

ESR in conducting polymers: Oxygen-induced contribution to the linewidth

E. Houz e and M. Nechtschein

D epartement de Recherche Fondamentale sur la Mati ere Condens ee/Service d'Etude des Structures et Architectures Mol eculaires, Laboratoire de Physique des M etaux Synth etiques, Commissariat   l'Energie Atomique-Grenoble, rue des Martyrs, 38054, Grenoble, Cedex 9, France*

(Received 25 September 1995; revised manuscript received 14 December 1995)

The oxygen-induced ESR line broadening has been investigated in the case of the conducting polymer polyaniline in powder and in film form. Pumping under vacuum results in a narrowing of the ESR linewidth. After initial pumping various oxygen containing gases have been applied to the sample (pure O₂, ambient air, dry air) and the linewidth has been measured as a function of time. The residual water in these gases was found to seriously affect the narrowing behavior of the linewidth. A theoretical calculation is proposed showing that the line broadening is proportional to the oxygen concentration and to the polaron mobility. Considering the linewidth dependence upon applied oxygen pressure an evaluation of the polaron mobility is obtained. This value is consistent with the values estimated from previous spin dynamics studies. An evaluation of the exchange integral is also given. [S0163-1829(96)06021-3]

I. INTRODUCTION

Conducting polymers have been the subject of a considerable amount of work for fifteen years. Among the various techniques of investigation, ESR has been used intensively, since it enables one to directly "see" the polaron, a paramagnetic charge carrier species, which plays a major role in the physics of conducting polymers. The width of the ESR signal is a particularly meaningful parameter: it is directly connected to the interactions of the spins with their environment and to their motion. According to the well known process of motional narrowing, the observation of a narrow line is expected to be an evidence for fast motion. The narrowness of the line should be a measure of the spin mobility. However, besides narrowing, possible processes of line broadening should also be considered. For instance, for a sample left in air, the oxygen contamination results in a line broadening due to magnetic interactions of the polarons with the molecular oxygen triplet state.¹⁻³ The observed linewidth is then the result of competing processes. The purpose of this paper is to specify the various parameters which determine the observed linewidth, paying a special attention to the links between the oxygen-induced line broadening and the motion of the spins.

It has been known for a long time that the ESR signal of the free spins in various compounds is reversibly broadened in the presence of air. As examples we mention (i) free radicals in solution: the resolution of the hyperfine structure is lost if the solution has not been properly degassed,^{4,5} (ii) phtalocyanine radicals such as lithium phtalocyanine,⁶⁻¹¹ (iii) alkali-DCNQI radical ion salts,¹² and (iv) amorphous silicon.¹³ We also mention the effect of oxygen in polyacetylene, which is only partly reversible.^{14,15}

Basically, the ESR line broadening relies on the magnetic interactions of the spins with the triplet state of the molecular oxygen contained in air. However, depending on the compounds, various mechanisms might be involved, and in many cases the broadening mechanism is not actually understood in details.

In this work, we present a comprehensive study of the origins of the ESR linewidth in polyaniline in the presence of oxygen and more generally in conducting polymers. Our notable, and rather unexpected, finding is that the oxygen-induced linewidth increases with the polaron mobility. This is contrary to the case of the motional narrowing, and also to the case of the line broadening of the conduction-electron spin resonance in metals by the Elliott mechanism.¹⁶

The paper is organized as follows. Section II describes the experimental results: the linewidth broadening in the presence of oxygen is thoroughly investigated. It has been known for a long time that oxygen broadens the line. However, the broadening was first believed not to persist, but to "relax" with time. We demonstrate that such a "relaxation" of the broadening is suppressed if stringent experimental conditions are used. In Sec. III, we develop the theory of the line broadening based on polaron-oxygen collisions. We establish that it is proportional to the polaron hopping frequency. Various situations of spin-exchange during the collisions are considered. Utilizations of the theoretical expressions are made in Secs. IV and V for estimating the polaron hopping frequency and the exchange value from the data in polyaniline.

II. EXPERIMENTS

A. Experimental conditions

The samples were powder or thin films of emeraldine salt form of polyaniline prepared by the conventional method developed by MacDiarmid *et al.*¹⁷ and protonated in 1 M HCl aqueous solution. The ESR experiments have been performed with an ER 200 Bruker ESR X band spectrometer. The sample was in a quartz cell placed inside the microwave cavity and connected to a pumping line. The ESR linewidth measurements have been automatized. The ESR linewidth (the full linewidth at half maximum, $\Delta H_{1/2}$, and the peak-to-peak linewidth, ΔH_{pp}) could be recorded as a function of time.

The starting point of the experiment is the following. If one takes a polyaniline sample, that has been left in ambient

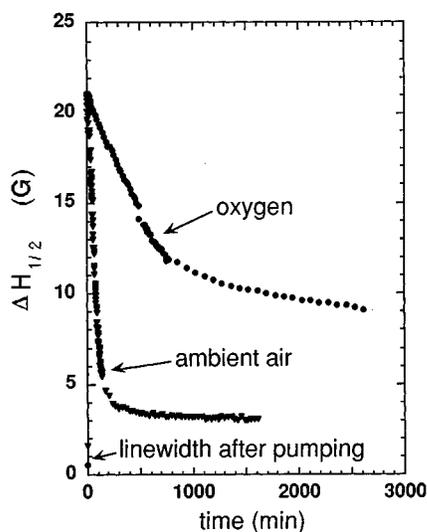


FIG. 1. ESR linewidth (full width at half maximum) of poly-aniline powder as a function of time. The sample is initially pumped under vacuum. At time $t=0$, atmospheric pressure of air, or 150 Torr of oxygen, is introduced.

air for a long time, say several months, its ESR linewidth is typically $\Delta H_{pp} \approx 2$ G. After pumping the sample (primary pumping), the linewidth decreases (in a few seconds for a powder) to $\Delta H_{pp} \approx 0.8$ G. This preliminary experiment gives evidence that ambient air has some broadening effect on the linewidth, since its removal by pumping results in a line narrowing: ΔH_{pp} decreases from 2 to 0.8 G. In the following, we report changes of the linewidth upon application of a gas pressure and as a function of time. The gas is introduced after a pumping stage which can be either short (a few minutes of primary pumping) or stringent (three days of secondary pumping). The linewidth evolution can be quite intricate, depending on the experimental procedure, but, at any time, pumping the sample always restores essentially the same value for the linewidth under vacuum. This is evidence that the various effects are reversible.

B. Summary of known results

Let us recall the results which have been previously obtained.^{1,18} After a short pumping stage (a few minutes of primary pumping), the sample was opened to the following gases: ambient air, N_2 and O_2 . Data of the linewidth versus time are shown in Fig. 1 for powder. The data of the film are presented in Ref. 1.

1. Effect of ambient air

After opening of the pumped sample tube to ambient air, one observes a fast increase of the linewidth (in a few seconds for the powder, in a few minutes for the film). Surprisingly, the linewidth reaches a much larger value than that of the sample left in ambient air for a long time. After this increase stage, a slow decay of the linewidth occurs. It can be qualitatively described with two characteristic times $\tau_a \approx 3$ hours and $\tau_b \approx 1$ day.

2. Effect of N_2

Opening the pumped sample to a given pressure of N_2 , the narrow line remains unchanged: $\Delta H_{pp} \approx 0.8$ G. N_2 seems to have no effect on the linewidth. Indeed, this behavior is consistent with the diamagnetic nature of the nitrogen molecules.

3. Effect of O_2

At $t=0$, the pumped sample is opened to an oxygen pressure: $P_i = 150$ Torr, i.e., the partial pressure of O_2 in air (in all the following the subscript i stands for "impurity"). The linewidth increases fast to the same value as with air. Then, the linewidth decays with time but significantly slower than with air. The decay can be qualitatively described with a single characteristic time of about 1 day; that is about the same as for the slow decay in ambient air.

4. Discussion

The broadening observed with O_2 and ambient air is due to the arrival of oxygen molecules into the polymer matrix. The large broadening observed is evidence that the magnetic interactions between polyaniline spins (polarons) and oxygen molecules ($S=1$) are strong and therefore that the oxygen molecules succeed well in coming close to the polarons. This can be visualized by the picture of a given O_2 molecule occupying an "active site" where a strong coupling exists between the spin of a polaron and the spin of the O_2 triplet state (whatever this coupling is exchange or dipole-dipole interaction).

The mechanism responsible for the linewidth decay remained unclear to us for a long time. In particular, the difference of behavior upon exposure to air or to oxygen was quite intriguing. Since N_2 seems at first to have no effect on the linewidth, the behavior with air ($O_2 + N_2$) would therefore have been expected to be essentially the same as with O_2 (using the same partial pressure). We proposed¹⁸ an explanation for the difference of behavior in the presence of air or oxygen in terms of a scenario of competition between O_2 and N_2 . Upon a sudden application of air, the O_2 molecules would arrive first at the active centers (hence the fast increase of the linewidth), and then would be progressively replaced by the N_2 molecules, according to their ratio in air (hence the slow decay). This assumption was consistent with the fact that upon application of oxygen alone, the decay with $\tau_a \approx 3$ h was not observed. However, this assumption failed in two respects. First, it did not explain the slow decay ($\tau_b \approx 1$ day), which remains in presence of oxygen alone. Second, it was postulated that the number of available sites was limited (so that, as they arrive, the nitrogen molecules have to expel the oxygen ones). But there is an evidence that only a small part of the active sites are occupied by the oxygen molecules. This is shown in Fig. 2, in which ΔH is given as a function of oxygen pressure. No significant saturation effect in the line broadening versus oxygen pressure appears for P_i close to the ambient pressure. In this range of pressures, there is thus plenty of sites available for gas molecules. The nitrogen molecules, when they arrive, need not to expel oxygen. Consequently, we came to the conclusion that the proposed assumption was incorrect. Moreover, the lack of competition between O_2 and N_2 allows us to explain

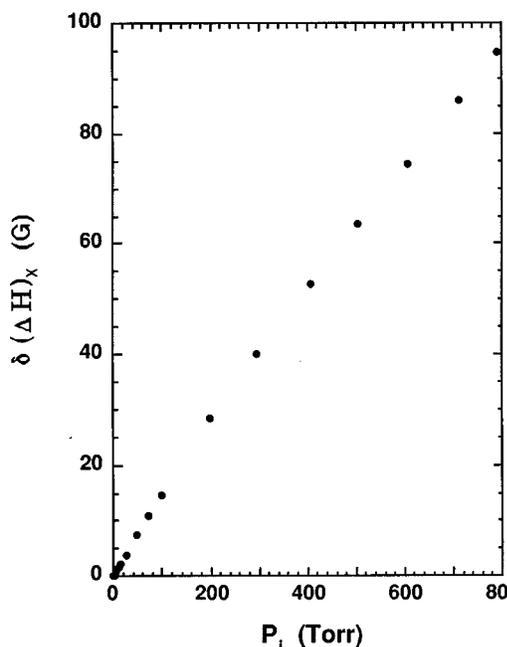


FIG. 2. ESR broadening (full width at half maximum) of polyaniline powder as a function of the applied oxygen pressure.

the same initial linewidth increase observed with ambient air and with $P_i=150$ Torr of O_2 : the presence of diamagnetic molecules (here the nitrogen molecules) does not prevent the oxygen molecules from reaching the active sites.

C. Effect of stringent drying

1. Effect of pumping conditions

In our previous reports,^{1,18} pumping over the sample meant a few minutes of primary pumping: for the reversibility of the observed phenomena it was indeed sufficient for coming back to the narrow line ($\Delta H_{pp} \approx 0.8$ G). Nevertheless, we decided to investigate the effect of the pumping conditions. A more drastic pumping was used: secondary pumping for three days. This led to a narrower line: $\Delta H_{pp} \approx 0.7$ G. Then an O_2 pressure of $P_i=150$ Torr was applied (at $t=0$). The linewidth change versus time is shown in Fig. 3(a).

At first, there is a rapid increase of the linewidth to $\Delta H_{pp}=13$ G. Then, the linewidth remains constant: *no significant decay was observed*. We were therefore led to the conclusion that, after the long pumping process, something had been eliminated from the polymer matrix, which was responsible for the linewidth decay previously observed. It is quite reasonable to conclude that this is water. Polyaniline is known to be very avid of water, and extracting all the water molecules from polyaniline has been shown to require a drastic pumping.^{19,20}

We are thus led to the conclusion that the presence of residual water molecules was responsible for the decay of the linewidth after exposure to oxygen.

2. Effect of air drying

Considering the fact that ambient air also contains some moisture, we decided to introduce dry air (ambient air passed

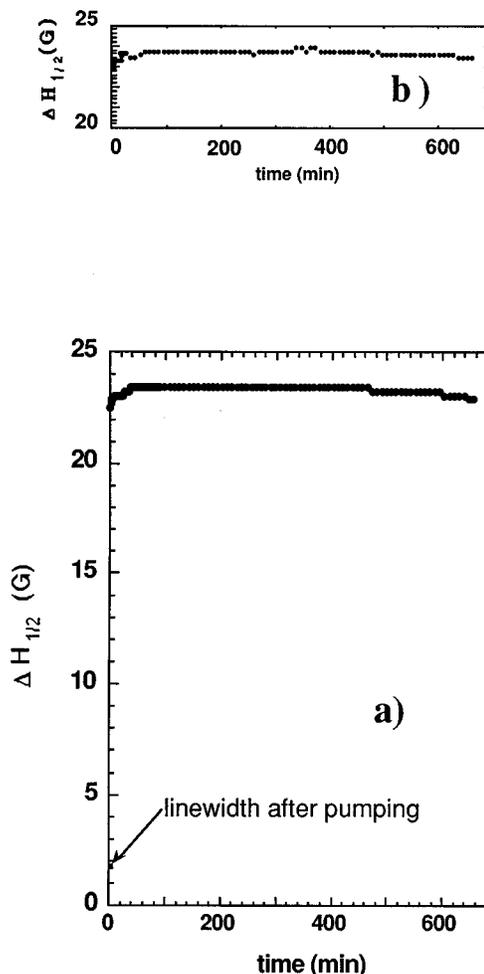


FIG. 3. ESR linewidth (full width at half maximum) of polyaniline powder as a function of time. The sample is initially pumped for three days under secondary vacuum. At time $t=0$, a pressure of 150 Torr of oxygen (a), or dried air (b), is introduced.

through a column of KOH) on the sample which had been previously pumped as explained in Sec. II C 1. The behavior was exactly the same as the one obtained with oxygen: first, the linewidth increased very fast to $\Delta H_{pp}=13$ G; then, it remained constant. See Fig. 3(b).

This experiment clearly proves that N_2 has no influence on the linewidth behavior. It shows that the linewidth decay observed with ambient air was due to water molecules as for the case of oxygen.

The two characteristic times observed in the case of ambient air, $\tau_a \approx 3$ h and $\tau_b \approx 1$ day, can be explained in terms of two water reservoirs: (a) water molecules contained in ambient air, and (b) residual water molecules in the polymer matrix, corresponding to the time constants τ_a and τ_b , respectively. In the case of oxygen applied after primary pumping only the process with $\tau_b \approx 1$ day is left.

What is the mechanism for the linewidth narrowing in presence of water? One can imagine that, through hydrogen bonds, H_2O molecules can be more intimately tied to the chain than O_2 . They can thus have a shielding effect between O_2 and polarons, resulting in a decrease of the magnetic interaction and, consequently, in a narrowing of the line. The decay time constants are representative of the time for the

H₂O molecules to reach the active sites. A microscopic picture of the water action has not yet been elaborated.

III. THEORY

As previously emphasized, the oxygen-induced line broadening relies on the magnetic interactions of the spins of the sample with the triplet state of the molecular oxygen. These interactions can be either dipole-dipole or exchange coupling. In this work only the latter will be considered.

A. Collision and exchange frequencies

Let us consider two mobile paramagnetic species A and B with spins S_A and S_B , respectively. They have two different Larmor frequencies ω_{0A} and ω_{0B} corresponding to the gyromagnetic ratios γ_A and γ_B , respectively. The difference between the Larmor frequencies will be denoted by $\delta\omega_0 = |\omega_{0A} - \omega_{0B}|$, and the spin-lattice relaxation of A (resp. B) by T_1^A (resp. T_1^B). The two species undergo collisions during which they interact through exchange coupling. Our aim is to determine the ESR linewidth of species A , taking into account the collision and exchange processes with the B species. Keeping in mind that the exchange integral drops off very rapidly with increasing distance we assume that the exchange is only efficient during the collision duration, t_c . Let us denote by J the value of the exchange integral during this time. Following the usual formalism developed for the description of spin exchange between paramagnetic species in solution,²¹⁻²³ we introduce the following quantities.

The *collision frequency* ω_{cA} is defined for A as the frequency of collision of a given A particle against any B particle. We only take into account the nonidentical particle collisions (i.e., collisions between A and B) since they are much more efficient in line broadening. For a given A particle the probability to collide with a B particle is proportional to the concentration C_B of B in the solution and to the relative mobility of the particles. Its collision frequency ω_{cA} (resp. ω_{cB}) is then written as

$$\omega_{cA} = K_d C_B, \quad (3.1)$$

where K_d is a characteristic diffusion frequency. A collision frequency, ω_{cB} , can be symmetrically defined for B as

$$\omega_{cB} = K_d C_A. \quad (3.2)$$

The value of K_d depends on the relative motion of the particles. In a liquid, if the displacement λ of a particle during an elementary diffusion step is less than the effective radius r_i of the spin-exchange region, it has been shown²⁴ that $K_d = 4\pi D r_i$ where $D = D_A + D_B$ is the sum of the diffusion coefficients of the colliding partners. As $D \propto 1/\eta$, where η is the viscosity of the solvent, K_d is inversely proportional to the viscosity of the solvent. In our system (polyaniline in the atmosphere of oxygen), the polarons are hopping from site to site with a frequency ω_{hop} and they collide with the oxygen molecules adsorbed on active sites. Whereas the polarons are mobile, the oxygen molecules can be considered as fixed. Thus, if the exchange interaction region is limited to one unit cell (one aniline ring), one can write

$$K_d = \omega_{\text{hop}}. \quad (3.3)$$

The *exchange frequency*, ω_{xA} , represents the flip-flop frequency of the spin of a given A particle due to its collisions with the B spins. This exchange frequency can be written as $\omega_{xA} = p_A \omega_{cA}$, where p_A is the flip-flop probability during a collision. The following expression is therefore obtained:

$$\omega_{xA} = p_A K_d C_B. \quad (3.4)$$

An *exchange frequency*, ω_{xB} , can be symmetrically defined for B as

$$\omega_{xB} = p_B K_d C_A. \quad (3.5)$$

B. Different exchange situations

Depending on the relative values of $\delta\omega_0$, T_1^B , ω_{xA} , and ω_{xB} on the one hand, J and t_c on the other hand, several situations should be distinguished: separate spins versus single spin reservoir case and weak versus strong exchange.

1. Separate spins versus single spin reservoir

According to the value of the exchange-induced flip-flop frequency ω_x ($\omega_x = \omega_{xA}$ or ω_{xB}) compared to $\delta\omega_0$ or T_1^B , one can deal with the two cases as follows.

Case of separate spins. For two species having short spin-lattice relaxation rates $1/T_1^{A,B}$ compared to $\delta\omega_0$ (like free radicals in solution), two separate spin reservoirs can be defined if $\max\{\omega_{xA}, \omega_{xB}\} \leq \delta\omega_0$ (slow exchange). However, if one of the partners (for instance B) can be considered as a diluted species in the sea of the majority species (A) ($C_B \ll C_A$) and, moreover, has a relaxation time T_1^B so short that the condition $\delta\omega_0 \leq 1/T_1^B$ is satisfied, the separate spins condition has to be written $\omega_{xB} \ll 1/T_1^B$.²⁶ Indeed, the B spins then appear for the A spins as if they were always in thermal equilibrium with the lattice. They have therefore to be treated as two different kinds of spins even if the condition $\max\{\omega_{xA}, \omega_{xB}\} \leq \delta\omega_0$ is satisfied. Under the separate spins condition the lines of the two partners broaden independently.

Case of single spin reservoir. The condition for having one single spin reservoir can be written as $\max\{\omega_{xA}, \omega_{xB}\} \geq \delta\omega_0$ (fast exchange) and $\omega_{xB} \gg 1/T_1^B$. This condition leads to the well known exchange narrowing phenomenon: the lines of the two paramagnetic species merge into one single narrow line at the center of the spectrum.²⁵

These results can be obtained by a statistic approach based on a Markovian frequency migration process,²⁵ or by a quantum calculation of the second and fourth moments. Let us recall briefly the basic ideas of the latter, in order to clarify the physical process which governs the line broadening or narrowing. The contribution of the exchange Hamiltonian $\mathcal{H}_x = -J \mathbf{S}_A \cdot \mathbf{S}_B$ to the second and fourth moments is given by

$$M_2 = -\frac{1}{\hbar^2} \frac{\langle [\mathcal{H}, S^x]^2 \rangle}{\langle S^x^2 \rangle},$$

$$M_4 = \frac{1}{\hbar^4} \frac{\langle [\mathcal{H}, [\mathcal{H}, S^x]]^2 \rangle}{\langle S^x^2 \rangle}, \quad (3.6)$$

where

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_x,$$

$$\mathcal{H}_A = -\gamma_A H_0 S_A^z - \gamma_A H_1 S_A^x, \quad (3.7)$$

and

$$\mathcal{H}_B = -\gamma_B H_0 S_B^z - \gamma_B H_1 S_B^x. \quad (3.8)$$

H_0 and H_1 are the static and alternating fields, respectively.

Let us describe briefly the moment approach.²⁵ From the above expressions of M_2 and M_4 , it is clear that when the moment of a resonance line is computed, only those spins which participate in that particular resonance should be included in the transverse magnetic moment S^x . Note that \mathcal{H}_x commutes with the total spin $S^x = S_A^x + S_B^x$ but not with the individual spins S_A^x and S_B^x . In the separate spins case, we have to consider $[\mathcal{H}_x, S_A^x]$ and $[\mathcal{H}_x, S_B^x]$, independently, which have nonzero values. It follows therefore that exchange contributes to M_2 of each resonance line and hence to their linewidth. Each resonance is broadened by exchange with the other one.

In contrast to this case, for the single spin reservoir, the spins are indistinguishable. We have therefore to consider $[\mathcal{H}_x, S^x]$ where $S^x = S_A^x + S_B^x$. Since $[\mathcal{H}_x, S^x] = 0$, the exchange Hamiltonian does not contribute to M_2 ; however, owing to crossed terms like $[\mathcal{H}_x, [\mathcal{H}_A, S^x]]^2$ or $[\mathcal{H}_x, [\mathcal{H}_B, S^x]]^2$, the exchange Hamiltonian contributes to M_4 . As a consequence, the narrowing phenomenon is observed.²⁵

This interpretation has been extensively developed by Gulley and Jaccarino in their studies of the bottleneck effect in exchange-coupled paramagnets.²⁶

2. Weak versus strong exchange

Two limiting cases must be considered depending on the value of the exchange time $(J/\hbar)^{-1}$ as compared to the collision duration t_c .

Strong exchange: $(J/\hbar)t_c \gg 1$. Many flip-flops can proceed during a collision. It will be shown in the next paragraph that this condition leads to flip-flop probabilities p_A and p_B which are independent of J and t_c . The exchange frequencies are then given by

$$\omega_{xA} = p_A K_d C_B \propto K_d C_B,$$

$$\omega_{xB} = p_B K_d C_A \propto K_d C_A. \quad (3.9)$$

In the case of strong exchange, an increase of K_d leads therefore to an increase of the exchange frequency.

Weak exchange: $(J/\hbar)t_c \ll 1$. The flip-flop probability during a collision is now dependent on J and t_c . More precisely, it can be shown that this condition leads to flip-flop probabilities p_A and p_B proportional to $J^2 t_c^2$. Moreover, assuming that the collision duration t_c is given in terms of the characteristic time of diffusion, we can write

$$t_c \propto \frac{1}{K_d}. \quad (3.10)$$

The exchange frequencies are then given by

$$\omega_{xA} = p_A K_d C_B \propto J^2 \frac{C_B}{K_d},$$

$$\omega_{xB} = p_B K_d C_A \propto J^2 \frac{C_A}{K_d}. \quad (3.11)$$

In the case of weak exchange, an increase of K_d may result in a decrease of the exchange frequency. Studying the evolution of the exchange frequency in terms of the characteristic diffusion frequency (solvent viscosity or spin hopping frequency) should therefore be a means of discriminating between weak and strong exchange.

C. ESR linewidth and exchange

In the following, we develop a calculation of the exchange contribution to the linewidth under assumptions corresponding to our experimental conditions.

1. Physical assumptions

The spin exchange leads to a line broadening. Two separate spin reservoirs can therefore be considered.

To make the detailed calculation, we take $S_A = 1/2$ (polaron spin) and $S_B = 1$ (oxygen molecule spin).

The solution is considered to be dilute so that the time between two collisions is long compared to the collision duration; that is, $1/\omega_{cA}$ and $1/\omega_{cB} \gg t_c$. This assumption will permit a one-particle description.

The exchange integral J is constant during the collision duration.

In view of the instantaneous nature of the collision, all interactions except exchange in the evolution operator can be neglected. In the case of a fast relaxing impurity B , this assumption implies that $T_1^B \gg \tau_c$ so that the spin-lattice relaxation of B during the collision can be neglected.

2. Calculation

The calculation is based on a one particle description using the density matrices ρ_A and ρ_B . The equations of evolution have the general form

$$\frac{\partial \rho}{\partial t} = -i\hbar^{-1}[\rho, \mathcal{H}] + \Gamma(\rho - \rho^0) + \Phi(\rho), \quad (3.12)$$

where \mathcal{H} is the total spin Hamiltonian of the particle allowing for interaction with the static field H_0 and the alternating field H_1 , ρ^0 is the equilibrium density matrix, $\Gamma(\rho - \rho^0)$ is the relaxation matrix, and $\Phi(\rho)$ is the collision term describing the effect of Heisenberg exchange (exchange relaxation matrix). In this calculation we are only interested in the influence of exchange on the density matrix evolution: the relaxation matrix Γ will therefore be ignored. Moreover, the collision term will only take into account the nonidentical particle interactions (i.e., interactions between A and B). Just after the beginning of the collision, the density matrix of the colliding particle complex $A-B$ is represented by the external product $\rho_A \otimes \rho_B$. At the end of the collision, the density matrix $\rho_A \otimes \rho_B$ has become $U\rho_A \otimes \rho_B U^{-1}$, where U is the Heisenberg evolution operator $U = \exp[-i(J/\hbar)\mathbf{S}_A \cdot \mathbf{S}_B t_c]$. Then the A particle density matrix after collision is $\rho_A(t_c) = \text{Tr}_B(U\rho_A \otimes \rho_B U^{-1})$ where Tr_B is the trace in the B

spin space. The latter expression must be averaged over the collision duration distribution. For the general case, the averaging can be carried out if we assume, as in the liquid case, that the distribution of collision times obeys the law of radioactive decay $P(t_c) = (1/t_w) \exp[-(t_c/t_w)]$, where t_w is the width of the duration distribution. The A particle density matrix can finally be written after the collision as $\overline{\text{Tr}_B(U\rho_A \otimes \rho_B U^{-1})}$, where $\overline{(\dots)}$ denotes the average over the t_c distribution. For the B particle matrix there is an analogous expression. Then equations for the density matrices can be written as

$$\begin{aligned} \frac{\partial \rho_A}{\partial t} &= -i\hbar^{-1}[\rho_A, \mathcal{H}_A] + \frac{\overline{\text{Tr}_B(U\rho_A \otimes \rho_B U^{-1})} - \rho_A}{t_A}, \\ \frac{\partial \rho_B}{\partial t} &= -i\hbar^{-1}[\rho_B, \mathcal{H}_B] + \frac{\overline{\text{Tr}_A(U\rho_A \otimes \rho_B U^{-1})} - \rho_B}{t_B}. \end{aligned} \quad (3.13)$$

$t_A(t_B)$ is the mean time between collisions of an $A(B)$ particle against a $B(A)$ particle. Accordingly with Eqs. (3.1) and (3.2), one can write

$$\begin{aligned} \frac{1}{t_A} &= \omega_{cA} = K_d C_B, \\ \frac{1}{t_B} &= \omega_{cB} = K_d C_A. \end{aligned} \quad (3.14)$$

The A resonance line is proportional to $\langle M_A^y \rangle = \text{Im}[\text{Tr}(\rho_A M_A^+)]$, where M_A is the A species magnetization and $M_A^+ = M_A^x + iM_A^y$. According to the assumption of separate spin reservoirs, the lines of the two species are indeed broadened independently. The B magnetization therefore gives no contribution to the A resonance line.

Remembering that $S_A = 1/2$, we obtain

$$\langle M_A^y \rangle = \left\langle -\frac{1}{2} \rho_A \left| \frac{1}{2} \right\rangle \right\rangle = \rho_{-1/2,1/2}^A. \quad (3.15)$$

The problem is now to calculate $\partial \rho_{-1/2,1/2}^A / \partial t$. The equation giving $\partial \rho_A / \partial t$ will be projected on the bra $\langle -\frac{1}{2} |$ and on the ket $| +\frac{1}{2} \rangle$. When carrying out this projection on U or U^{-1} , it is necessary to pass from individual to total spin, $S = S_A + S_B$, representation. As the state of total spin is the eigenstate of the operator $\mathbf{S}_A \cdot \mathbf{S}_B$, one has

$$\exp\left(\pm i \frac{J}{\hbar} \mathbf{S}_A \cdot \mathbf{S}_B t_c\right) |S\lambda\rangle = \exp\left(\pm i \frac{J}{\hbar} t_c q_S\right) |S\lambda\rangle, \quad (3.16)$$

where S, λ are the total spin of the colliding complex and its projection

$$q_S = \frac{1}{2} [S(S+1) - S_A(S_A+1) - S_B(S_B+1)]. \quad (3.17)$$

After carrying out the projection, we obtain

$$\begin{aligned} \frac{\partial \rho_{-1/2,1/2}^A}{\partial t} &= \rho_{-1/2,1/2}^A \left[-i\gamma_A H_0 + \frac{16}{27} K_d C_B \right. \\ &\quad \left. \times \left(-1 + \cos\left(\frac{3Jt_c}{2\hbar}\right) \right) \right] - H_1 M_A^0, \end{aligned} \quad (3.18)$$

where M_A^0 is the equilibrium magnetization of the A spins.

The variation of $\rho_{-1/2,1/2}^A$ due to spin exchange $(\partial \rho_{-1/2,1/2}^A / \partial t)_x$ is given by

$$\left(\frac{\partial \rho_{-1/2,1/2}^A}{\partial t} \right)_x = -\frac{16}{27} K_d C_B \rho_{-1/2,1/2}^A \left(1 - \cos\left(\frac{3Jt_c}{2\hbar}\right) \right). \quad (3.19)$$

We thus obtain the expression of the linewidth broadening due to exchange,

$$\delta(\Delta\omega)_x = \frac{16}{27} \frac{9 J^2}{4 \hbar^2} \frac{t_w^2}{1 + \frac{9 J^2}{4 \hbar^2} t_w^2} K_d C_B. \quad (3.20)$$

Remembering the general form of ω_{xA} given by Eq. (3.4), $\omega_{xA} = p_A K_d C_B$, one has

$$\delta(\Delta\omega)_x = \omega_{xA} \quad (3.21)$$

and

$$p_A = \frac{16}{27} \frac{9 J^2}{4 \hbar^2} \frac{t_w^2}{1 + \frac{9 J^2}{4 \hbar^2} t_w^2}. \quad (3.22)$$

In the case of weak exchange $Jt_w \ll 1$, we have $p_A \propto J^2 t_w^2$ as described previously. In the case of strong exchange $Jt_w \gg 1$, $p_A = 16/27$, which is independent of J and t_w .

IV. ESR LINEWIDTH AND POLARON HOPPING FREQUENCY

As shown in the previous section [Eq. (3.20)] the oxygen-induced linewidth $\delta(\Delta\omega)_x$ is directly connected to the characteristic diffusion frequency K_d and therefore, in our system, to the polaron mobility [Eq. (3.3)]. The aim of the present section is to take advantage of this connection to obtain a quantitative estimate of the polaron hopping frequency in polyaniline.

Polaron and oxygen spins can be considered as corresponding to spin systems A and B , respectively, and they are assumed to fulfill the conditions stated in Sec. III C 1. The oxygen-induced linewidth is then given by

$$\delta(\Delta\omega)_x = p \omega_{\text{hop}} C_i, \quad (4.1)$$

where ω_{hop} is the polaron hopping frequency, C_i the oxygen concentration (per aniline ring), and $p = p(J, t_w)$ is the spin flip-flop probability during a collision, which depends on the amplitude of exchange during collisions J , and on the characteristic collision duration t_w ,

$$p = \frac{16}{27} \frac{\alpha^2}{\alpha^2 + 1}, \quad (4.2)$$

with

$$\alpha = \frac{3}{2} \frac{J}{\hbar} t_w.$$

The ESR linewidth has been measured as a function of the oxygen pressure. The data are presented in Fig. 2. It appears that the linewidth increase is essentially linear with the oxygen pressure. Besides, the mass uptake of polyaniline samples as a function of the oxygen pressure has been measured by Rebattet *et al.*²⁷ The oxygen adsorption isotherms are also linear functions of the oxygen pressure, at least to a first order approximation [see Fig. 4(a)]. Rebattet's data enable us to convert the data of linewidth versus pressure into data of linewidth versus concentration, as shown in Fig. 4(b). Denoting by m the slope of the linewidth versus concentration, from Eq. (4.1) one has

$$\gamma m = p \omega_{\text{hop}}, \quad (4.3)$$

where γ is the electronic gyromagnetic ratio.

A fit of the data in Fig. 4(b) with a straight line gives

$$p \omega_{\text{hop}} \approx 4 \times 10^{11} \text{ rad/s}. \quad (4.4)$$

Generally speaking, p is a function of the characteristic collision duration t_w [cf. Eq. (4.2)] and therefore of ω_{hop} if we assume that $t_w \propto 1/\omega_{\text{hop}}$. However, according to Eq. (4.2), this function is limited [$0 < p(t_w) \leq \frac{16}{27}, \forall t_w$]. Equation (4.4) therefore gives

$$\omega_{\text{hop}} \geq 6 \times 10^{11} \text{ rad/s}. \quad (4.5)$$

Such a value is quite consistent with the values estimated from previous spin dynamics studies.²⁸ For the diffusion rates D_{\parallel} and D_{\perp} , along and perpendicular to chains, respectively, the following values have been found:

$$D_{\parallel} \approx 10^{12} - 10^{13} \text{ rad/s}$$

and

$$D_{\perp} \approx 10^{11} \text{ rad/s}.$$

For a comparison with the present determination based on polaron collisions against adsorbed oxygen molecules the relevant diffusion rate to be considered is more likely D_{\parallel} . Taking $\omega_{\text{hop}} = D_{\parallel}$, Eq. (4.4) gives an estimate for the spin flip efficiency factor:

$$p \approx 0.04 - 0.4, \quad (4.6)$$

which is near the strong exchange limit ($p = 16/27 \approx 0.6$). This relation will be discussed in more detail in the next section.

It is noteworthy that the mass uptake measurements by Rebattet are concerned with the total oxygen adsorbed in the polymer sample, while ESR linewidth is only sensitive to oxygen molecules whose spins can undergo a coupling with polarons. It has not been proved that all adsorbed oxygen molecules actually contribute to the linewidth. However, we have obtained other results, which are consistent with the assumption that all oxygen molecules adsorbed in the polymer participate to the linewidth broadening. A set of polyaniline samples containing various known amounts of Fe^{3+} in the dopant counterion has been prepared. It turns out that

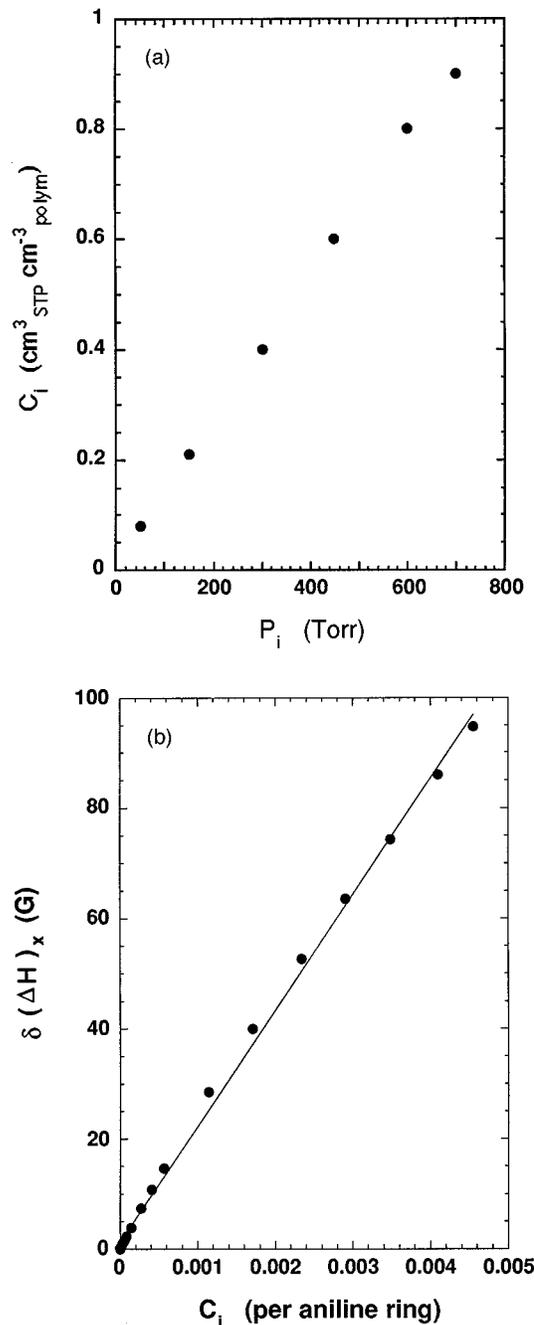


FIG. 4. (a) Sorbed oxygen concentration in polyaniline powder as a function of the applied oxygen pressure. (b) ESR line broadening (full width at half maximum) of polyaniline powder as a function of the sorbed oxygen concentration.

the linewidth increase is proportional to the Fe^{3+} concentration with a slope quite consistent with that obtained with oxygen.²⁹

V. EXCHANGE FREQUENCY AND EXCHANGE AMPLITUDE: DISCUSSION

It has been described in Secs. III and IV that for the efficiency of polaron-oxygen collisions in broadening, the line depends on the exchange amplitude during the collisions and on the duration of the collision. In a more general way,

in this section, we envisage the different possible situations for the polaron-oxygen exchange. Namely, on the one hand, the oxygen and polaron spins can be separated or included in a single reservoir, depending on the value of the exchange frequency compared to their Larmor frequency difference and to their spin-lattice relaxation rates; on the other hand, the collision can be strong or weak, depending on whether the lifetime of the spin pair entity formed during the collision is long enough to permit, or not, well defined exchange energy levels.

A. Separate spins versus single spin reservoir

1. Preliminary discussion

In the separate spins and single spin reservoir conditions, the leading terms are the exchange frequencies ω_{xA} , ω_{xB} of the two colliding spins, their spin-lattice relaxation rates $1/T_1^{A,B}$, and their Larmor frequency difference $\delta\omega_0$. In our case, the latter is not clearly known. Indeed, whereas the polaronic ESR spectrum consists of one line at $g \approx g_e$ (g_e is the free electron g factor), the gaseous oxygen spectrum contains many lines associated with transitions between rotational levels of the molecule.^{30–32} As for the adsorbed oxygen no line has been specifically observed, and $\delta\omega_0$ is unknown. However, we know that the gaseous oxygen spectrum broadens drastically for $P_i > 5$ Torr: under this pressure, the rotational lines rapidly overlap leading to one single very broad line. In the adsorbed state, the symmetry lowering leads to even broader lines. We are therefore led to assume that the adsorbed oxygen molecules have a spin-lattice relaxation rate $1/T_1^i$ so fast that the condition $1/T_1^i > \delta\omega_0$ is satisfied. Moreover, the adsorption isotherms [Fig. 4(a)] indicate that the oxygen concentration C_i is very low: $C_i \leq 0.005$ in the whole pressure range ($0 \leq P_i \leq 1$ bar). The oxygen molecules can therefore be considered as fast-relaxing impurities in a polaronic sea.

2. Separate spins versus single spin reservoir

Let us, first, recall the experimental data: (i) the polaron line is broadened in the presence of oxygen, the broadening being essentially proportional to the oxygen pressure and (ii) no line shift has been observed, even at high oxygen pressure (1 bar).

From these results, it is clear that the oxygen and polaron spins belong to separate reservoirs. As the oxygen molecules can be considered as fast relaxing impurities, the separate spins condition has to be written

$$\omega_{xi} \ll \frac{1}{T_1^i}, \quad (5.1)$$

where ω_{xi} is the oxygen exchange frequency. According to Eqs. (3.4) and (3.5),

$$\frac{\omega_{xp}}{\omega_{xi}} \sim \frac{C_i}{C_p}, \quad (5.2)$$

where ω_{xp} and C_p are the polaron exchange frequency and concentration, respectively. Since $\omega_{xp} = \delta(\Delta\omega)_x$ [see Eq. (3.21)], the separate spins condition (5.1) becomes

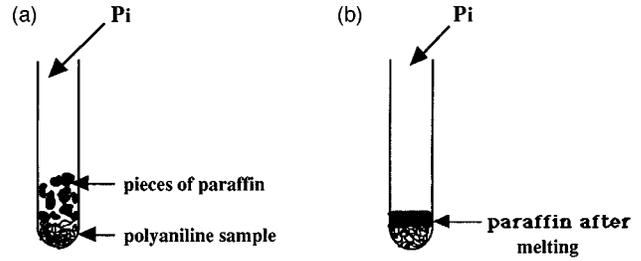


FIG. 5. An experiment to test a relaxation process via oxygen gas. (a) Oxygen gas at pressure P_i is applied on the sample; (b) the melted paraffin isolates the sample from the oxygen gas.

$$\frac{C_p}{C_i} \delta(\Delta\omega)_x \ll \frac{1}{T_1^i}. \quad (5.3)$$

This condition is all the more drastic as the oxygen pressure increases. At $P_i = 1$ bar, $C_p/C_i \approx 10$ and $\delta(\Delta\omega)_x \approx 100$ G; this yields $T_1^i \leq 10^{-10}$ s. It implies a strong relaxation mechanism for the oxygen spins. Different possible cases can be conceived to explain such an efficient relaxation process.

In the case of the relaxation via oxygen gas, the sample is surrounded by oxygen molecules in the gas state at a given pressure. They collide each other at a rate given by the gas kinetics theory. It is known that the molecule collisions govern the spin relaxation in the gas state. This process is so efficient that the ESR spectrum broadens drastically for $P_i > 5$ Torr. One possibility to envisage is that the relaxation in the gas state is the primary source which induces the relaxation in the solid state via collisions of the gas molecules against the surface. In order to test such a process we have carried out an experiment, which enables us to suppress the presence of gas oxygen around the sample. This was obtained by covering the sample with cuttings of paraffin. After melting the paraffin the sample was isolated from the gas reservoir (see Fig. 5). The polaron linewidth has been measured before and after this process. No change has been observed. Therefore, it seems that the presence of an oxygen gas reservoir is not required for the relaxation of the sorbed oxygen spins.

In the case of the relaxation by oxygen-oxygen collisions in the solid state, the relaxation originates from the collisions between adsorbed oxygen molecules. Let us evaluate the efficiency of such a relaxation process. The mean time τ between two collisions depends on the mean free path λ and on the diffusion coefficient D through the relation

$$\tau = \frac{\lambda^2}{D}. \quad (5.4)$$

According to the adsorption isotherms $C_p/C_i \approx 10$ at $P_i = 1$ bar; as the polaron concentration in polyaniline is $C_p \approx 0.05$ (1 polaron per 20 unit cells, i.e., aniline ring), two oxygen molecules are separated by 200 rings at this pressure. Taking the length d of a cycle as 5 \AA and assuming that $\lambda = 200d$, τ can be calculated using the value of the diffusion coefficient given by Rebattet *et al.*:²⁷ $D = 123 \text{ cm}^2/\text{s}$. The result is

$$\tau \approx 8 \times 10^{-2} \text{ s.}$$

Assuming that all the collisions lead to a flip-flop of the spins, one should have

$$T_1^i = \tau. \quad (5.5)$$

The value obtained for T_1^i is then much too large to satisfy the condition (5.3). Although the previous calculation is quite rough, it does not seem possible to obtain values of T_1^i as short as required by (5.3) by a relaxation process through collisions.

Since the oxygen-oxygen collisions, either in the solid state or via the gas state, seem not to be sufficient to explain the fast relaxation process, we are led to propose that this process is induced by the spin-orbit coupling of adsorbed oxygen molecules.

B. Estimate of the polaron-O₂ exchange integral

From Eq. (3.22) and with Eq. (4.6) the exchange during the polaron-oxygen collisions can be estimated

$$\frac{Jt_w}{\hbar} \sim 0.2 - 1. \quad (5.6)$$

Preliminary data in samples of different conductivities show that the linewidth varies like the conductivity, consistently with the strong exchange limit.³³ Besides, assuming that the polaron motion is not disturbed by the presence of oxygen molecules, we can conclude that the collision duration is governed by the polaron diffusion. Polarons are usually described as quasiparticles extended over L lattice units. As their motion is a random walk along the chain, they spend a time $t_w \approx L^2/\omega_{\text{hop}}$ near a given fixed oxygen molecule. With $L=4$, as usually admitted, one obtains $J/k \sim 0.4-0.9$ K.

VI. CONCLUSION

We have presented a comprehensive study of the oxygen-induced linewidth broadening in the conducting polymer polyaniline. At a first stage, the influence of the experimental conditions has been emphasized. If anhydrous experimental conditions are not used, the broadened linewidth exhibits a decay with time. Residual water is therefore responsible for the linewidth "relaxation" previously reported.¹ The detailed mechanism for this water-controlled linewidth narrowing is not known. Generally speaking, one can say that residual water leads to a decrease of the magnetic interactions between the polarons and the oxygen molecules. One can for instance imagine that H₂O molecules remove O₂ molecules from the adsorption sites thus having a shielding effect between O₂ and the polarons. This picture is consistent with the high water avidity of polyaniline.

The effect of water upon the linewidth being clearly iden-

tified, we were able to carry out careful studies, that is, to obtain only the real oxygen-induced linewidth $\delta(\Delta H)_x$. The theory of the line broadening upon polaron-oxygen collisions has been developed. We have shown that the line broadening observed in the whole oxygen pressure range ($0 < P_i < 1$ bar) requires the oxygen and the polarons to belong to separate reservoirs. In our system where oxygen molecules can be considered as fast-relaxing impurities, two separate spin reservoirs can be defined. This implies the oxygen exchange frequency to be much lower than its spin-lattice relaxation rate. This drastic condition leads to an oxygen spin-lattice relaxation time much shorter than 10^{-10} s. A strong relaxation mechanism must exist for the oxygen spins, likely originating from the spin-orbit coupling. Since the gaseous oxygen molecule has a fundamental electronic state with no angular momentum and therefore no spin-orbit coupling, the adsorbed oxygen molecule may have a deformed electronic cloud allowing for a strong spin-orbit coupling.

Another interesting theoretical result is that the line broadening can be either proportional or inversely proportional to the polaron mobility depending on the value of the exchange time $(J/\hbar)^{-1}$ as compared to the collision duration t_c (weak and strong exchange). In our case, the evaluation of the collision efficiency p indicates that we are in an intermediate case. However, preliminary data have shown that the linewidth broadening increases with the polaron hopping frequency and therefore with the conductivity of the sample.³³ This is contrary to the case of the motional narrowing, and also to the line broadening of the conduction-electron spin resonance in metals by the Elliott mechanism. We note that qualitatively similar broadening effects have been mentioned for free radicals in solution,²¹ in magnetic insulator containing spin impurities,²⁶ and in amorphous silicon.³⁴

Lastly the theoretical expression of the line broadening allows us to estimate the polaron hopping frequency and the exchange integral from the ESR data. The value obtained for ω_{hop} is quite consistent with the values estimated from previous spin dynamics studies using NMR. This result reveals that the oxygen spins act as a nanoscopic probe of the polaron dynamics. The phenomenon of line broadening by fixed spins could therefore provide a new method for spin dynamics studies.

ACKNOWLEDGMENTS

We are grateful to J. P. Travers and F. Genoud for many fruitful discussions. We also acknowledge O. Chauvet, who drew our attention to the Movaghar and Schweitzer process for the line broadening.

*Member of Centre National de la Recherche Scientifique.

¹M. Nechtschein and F. Genoud, *Solid State Commun.* **91**, 471 (1994).

²A. Bartl, L. Dunsch, H. Naarmann, D. Schmeisser, and W. Gopel, *Synth. Met.* **61**, 167 (1993).

³M. Inoue, M. B. Inoue, Ma. M. Castillo-Ortega, M. Mizuno, T. Asaji, and D. Nakamura, *Synth. Met.* **33**, 355 (1989).

⁴G. E. Pake and T. R. Tuttle, *Phys. Rev. Lett.* **3**, 423 (1959).

⁵M. J. Povich, *Anal. Chem.* **47**, 346 (1975).

⁶Ph. Turek, J. J. André, and J. Simon, *Solid State Commun.* **63**, 741 (1987).

⁷P. Petit, K. Holczer, and J. J. André, *J. Phys. (Paris)* **48**, 1363 (1987).

⁸Ph. Turek, M. Moussavi, and J. J. André, *Europhys. Lett.* **8**, 275 (1989).

⁹F. Bensebaa, P. Petit, and J. J. André, *Synth. Met.* **52**, 57 (1992).

¹⁰X.-S. Tang, M. Moussavi, and G. C. Dismukes, *J. Am. Chem. Soc.* **113**, 5914 (1991).

¹¹D. Duret, M. Moussavi, C. Jeandey, and M. Beranger, *Sensors Actuators B*, 266 (1992).

¹²S. Hamm, J. U. von Schutz, H. Wachtel, and H. C. Wolf, *J. Phys. D* **25**, 1354 (1992).

- ¹³M. Hoinkis, E. D. Tober, R. L. White, and M. S. Crowder, *Appl. Phys. Lett.* **61**, 2653 (1992).
- ¹⁴K. Holczer, J. P. Boucher, F. Devreux, and M. Nechtschein, *Phys. Rev. B* **23**, 1051 (1981).
- ¹⁵F. Genoud, F. Devreux, M. Nechtschein, and J. P. Travers, *J. Phys. (Paris) Colloq.* **44**, C3-291 (1983).
- ¹⁶R. J. Elliott, *Phys. Rev.* **96**, 266 (1954).
- ¹⁷A. G. MacDiarmid, J. C. Chiang, A. F. Richter, N. L. D. Soma-siri, and A. J. Epstein, in *Conducting Polymers, Special Appl.*, edited by Alcacer Luis (Reidel, Dordrecht, 1987), p. 105.
- ¹⁸K. Aasmundtveit, F. Genoud, E. Houzé, and M. Nechtschein, *Synth. Met.* **69**, 193 (1995).
- ¹⁹J. P. Travers and M. Nechtschein, *Synth. Met.* **21**, 135 (1987).
- ²⁰E. S. Matveeva, R. Diaz Colleja, and V. P. Parkhutik, *Synth. Met.* **72**, 105 (1995).
- ²¹Yu. N. Molin, K. M. Salikhov, and K. I. Zamaraev, *Spin Exchange*, Springer Series in Chemical Physics Vol. 8 (Springer-Verlag, Berlin, 1980).
- ²²Ruth M. Lynden-Bell, *Mol. Phys.* **8**, 71 (1964).
- ²³V. Yu. Zitserman, *Mol. Phys.* **20**, 1005 (1971).
- ²⁴A. L. Buchachenko, R. Z. Sagdeev, and K. M. Salikhov, *Magnetic and Spin Effects in Chemical Reactions* (Nauka, Novosibirsk, 1978).
- ²⁵A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).
- ²⁶J. E. Gulley and V. Jaccarino, *Phys. Rev. B* **6**, 58 (1972).
- ²⁷L. Rebattet, thesis, Lyon, 1994; L. Rebattet, M. Escoubes, M. Pineri, and E. M. Genies, *Synth. Met.* **71**, 2133 (1995).
- ²⁸K. Mizoguchi, M. Nechtschein, J.-P. Travers, and C. Menardo, *Phys. Rev. Lett.* **63**, 66 (1989).
- ²⁹E. Houzé, M. Nechtschein, and A. Pron (unpublished).
- ³⁰A. Meckler, *J. Chem. Phys.* **21**, 1750 (1953).
- ³¹M. Tinkham and M. W. P. Strandberg, *Phys. Rev.* **97**, 937 (1955).
- ³²M. Tinkham and M. W. P. Strandberg, *Phys. Rev.* **97**, 951 (1955).
- ³³F. Genoud, M. Nechtschein, R. Racine, M. F. Planche, and J. C. Thiéblemont, *J. Chim. Phys. (Paris)* **92**, 995 (1995).
- ³⁴B. Movaghar, L. Schweitzer, and H. Overhof, *Philos. Mag. B* **37**, 683 (1978).