Electron Spin−Echo Envelope Modulation Induced by Slow Intramolecular Motion

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A new type of electron spin−echo envelope modulation (ESEEM) was observed in a three-pulse stimulated echo experiment on nitroxides in a molecular glass. With fixed interval T between the second and the third pulses and variable interval τ between the first and the second ones, it appears in the frequency domain as a broad peak around ~5 MHz. It is attributed to a sudden change of the EPR resonance frequency due to reorientation of the methyl groups of the nitroxide during the T interval. The rate of the growth of this peak with increasing T reflects the methyl group reorientation rate, which was found to be strongly temperature dependent.

Introduction

Electron spin−echo envelope modulation (ESEEM) is widely used for structural investigations.[1,2] Modulation appears as a result of a sudden change of spin interactions (electron−nuclear or electron−electron) by the applied microwave pulses.

However, spontaneous processes may also change spin interactions and, under proper experimental conditions, result in ESEEM. This was observed recently for the stimulated echo sequence $\pi/2-\tau-\pi/2-T-\pi/2-\tau-$echo, applied to a nitroxide biradical.[3] The sudden change of the resonance frequency takes place during the T-period due to longitudinal relaxation of the partner electron spin. It was found that the stimulated echo, with fixed T and variable τ, is strongly modulated with the frequency of the electron dipole−dipole interaction. The modulation appears for a slow process, $\Delta\omega\tau_c \gg 1$, where $\Delta\omega$ is the shift of resonance frequency and τ_c is the correlation time (spin−lattice relaxation time for this particular process). The fact that longitudinal relaxation of the partner spin influences the variation of the amplitude of the stimulated echo with τ and that this effect depends on the choice of T was first noted in ref 4. To observe ESEEM, one more requirement is that $\Delta\omega$ should not exceed the microwave pulse amplitude that is normally around 10−20 MHz.

Another possible spontaneous process of that kind might be an intramolecular motion, for example, methyl group reorientation. For methyl groups in nitroxides, $\Delta\omega$ does not exceed 10 MHz. By an appropriate choice of temperature one may find conditions where the ESEEM may be observed. Such observation is the subject of the present paper. We will show also that the reorientation rate may be easily derived from the experiment.

If the hyperfine structure of the exchanging lines is resolved, an inversion−recovery technique may be used for investigation of slow methyl group rotation.[5] In the case of fast reorientation, $\Delta\omega\tau_c \ll 1$, methyl group reorientation leads to the decrease of the apparent phase memory time T_2.[6,7] Rotation of solvent methyl groups also may be studied via relaxation of ESE.[8] ESEEM arising from mixing of rotational and electron spin states for tunneling methyl rotors was discussed in ref 9.

Reorientation of a Methyl Group and Stimulated ESEEM

It is well-known that spectral diffusion influences stimulated echo.[4] Here we describe this influence in more detail, for the particular case of spectral diffusion induced by reorientation of a methyl group. Let us consider the simplified case of a nitroxide with only one methyl group attached. For simplicity we assume that the nonsecular part of the hyperfine interaction (hfi) is weak as compared with the nuclear Zeeman interaction. This allows neglecting the electron−nuclear ESEEM induced by simultaneous excitation of allowed and forbidden spin transitions. In this case, nuclear spins are quantized along the direction of the external magnetic field $\mathbf{B_0}$ (Z-axis in the laboratory frame). The spin Hamiltonian may be written as

$$H = \omega_s S_z + S_z(a_1 I_{1z} + a_2 I_{2z} + a_3 I_{3z}) \qquad (1)$$

where $\mathbf{S}$ is the electron spin operator, ω_s is the electron Larmor frequency that takes into account all electron spin interactions except the hfi with methyl protons, $\mathbf{I}_1$, $\mathbf{I}_2$, and $\mathbf{I}_3$ are the spin operators of these protons, and a_1, a_2, and a_3 are the secular hfi constants. Nuclear Zeeman terms are omitted in (1).

Let us consider evolution of the spin system under the combined action of the stimulated echo pulse sequence and methyl group reorientation. We assume that spin relaxation is slow at the time scale of the experiment. Thus, the Z-projections of the nuclear spins are considered as parameters $m_i = \pm{}^1/_2$, $i = 1, 2, 3$. In the case of slow motion, $\Delta\omega\tau_c \gg 1$, the EPR spectrum consists of a set of well-resolved distinct lines. For a moment, let us additionally assume that $\tau_c > \tau \approx 10^{-6}$ s, so that one may neglect the reorientation during the τ period. But the T interval may be still comparable with τ_c.

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The first $\pi/2$ pulse converts Boltzmann Z-magnetization into the XY plane where it precesses during the τ period. The second $\pi/2$ pulse creates nonequilibrium Z-magnetization stored during the T period. During this period a sudden change of the Hamiltonian (1) occurs due to reorientation. This change may be treated as a cyclic permutation of the hfi constants a_1, a_2, and a_3. This in turn causes the shift of the electron Larmor frequency $\Delta\omega$. The third $\pi/2$ pulse creates transverse magnetization. So, during the first and the second τ periods, the magnetization precesses with different frequency. This leads to incomplete refocusing of the spin packets at the moment of the stimulated echo detection, $t = 2\tau + T$, so that the echo amplitude is proportional to $\cos(\Delta\omega\tau)$.

The methyl group does not change its position during the T period with probability

$$P_0 = \frac{1}{3}(1 + 2\exp(-T/\tau_c)) \tag{2}$$

The two other cases (clockwise and counterclockwise methyl group rotation) have equal probabilities

$$P_+ = P_- = (1 - P_0)/2 = \frac{1}{3}(1 - \exp(-T/\tau_c)) \tag{3}$$

If the methyl group rotates, $\Delta\omega$ may be either zero, if all the m_i values are equal (with the probability $^1/_4$), or it attains one of the six values $\pm(a_1 - a_2)$, $\pm(a_1 - a_3)$, or $\pm(a_2 - a_3)$, for the other combinations of the nuclear spin projections (each value with the probability $^1/_8$). Hence

$$P(\Delta\omega = 0) = P_0 + (P_+ + P_-)/4 = \frac{1}{2}(1 + \exp(-T/\tau_c)) \tag{4}$$

$$P(|\Delta\omega| = |a_1 - a_2|) = P(|\Delta\omega| = |a_1 - a_3|) = P(|\Delta\omega| = |a_2 - a_3|) = (P_+ + P_-)/4 = \frac{1}{6}(1 - \exp(-T/\tau_c)) \tag{5}$$

Thus, the amplitude of the stimulated echo is

$$M_y(2\tau + T) = \frac{1}{2}(1 + \exp(-T/\tau_c)) + \frac{1}{6}(1 - \exp(-T/\tau_c))[\cos((a_1 - a_2)\tau) + \cos((a_1 - a_3)\tau) + \cos((a_2 - a_3)\tau)] \tag{6}$$

Equation 6 predicts that, after cosine Fourier transform with respect to τ, three peaks appear at frequencies $|a_1 - a_2|$, $|a_1 - a_3|$, and $|a_2 - a_3|$. The intensity of these peaks increases with increasing T.

We neglected here the relaxation of the electron spin magnetization. It may be taken into account in a phenomenological way by multiplying the expression (6) by the relaxation factor $\exp(-2\tau/T_2 - T/T_1)$.

If methyl group reorientation occurs during the τ intervals, the phase of the electron spin magnetization at the moment of echo detection is shifted. After averaging over all possible reorientation times, this results in relaxation of stimulated echo, that is, in nonmodulated smooth decay.

If the molecule has several methyl groups, different combinations of the electron frequency shifts $\Delta\omega$ may appear. In the case of different hfi constants and for polyoriented samples, one may expect that broad unresolved lines appear in the frequency domain. The nonsecular part of the hfi results in a nonzero probability of forbidden transitions. Then methyl group rotation induces a complicated exchange between allowed and forbidden EPR lines. This eventually will result in further broadening and smoothing the frequency spectra.

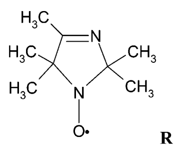
Thus, one may expect that broad unresolved lines appear in the frequency domain instead of only three frequencies.

The simultaneous excitation of allowed and forbidden transitions provides an additional contribution to ESEEM (usual electron−nuclear ESEEM[1,2]). These two contributions must be multiplied in the time domain. As both contributions normally contain a large nonmodulated part (see eq 6 and refs 1 and 2 for electron−nuclear ESEEM), one may expect that peaks at combination frequencies in the frequency domain are not large. However, for more detailed quantitative analysis these peaks may be important.

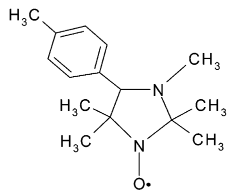
Experimental Section

The experiments were performed on a Bruker ESP 380E pulse X-band EPR spectrometer. A homemade rectangular resonator was used, with a quartz dewar containing liquid nitrogen or liquid oxygen. The resonator quality was adjusted to obtain the dead time of 104 ns. The lengths of the $\pi/2$ pulses were 16 ns.

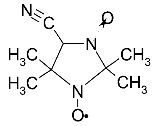
Nitroxides were used:



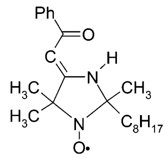
R1



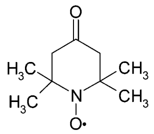
R2



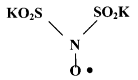
R3



R4



TEMPON



Fremy Salt

The synthesis of imidazoline radicals R1−R4 is described in ref 10. Nitroxides were dissolved in toluene, or in ethanol, or in a 1:1 wt/wt water/glycerol mixture. The nitroxide concentrations were about 2 mM in all samples. All samples were in a glassy state obtained by fast freezing at 77 K.

The time domain traces of the stimulated echo were acquired with a τ increment of 8 ns (200 points).

Results

If not stated otherwise, the microwave excitation was applied at the low-field maximum of the nitroxide EPR spectrum. This was done to provide an appropriate orientation selectivity of the experiment. Indeed, when the low-field maximum of the EPR spectrum is excited, the echo is formed predominantly by the nitroxides with the axis of the unpaired π-electron orbital parallel to the magnetic field $\mathbf{B_0}$. In that case all four methyl groups become nearly magnetic equivalent, and their reorientation contributes to the ESE modulation with the same frequency.

Figure 1 shows the initial part (100 points) of the τ dependence of the stimulated echo amplitude for R1 in toluene at 77 K, with two different T values, 3 and 50 μs. The echo decay curve was approximated by an exponential which was

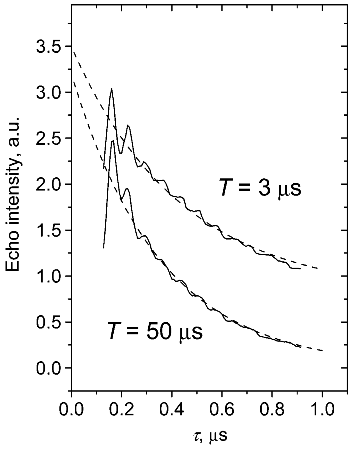


Figure 1. Time domain stimulated ESEEMs for R1 in toluene at 77 K with $T = 3$ μs and $T = 50$ μs. The amplitude of the latter trace is increased to match the amplitude of the former one. The dashed lines present exponential fitting to the experimental traces.

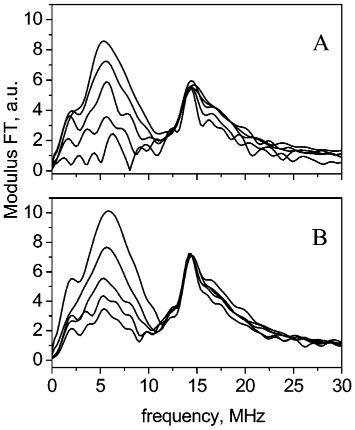


Figure 2. (A) Modulus FT spectra of stimulated ESEEM for R1 in toluene at 77 K. The values of T are 3, 20, 50, 100, and 130 μs (with increasing T, the peak at 5.5 MHz increases). The spectra are normalized to the initial amplitude of the exponential fitting (see Figure 1). (B) The same experiment at 90 K, with T values 2, 3, 5, 10, and 15 μs.

then subtracted. To normalize data for different T values, they were divided by the initial amplitude of this exponential.[3] Note that signal decay due to spin−lattice relaxation is compensated in that way. The data were zero-filled up to 512 points, and modulus Fourier transform was done. No mathematical dead time recovery was used because it is not efficient for the case of broad distribution of modulation frequencies.[1]

The resulting frequency domain spectra for R1 in glassy toluene are shown in Figure 2. The peak with maximum at 14.5 MHz (proton Larmor frequency) represents well-known electron−proton ESEEM. The change of its amplitude and shape with increasing T is negligible.

In contrast, a peak with maximum around 5.5 MHz appears and grows substantially with increasing T. An exponential fit (see Figure 3) gives the characteristic time of the growth, $T_e = 55 \pm 10$ μs at 77 K and 8 ± 3 μs at 90 K.

Frequency spectra for R1 frozen in other solvents (ethanol, water/glycerol mixture; data not shown) are very similar to those in toluene (Figure 2). This testifies that the appearance of the growing peak is an intrinsic property of nitroxides.

Similar results were obtained for other nitroxides; see Figure 4. For R4 (Figure 4c) the growing peak is rather broad. For TEMPON in toluene (Figure 4d), peaks are seen at the frequencies 3.4 and 6.7 MHz. For Fremy salt (Figure 4e), no peaks with frequency higher than 2 MHz are seen.

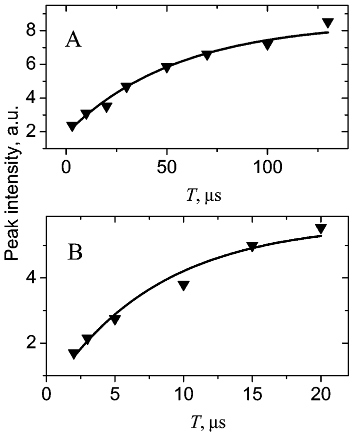


Figure 3. Amplitude of the peak at 5.5 MHz in Figure 2 as a function of T. The solid line represents exponential fitting: A, 77 K; B, 90 K.

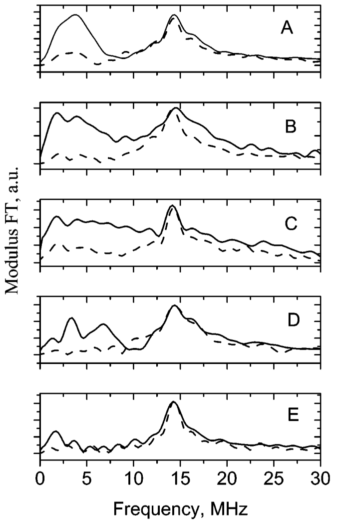


Figure 4. Modulus FT spectra of the stimulated ESEEM for different nitroxides: (dashed line) the lower T value; (solid line) the higher T value; (A) R2 in toluene, 77 K, $T = 3$ μs and 50 μs; (B) R3 in 2-propanol, 77 K, $T = 3$ μs and 20 μs; (C) R4 in toluene, 77 K, $T = 3$ μs and 20 μs; (D) TEMPON in toluene, 90 K, $T = 2$ μs and 10 μs; (E) Fremy salt in water/glycerol mixture, 77 K, $T = 3$ μs and 50 μs.

Discussion

The appearance of the additional peak and its growth with increasing T may be traced back to methyl group reorientation, in line with the above consideration. The appearing frequencies are in the range of hfi constants typical for methyl protons of nitroxides, 2−9 MHz.[11]

The weak peak near zero frequency seen in Figures 2 and 4 (at 1.5−2 MHz) most probably is an artifact of the Fourier transform arising from some discrepancy of the exponential fitting.

Equation 6 allows relating the rate of the peak growth to the characteristic time of methyl group reorientation. For R1 an estimate of the Arrhenius parameters gives the preexponential factor $A \approx 1.5 \times 10^{10}$ s^{-1} and the activation energy $E_a/k \approx 1050$ K, where k is the Boltzmann constant. These values agree well with those obtained from the study of primary ESE relaxation in imidazoline nitroxides[7] for higher temperatures (100−180 K), $A = (1.3-2) \times 10^{10}$ s^{-1} and $E_a/k = (1000 \pm 100)$ K. A similar value, $E_a/k = 1100$ K, was obtained for TEMPON from the temperature dependence of its ENDOR spectrum.[11] The unusually low value of the preexponential factor is caused probably by synchronized rotation of two methyl groups attached to the same carbon atom.

Note that for TEMPON at 77 K we did not observe this peak, probably because motion becomes slower than spin−lattice relaxation.

The growing peak at 5.5 MHz was also observed in analogous experiments with excitation of the central maximum of the EPR spectrum of R1 (data not shown). In this case the peak amplitude was nearly 2 times less than that in the case of the low-field maximum excitation. This may be explained by the absence of orientation selectivity and, as a consequence, broader distribution of $\Delta\omega$. Note that in our previous work[3] growing peaks due to methyl group rotations were also seen but not interpreted as such at that time.

Finally, let us discuss other possible sources of slow spectral diffusion, which may also result in similar effects. It may be spontaneous nuclear spin flips (nuclear spin relaxation), reorientation of a nitroxide, conformational transitions, isomerization, and so forth.

Nuclear spin−lattice relaxation in nitroxides indeed may be fast enough to be detected in this experiment. This relaxation becomes effective when the correlation time of the molecular motion matches the nuclear resonance frequency. For ^{14}N nuclei in the paramagnetic fragment of nitroxides, spin−lattice relaxation time in glassy solids may go down to several tens of microseconds.[12] The spectral shift induced by such relaxation is determined by the hfi and may be expected in the frequency range from 15 to 100 MHz. In the described experiment this shift was not observed, most probably because of slow relaxation and large spectral width. For other nuclei in the vicinity of nitroxide (protons, nitrogen in the third ring position), hfi is also the most important time-dependent interaction, because of intensive librational motion of nitroxide.[12,13] As for these nuclei hfi is several times smaller, one may expect nuclear relaxation to be at least 1 order of magnitude slower, falling to the millisecond time region.

Except for nuclear spin−lattice relaxation, spin diffusion[4,14] may also result in the fluctuation of the local magnetic field. However, in the vicinity of the unpaired electron this diffusion is suppressed because of high hyperfine field.[4,14]

Reorientation of a nitroxide as a whole also shows up in these experiments.[15] In principle, this may lead to ESEEM provided that reorientations take place between some resolved orientations. The same is valid for conformational transitions of nitroxides. To distinguish this mechanism, one may conduct measurements at the different field positions across the resonance line. At the edges of the spectrum (parallel canonical orientation of the nitroxide), the fluctuation of the resonance frequency due to motion is close to zero,[13] so for these field positions the spectral shift must be remarkably smaller than those for others. This was not observed in our experiment (see above), which suggests that reorientation is slow in our case or that the resulting spectral width is large.

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