁻⁸ to 1.4 · 10⁻⁹ sec, while the temperature dependence deviates from the Arrhenius law. At the same time, we observe substantial redistribution of intensities between narrow and broad components with preservation of the total integrated intensity of the forbiddentransition line. The data obtained allow us to draw the conclusion that relaxation in the studied system is nonuniform in the temperature interval -90° to -60° C. Both the structural nonhomogeneity of the matrix and even the coexistence of several different forms of the biradicals in the system may be sources of the polychromatic relaxation. The presence of biradicals of different structures should be reflected in the allowed $\Delta M_s = 1$ transition line shape, which is not observed. Thus, the complex form of the $\Delta M_s = 2$ transition EPR line reflects the structural nonhomogeneity of the matrix. In the simplest case we may consider the system as consisting of two phases: "soft" and "hard." Raising the temperature changes the ratio of the phases, and the deviation from the Arrhenius law at high temperatures for the "soft" phase may be evidence for its melting - that is, for the occurrence of a third, still softer, phase.

It is not necessary to reevaluate what we have obtained above by analysis of detailed information on transformations in the system. The actual composition of the matrix, of course, may involve more than two components. Nevertheless, we may consider it firmly established that the number of components of the system is not less than two — that is, that the structure of the matrix is nonhomogeneous.

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