

# Electron Spin Resonance Spectroscopic Investigation of the Rotational Motion of Self-Assembled Fatty Acid Films on Al<sub>2</sub>O<sub>3</sub>/NiAl(110)

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We report on the first electron spin resonance (ESR) investigation of the molecular rotational motion of self-assembled monolayers. We present results on fatty acid films grown on a thin Al<sub>2</sub>O<sub>3</sub> film. The spectra reveal a distinct temperature and coverage dependence. The changes in the line shape with variation of the spin labels location along the alkyl chain allow insight into the internal dynamics of self-assembled films.

The study of ultrathin organic films prepared by the Langmuir–Blodgett (LB) method or by self-assembly has been of considerable interest over the last years.<sup>1</sup> Although a vast array of methods has been used to characterize various properties of those films, most of the studies dealt with static properties. Fast infrared spectroscopy and nonlinear optical methods<sup>2</sup> are now frequently used to study dynamical properties on surfaces, but there is still a lack of methods covering the time scale between 10<sup>-6</sup> and 10<sup>-10</sup> s. Electron spin resonance (ESR) spectroscopy could provide insight into rotational motion on the required time scale because the line shape of the ESR spectrum reflects the motion directly. Therefore ESR spectroscopy has been applied in various fields, for example, in biological systems.<sup>3</sup> Studies of Baberschke et al.<sup>4–6</sup> on metal single crystals and of Schlienz et al.<sup>7</sup> on well-ordered oxide surfaces have shown that it is possible to examine submonolayers of paramagnetic adsorbates by ESR spectroscopy.

In this report we present the first ESR measurements on the molecular dynamics of self-assembled fatty acid films. It is known from the literature<sup>8–10</sup> that fatty acids form self-assembled monolayer on oxide surfaces. Therefore we have used an Al<sub>2</sub>O<sub>3</sub> film as substrate. Since the order of the films increases with increasing chain length, we have used stearic acid (C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>) films as a model system. In order to investigate the films by ESR spectroscopy we use spin labels, namely, *n*-doxyl stearic acid (*n*-DXSA), as probe molecules. These nitroxides, with an oxazolidinyl ring as the paramagnetic group connected to different positions of the aliphatic chain, are well-known as paramagnetic probes, for example, in the study of natural and synthetic membranes.<sup>11</sup>

The experiments have been performed in a combined ultrahigh vacuum (UHV)-ESR apparatus equipped with a low-energy electron diffraction (LEED), Auger, and a

temperature-programmed desorption (TPD) unit in order to characterize the Al<sub>2</sub>O<sub>3</sub> substrate. The details of the experimental setup have been described elsewhere.<sup>12</sup> The Al<sub>2</sub>O<sub>3</sub> substrate has been grown under UHV conditions as a thin, well-ordered epitaxial film on a NiAl(110) single crystal. The preparation procedure and the properties of the film have been reported in literature.<sup>13</sup>

The fatty acid films were prepared by immersion of the Al<sub>2</sub>O<sub>3</sub> substrate into a 1 mM mixture of *n*-DXSA and stearic acid in toluene at room temperature. The immersion times were varied between 24 and 100 h without effect on the resulting ESR spectra. After being removed from the solution, the sample was rinsed several times with toluene and subsequently with chloroform and water. Afterward the crystal was transferred into the vacuum chamber. The ESR spectra were recorded under high vacuum with a base pressure lower than 10<sup>-7</sup> mbar. Under these conditions the self-assembled films were stable for weeks.

In Figure 1 ESR spectra for different concentrations of labeled molecules are shown. The amount of labeled molecules given in Figure 1 refer to the molar fraction in the solution. However, the concentration of labeled molecules in the film is difficult to measure, because there is no easy way to determine the total number of molecules on the surface. In Figure 1 the dramatic line shape variation of the ESR spectra with concentration can easily be recognized. Whereas the spectra of the pure labeled film show exchange narrowing, at concentrations lower than 20% the spectra reveal a distinct resolution of the <sup>14</sup>N hyperfine components. Although it is in general not possible to extract information on the molecular motion from exchange narrowed spectra, the line width of the spectra compared to other dense packed molecular arrangements can give a hint at the density of the self-assembled film. Comparing the 19 G broad signal of the pure labeled film in Figure 1 with the line width of bulk crystalline 5-doxyl stearic acid, 18 G, we can conclude that the mean distance between the spin labels is approximately the same in both molecular arrangements. In contrast the LB film of 5-doxyl stearic acid in refs 14 and 15 reveals a signal of 24–26 G width. The enhanced line width is indicative of a higher mean distance between the spin labels and was interpreted by the authors as a more open structure compared to the bulk. Furthermore

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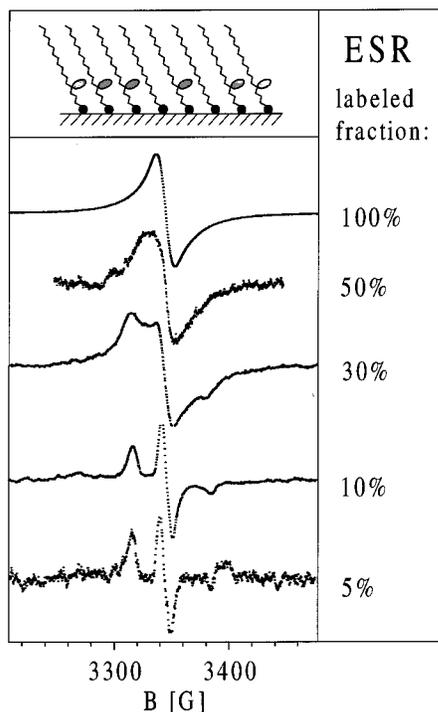
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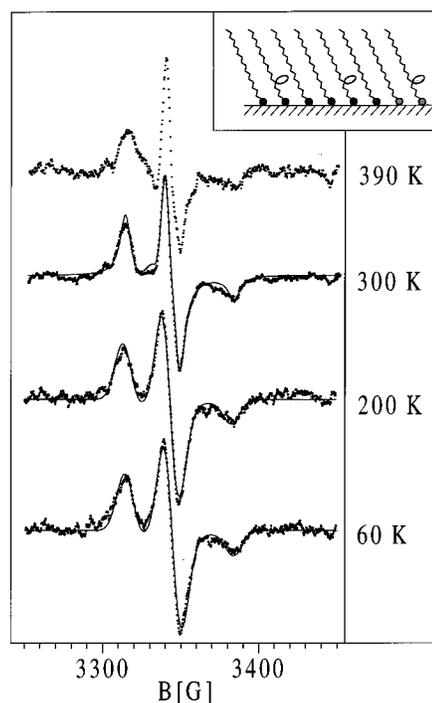


**Figure 1.** Concentration dependent ESR spectra of 5-doxyl stearic acid at room temperature. Intensities are normalized.

the aim of the present investigation was to elucidate the molecular dynamics of surface bound molecules whereas the experiments on LB films dealt with multilayer systems where the interaction with the surface is negligible. We have performed temperature dependent ESR measurements on self-assembled films over a wide range as will be presented further below in order to characterize the motion.

Focusing on the last two spectra with a concentration of 10% and 5%, respectively, it can be seen that the line shape of both spectra is approximately the same. This observation is corroborated by computer simulations that revealed the best fit for a line width of 7.5 and 7.4 G assuming a rigid limit spectrum with the same  $g$ - and  $A$ -tensor components for both spectra. However, the intensity of the spectra and by that the signal to noise ratio is reduced considerably with decreasing concentration. This means that either the mean distance between the molecules does not decrease with decreasing concentration for example due to inhomogeneous growth modes or the line widths of the spectra are determined by unresolved interaction between the unpaired electron and its surroundings. The second explanation is supported by the fact that rigid limit spectra of several highly diluted  $n$ -doxyl spin probes reveal approximately the same line width. We have undertaken studies of di-*tert*-butyl-nitroxide (DTBN) adsorbate where the limit of very low concentration can be reached.<sup>16</sup> The ESR spectra of DTBN are very similar to the spectra of the spin label and may, therefore, be directly compared. We can conclude that it is possible to prepare films with such a low concentration of the spin labels that their magnetic interaction becomes negligibly small. Those labels can be regarded as reasonable probes for the dynamics of the films. Therefore we used films grown in 10% solution of  $n$ -DXSA for all the following investigations.

Figure 2 shows ESR spectra of 5-DXSA at different, selected temperatures. The line shape of the spectra for



**Figure 2.** Temperature dependent ESR spectra of a 5-doxyl stearic acid film. Intensities are normalized.

temperatures up to 200 K remains unchanged, whereas the intensities decrease according to Curie's law. Increasing the temperature to values higher than 200 K results in a decrease of the line width (see, e.g., the spectra at 60 and 300 K in Figure 2). However, the positions of the characteristic spectral features remain unchanged. This behavior may be interpreted in terms of very slow motion of the spin label but it is difficult to understand, because it is known from the literature<sup>17</sup> that the line width of the spectra should increase first before changes in line positions occur. An alternative mechanism for line broadening at low temperatures is inhomogeneous broadening due to unresolved proton superhyperfine interactions. Apart from an increasing line width, this mechanism should change the line shape from Lorentzian to Gaussian.<sup>18</sup> This can be shown to be the case (see ref 19 for details): The solid lines in Figure 2 represent computer simulations of the spectra assuming a rigid, randomly oriented ensemble of spin labels. Whereas the spectrum at 300 K is computed with Lorentzian lines, the spectra at 200 and 60 K are calculated using Gaussian line shapes. The change from Lorentzian to Gaussian line shape is necessary in order to fit the rigid limit spectra with a single set of  $g$ - and  $A$ -tensors. This indicates that the changes in the line width above 200 K are due to the motion of the protons in the surroundings of the spin label. On subsequent raising of the temperature higher than 315 K, the line shape changes again. But now the changes of the line shape, namely, the growth of a structure between the two maxima of the spectra, are indicative of the motion of spin labels connected to the alkyl chains themselves.<sup>20</sup>

In self-assembled films one end of the long chain molecule is rigidly connected to the surface through the chemisorbed headgroup. For those systems the motion of

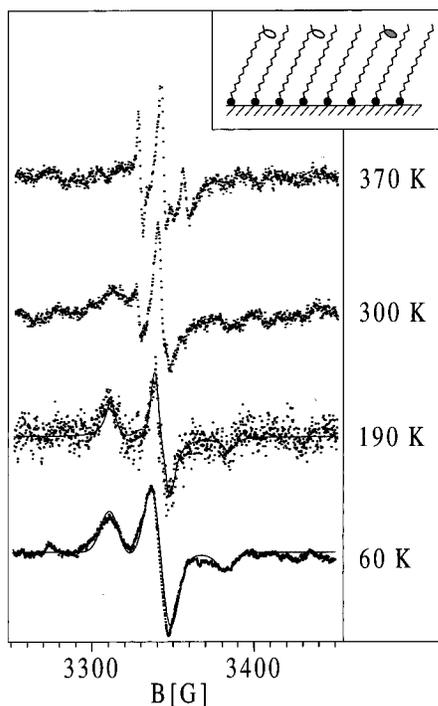
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**Figure 3.** Temperature dependent ESR spectra of a 16-doxyl stearic acid film. Intensities are normalized.

the chain tends to be more pronounced as the distance to the surface increases, as predicted by theoretical calculations; see, e.g., ref 21. In order to examine this effect, we have investigated films of 16-DXSA diluted in stearic acid to a 10% concentration with an almost maximal distance between the spin label and the surface. A series of ESR spectra at selected temperatures is shown in Figure 3. On comparison of the spectrum at 60 K with the equivalent spectrum of 5-DXSA, no pronounced differences occur. This behavior is expected because both spectra reflect an ensemble of static molecules. The situation changes at higher temperatures: Whereas the spectrum of 5-DXSA at 200 K could be described as a rigid limit spectrum with Gaussian line shape due to unresolved proton super-hyperfine interactions, the equivalent spectrum of 16-DXSA is a rigid limit spectrum as far as the spin label is concerned, but the line shape is almost Lorentzian. The onset of the protons motion for the 16-DXSA is approximately at 140 K. This is in good agreement with helium atom scattering experiments of Scoles et al.,<sup>22</sup> who observed a loss of the ordered structure above 100 K and attribute this effect to the motion of the terminal alkyl groups.

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The two high-temperature spectra clearly indicate the motion of the spin label itself. Compared to the 5-DXSA films the motion is considerably more excited. In an attempt to understand the dynamics in terms of liquid-like motion, the increase of the rotational constants should lead to a shift of the whole structure at the high- and low-field extrema toward the isotropic values. The surprising point of the dynamical spectra (300 K) presented here is that although a distinct feature at the position of the isotropic value appears, there is still a pronounced component with the  $A_z$  splitting of the rigid limit spectrum. Furthermore the components at the rigid limit positions decrease continuously with increasing temperature without any shift in the positions.

One explanation of this behavior could be the existence of at least two species with different rotation constants. In addition, one has to assume an equilibrium between the states in order to explain the continuous decrease of the intensities at the high- and low-field extrema.

A similar behavior of the ESR line shape has been observed for the motion of lipid side chains in lipid protein interaction.<sup>20</sup> For this case Ge and Freed have shown that it is possible to simulate the experimental spectra quantitatively by assuming a distribution of ordering potentials instead of different species with drastic different motional rates. First simulations within this framework have shown that an analysis of the motion by means of ordering potentials may also be suitable for the presented data. Detailed simulations to analyze the dynamical behavior are in progress. For a simpler adsorbate, namely DTBN, more elaborate simulations have been carried out.<sup>16</sup>

In summary, we have shown concentration and temperature dependent ESR spectra of self-assembled stearic acid films containing different *n*-doxyl stearic acids as spin probes. The concentration dependence of the spectra reveals magnetically independent spin labels for concentrations lower than 10%. The temperature dependent ESR spectra of 16- and 5-DXSA reveal two main aspects. Firstly, it is possible to distinguish two different kinds of molecular motions, on the one hand the motion of protons surrounding the spin label and on the other hand the dynamic of the spin label itself. Secondly, comparing the motional behavior of 5-DXSA and 16-DXSA we find a drastic shift in the onset temperature of the motion toward lower temperatures when switching from 5- to 16-DXSA.

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