

# The High-Frequency EPR Spectra of Polyaniline: Line Narrowing Due to the Spin Exchange<sup>1</sup>

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Received July 2, 1998;

Revised Manuscript Received September 17, 1998

**Abstract**—High-field EPR spectroscopy at 250 and 170 GHz was used to study polyaniline (PA) in the 100–300 K temperature range. Splitting of the EPR spectrum was observed which depended linearly on the magnetic field strength. The line shape for a PA sample was found to depend on the temperature. The spectra were simulated using the dynamic model of spin exchange.

## INTRODUCTION

Polyaniline (PA) is a well-known representative of a big family of conducting polymers which is very attractive due to its high resistance to oxidation and degradation. The EPR signal of PA in the solid state is known to be a singlet line without any visible structure. Of course, in the spectra of polyaniline solutions, the signal can be obtained with high resolution [1]. The most probable and evident explanation for the absence of line structure in the EPR spectra of PA is that, at the conventional EPR frequencies, the rate of spin exchange between paramagnetic centers is very high, and the signal is averaged to yield a singlet line. An alternative explanation is a high diffusion rate of charge carriers (also possessing a spin) [2].

In principle, it is possible to reach sufficiently high EPR frequencies where the line begins to broaden and some resolved structure can be observed. It is an anisotropy of the  $g$  tensor that is manifested in the EPR spectra measured at higher fields and frequencies. Figure 1 shows the EPR spectra of PA recorded at 250 GHz for three different temperatures. The bottom spectrum, measured at room temperature, corresponds to a paramagnetic center having the  $g$  tensor of axial symmetry which is substantially smoothed due to a high degree of spin exchange.

The temperature dependence of the linewidth (for the 3 cm waveband) in the 77–350 K range reported in [3] can be explained by the same spin-exchange mechanism, where the linewidth increases with decreasing temperature. In this paper, a similar effect is reported for a better resolved EPR signal recorded for

polyaniline at 250 GHz in the 113–323 K temperature range.

## EXPERIMENTAL

Polyaniline was synthesized in an alcohol solution [4] and then doped by the HCl vapors. The room-temperature conductivity of the initial PA sample was  $10^{-1} \Omega^{-1} \text{ m}^{-1}$ , and the density of spins was  $1 \times 10^{20} \text{ cm}^{-3}$ . These are typical values for polyaniline exhibiting record-breaking values neither in conductivity nor in the spin concentration.

We measured the samples on a 1-mm-waveband EPR spectrometer [5] for the 250 GHz resonance frequency and a 2-mm-waveband spectrometer [6] for the 170 GHz frequency. According to the Curie–Weiss law, the signal intensity is proportional to  $1/T$ . However, significant deviations from this law were observed on heating the sample even slightly above room temperature (Fig. 2). It is seen that some points at elevated temperatures lie below the straight line describing the low-temperature data. This behavior (i.e., the more rapid decrease in intensity than that expected according to the Curie–Weiss law) results evidently from a change in the  $Q$  value of the resonator. The PA conductivity increases with the temperature (up to  $\sim 350$  K, which is outside the temperature range of our experiments). Thus, the  $Q$  value of the resonator will decrease, which results in the observed deviation from the Curie–Weiss law.

The most interesting observation was the effect of line splitting in the EPR spectrum of polyaniline in the range of very high frequencies (250 GHz). At these frequencies, the EPR signal of PA is no longer a singlet. The line splits due to anisotropy of the  $g$  tensor, but its shape still correlates with the temperature. The temperature rise leads to an increase in the sample conductivity.

<sup>1</sup> This work was supported by the National Science Foundation (USA), grant no. CHE931367.

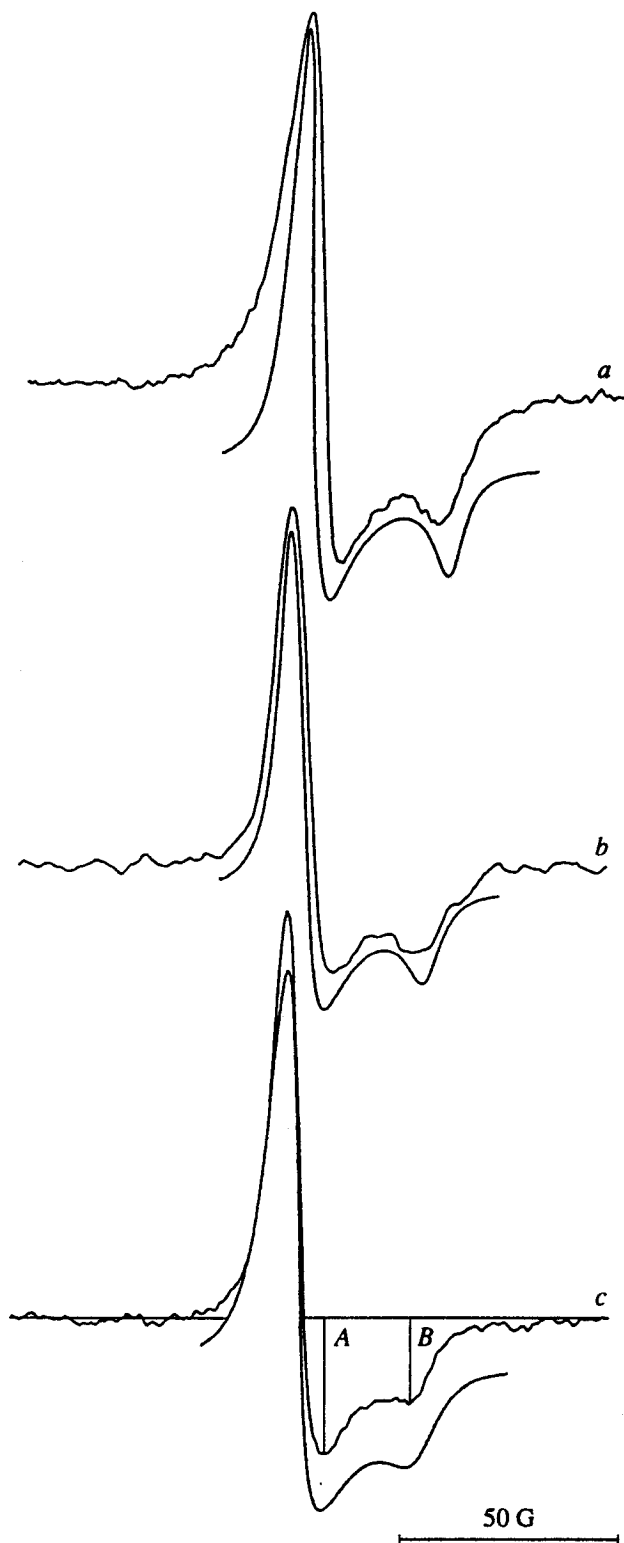


Fig. 1. EPR spectrum of polyaniline in the 250 GHz range at various temperatures: (a) 113, (b) 223, and (c) 290 K. The magnetic field is scanned around the central value of 8.9 T. The parameters *A* and *B* are defined in the bottom spectrum. The simulated spectrum is presented below every experimental spectrum.

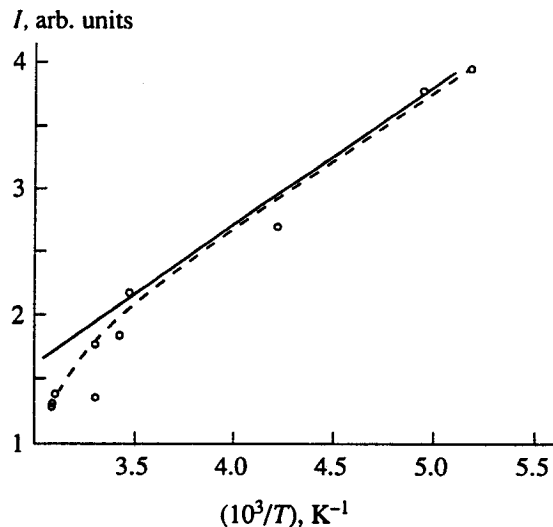


Fig. 2. Temperature dependence of the EPR signal intensity in polyaniline at 250 GHz. The solid line represents the Curie-Weiss law, and the dashed one, the experiment.

ity and, hence, to changes in the EPR line shape. These variations of the line shape with the temperature are shown in Fig. 1. Below each experimental curve is placed a curve obtained by computer simulation. This simulation was based on the Heisenberg model of spin exchange between the paramagnetic centers having axially symmetric *g* tensors [7, 8]. Figure 3 shows the temperature dependence of the *A/B* ratio (these quantities are defined in Fig. 1). The values of the spin exchange constant obtained by the computer simulation are presented in the right-hand part of the figure.

Figure 4 shows the room-temperature EPR spectrum of polyaniline recorded at 170 GHz. One can see that the distance between the maxima *A* and *B* increases linearly with the frequency. Let  $H_A$  and  $H_B$  be the magnetic field values corresponding to the maxima *A* and *B*, respectively. The ratio of the difference  $H_A - H_B$  at 250 GHz to the  $H_A - H_B$  value at 170 GHz is

$$(H_A - H_B)_{250} / (H_A - H_B)_{170} = 1.57,$$

which is close to the ratio  $250/170 = 1.47$ . This supports our suggestion that the splitting of signal can be related to anisotropy of the *g* tensor.

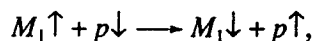
## RESULTS AND DISCUSSION

The results of simulation of the Heisenberg spin exchange are presented in Fig. 1. It can be seen that the description is quite adequate, except for the wings of the lines. From the spectrum obtained at 113 K, we have  $g_{\perp} = 2.0026$  and  $g_{\parallel} = 2.0018$ . The optimum intrinsic linewidth describing the results for all temperatures (113–340 K) is 3.5 G. In the limiting case of solid PA at 250 GHz, the ratio  $A/B = 1.23$ . For a very strong

exchange, this ratio depends on the linewidth and can reach a value of 10, where there is no visible asymmetry (practically, this ratio can acquire any value when the exchange-induced narrowing increases). Experimental points in Fig. 4 correspond to the exchange parameter ranging from  $2 \times 10^7$  l/(mol s) (at 193 K) to  $1.1 \times 10^8$  l/(mol s) (at 323 K).

We propose the following model, which seems to describe the above results in the most adequate way. The model considers the spin carriers in polyaniline belonging to the two main types. The spin carrier of the first type have low mobilities. In this case, the spectrum with well resolved components of the  $g$  tensor of axial symmetry should be observed due to a long relaxation time for these spins. There can exist the second type of spin carriers, representing the conduction polarons. These have a high mobility and can effectively sharpen the EPR lines. The exchange between the spins of two types  $M_1\uparrow$  and  $M_2\downarrow$  is provided by an intermediate polaron  $p\downarrow$  carrying both spin and charge.

The reaction of exchange is described as follows:



The character of the EPR signal produced by polarons is a challenging problem. It is well known that the EPR signal produced by the conduction electrons in real metals is very weak and is lower by two orders of magnitude than the signal from the same number of spins [9]. Moreover, the former signal is represented by a very broad line, which in many cases renders this signal unobservable. We assume that the EPR signal from the conduction polarons is similar to this type of signal: it is very broad and virtually invisible because of the very short spin relaxation time.

Thus, it is possible to suggest that the line narrowing results from the action of intermediate carriers responsible for the conductivity.

There are some other possible explanations of the obtained results. The explanation proposed in [2] suggests the change in the linewidth to result from changes in the spin mobility. The expression presented in [2] leads to another type of the frequency dependence, whereby the linewidth varies with the frequency (in the 10–24 MHz range) as  $\omega^{-1/2}$ , while our results show evidence of the linear frequency dependence of the linewidth. It may be necessary to revise the expression from [2] for higher frequencies. For the expression presented in that paper to be valid, the free path of carriers should be sufficiently high compared to the distance between radicals (i.e., the diffusion approximation is valid provided the path covered by the spin during a time interval of the order of  $1/\Omega$  is longer than the distance between the spins).

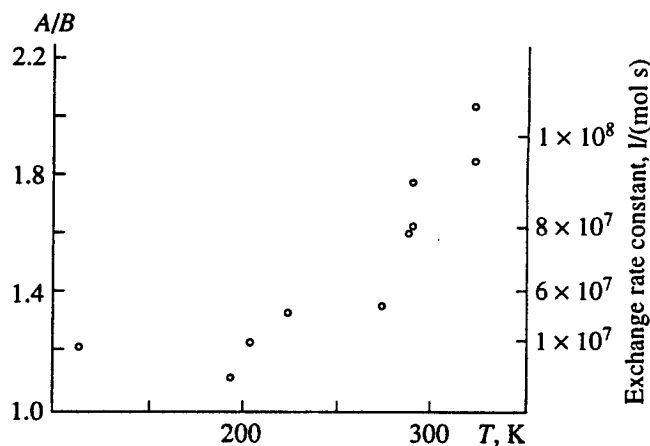


Fig. 3. Temperature dependence of the  $A/B$  ratio (250 GHz) for the polyaniline samples under study. The right-hand scale is in the units of exchange frequency.

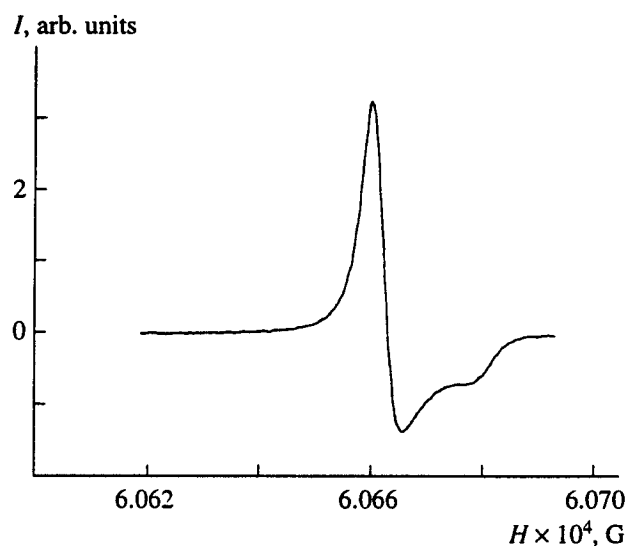


Fig. 4. The EPR spectrum of polyaniline at 170 GHz and 290 K.

The glass transition temperature of polyaniline lies near  $220^\circ\text{C}$  [10]; that is, all our experiments are conducted below the glass transition point, where the  $\alpha$  process responsible for the segmental mobility is frozen [11]. So, we can neglect the averaging of the EPR linewidth resulting from the mobility of molecules carrying the paramagnetic centers (which would sharpen the EPR lines in a liquid).

The EPR linewidth at room temperature is not determined by the unresolved hyperfine structure. This has been demonstrated in [12], where it was found that deuteration does not affect the EPR linewidth. Hence, there is no contradiction in the fact that the anisotropy of  $g$  tensor is manifested with increasing frequency while the anisotropy of hyperfine splitting is not exhibited.

## CONCLUSION

The splitting of the EPR signal of polyaniline is observed at very high frequencies: 170 and 250 GHz. The temperature dependence of the EPR line shape is described within the framework of the mechanism of spin exchange involving conduction polarons as intermediate carriers.

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