Echo-induced EPR spectra of nitroxides: Study of molecular librations

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Abstract – The shapes of echo-induced EPR spectra (i.e. field dependence of ESE signal intensity) for nitroxides in organic glasses are in good agreement with those computed for the model where magnetic relaxation is caused by low-amplitude stochastic orientational motion of a molecule near its equilibrium position. The echo-induced spectra depend on a single parameter only – the product $2\tau\overline{\alpha^2}\tau_c$, where τ is the time interval between two echo-forming pulses, $\overline{\alpha^2}$ – mean squared angle of torsional motion, τ_c – correlation time for stochastic process of motion. This motional type seems to be common for disordered molecular media with different structures. In a crystalline state this motion does not exist. So this effect could be used for a phase state determination in complex multicomponential systems (e.g. biological) using spin labeling.

INTRODUCTION

Spin probes and labels are widely used in physico-chemical and biological studies. They allow one to obtain very important information on dynamical properties of systems investigated (ref. 1). This include data on rotational (ref. 1) and translational (refs. 1,2) mobilities. In the present paper the possibility of studying orientational vibrational motions (librations) for spin probes and labels is discussed.

This possibility arises when one applies electron spin echo (ESE) spectroscopy. The echo amplitude taken as a function of the magnetic field H_0 is called the echo-induced EPR spectrum. The time interval τ between two echo-forming microwave pulses (in the primary echo technique) in these measurements is kept fixed. The shapes of these spectra may differ from those obtained with a continuous wave (cw) EPR spectrometer being dependent on τ. This is a consequence of different magnetic relaxation rates for different H_0s. This effect can arise due to a few relaxational mechanisms. The most important among them are "instantaneous diffusion" in ESE (ref. 3) which results in relatively high relaxation

rate for high-amplitude spectral lines (ref. 4), and molecular orienta-
tional motions (ref. 5). As Freed and coworkers have shown (ref. 5) dif-
ferent motional models usually used in the theory (jump, Brownian or
free diffusion) lead to noticeably different dependences on H_0 for the
transverse relaxation rate. For nitroxides in organic glasses, good ag-
reement has been achieved (ref. 6) for the model involving low-amplitude
orientational motion of the molecule near its equilibrium position To
confirm this model, the ^{15}N-substituted nitroxides are prefered because
in this case some special features of echo-induced spectra could be
observed which are hidden for ^{14}N due to the overlap of different hfs
components.

In the present paper the theoretical and experimental problems for stu-
dying molecular librations using echo-induced EPR spectra of nitroxides
are discussed as well as possible applications.

EXPERIMENTAL DETAILS

In measurements described here the nitroxide concentrations were about
$2 \ 10^{18}$molecules/g. On the one hand in this case the ESE signal intensity
is sufficient for measurements, on the other the spectral distortions
due to instantaneous diffusion (see Introduction) are not great.

We employ an ESE spectrometer operating at X-band. The microwave pulse
power is about 1 kW. A conventional two-pulse sequence 90^0-τ-180^0-τ-echo
was utilized. The pulse lengths were 40 ns and 80 ns respectively. So
the estimated microwave field strengh was 2.2 G. The sequence repetition
frequency normally was 1000 Hz. The spectrometer dead time (the minimum
τ at which an echo signal can be distinguished above the background of
resonator ringing) is about 150 ns. The upper τ limit is determined by
the signal intensity and the rate of relaxation. The magnetic field was
swept using a digital NMR-stabilizer. The echo signal amplitudes were
recorded with a multichannel analyzer.

ECHO-INDUCED EPR SPECTRA OF NITROXIDES

Typical examples of echo-induced EPR spectra are shown in Fig. 1. Two
types of samples were investigated: one glassy and one crystalline. In
both cases the samples were TEMPON dissolved in toluene. On rapid free-
zing by immersion in liquid nitrogen, the sample became a transparent
glass. With slow warming it converted into a polycrystalline form. The
spectra are taken at two different times τ. With τ increase, in the gla-
ssy state a spectral transformation is observed which is most noticeable
for the high-field component. One can see the additional minimum appea-
ring here. For the crystalline state this transformation is negligible.

EPR spectrum for nitroxides consists of three hyperfine structure (hfs)
components (see Fig. 1) for the ^{14}N nucleus with spin equal to 1. Each
component is inhomogeneously broadened by Zeeman interaction and by ani-
sotropic hyperfine interaction (hfi). Approximate spectral line posi-
tions for parallel and perpendicular orientations for all hfs components

are also shown in Fig. 1. Other possible orientations correspond to in-
termediated spectral line positions. Note that the exact correspodence
between orientation and spectral line position does not exist due to
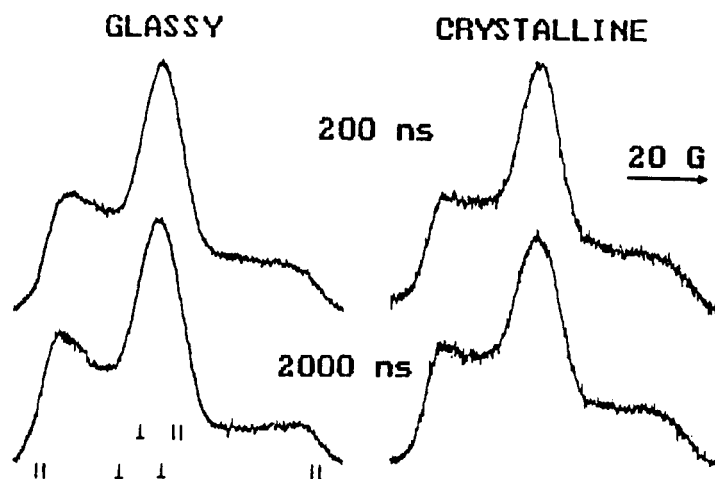unresolved hfi with matrix nuclei (see for details the next section).

Fig.1. Echo-induced EPR spectra for TEMPON in glassy and crystalline toluene at 77 K. The spectra are taken at two dif ferent times τ. When τ increase, in the glassy state a spect ral transformation is observed (see the text).

One can see from the data of Fig. 1 that for parallel orientation the
relaxation is slower than for others. This leads to a comparatively
small descrease in the intensity of spectral lines corresponding to this
orientation. Investigations with ^{15}N nitroxides (ref. 6) showed that
this is observed also for perpendicular orientations.

THEORY

Let us consider a nitroxide molecule undergoing the low-amplitude orien-
tational motion near its equilibrium position. Note that the usual har-
monic oscillations can not provide experimentally observable relaxation
rates due to the very high frequences of these oscillations (10^{12} – 10^{13}
Hz for molecular solids). This is clearly follows from the formulae gi-
ven by Abragam (ref. 7, chapter 10). But in the case of an anharmonicity
in these oscillations the non–oscillating shift will appear which de-
pends on the vibrational level number and fluctuates because of transi-
tions between different levels. Then the relaxation time τ_c of these
excitations will be the most important time parameter for the magnetic
relaxation. The other possible situation is when there are closely-
situated minima of potential energy where the molecule can perform
transitions due to thermal fluctuations. Then τ_c would be the
correlation time for the stochastic process of these transitions.

The spin-hamiltonian for nitroxides undergoing the librational motion
can be taken in the form (ref.6):

$$\hat{H} = \beta H_0 g_{zz} S_z + \hbar S_z (A_{zx} I_x + A_{zy} I_y + A_{zz} I_z) \qquad (1)$$

where β is the Bohr magneton, $\vec{H}_0$ is the magnetic field strengh vector,

g_{zz} and A_{zx}, A_{zy}, A_{zz} are components of g and hfi tenzors. S_z and I_x, I_y, I_z are operators of electron and nitrogen nuclear spins. The Z axis is assumed to be directed along $\vec{H}_0$.

The values of $\hat{g}$ and $\hat{A}$ tensor elements in (1) undergo motionally-induced fluctuations. For the low-amplitude motion near the equilibrium position, one may speak about their mean values. So let's divide the hamiltonian in two parts: permanent and variable. The first one is of the a form:

$$\hat{H}_0 = \beta H_0 \overline{g_{zz}} S_z + S_z (\vec{A}_0 \vec{I}), \tag{2}$$

where the line means time averaging. Vector $\vec{A}_0$ is determined by the mean values of hfi tensor elements: $\vec{A}_0 = (\overline{A_{zx}}, \overline{A_{zy}}, \overline{A_{zz}})$. Eigenfunctions of (2) are $|m_s m_I\rangle$ where m_s is the electron spin projection onto $\vec{H}_0$, m_I is the nuclear spin projection onto $\vec{A}_0$.

The variable part of the hamiltonian is:

$$\hat{H}_1(t) = \beta H_0 (g_{zz} - \overline{g_{zz}}) S_z + \hbar S_z (\vec{A} - \vec{A}_0) \vec{I} \tag{3}$$

where $\vec{A} = (A_{zx}, A_{zy}, A_{zz})$.

We shall assume that τ_c is small: $\tau_c \ll T_2$, where T_2 is motionally-induced transverse relaxation time. This should be valid for low-amplitude motion, $\tau_c \Delta\omega \ll 1$, where $\Delta\omega$ is the scale of motionally-induced spectral diffusion. Under these assumptions, one can use Redfield's equations (ref. 7) to compute the electron spin relaxation induced by the variable hamiltonian (3).

Using directly the formulae given in (refs. 7,8) for nuclear spin I=1/2 one can obtain:

$$T_2^{-1} = \frac{1}{T_2^a} + \frac{1}{T_2^{na}}, \tag{4}$$

where the first term presents the adiabatic rate constant:

$$\frac{1}{T_2^a} = \tau_c \left\{ \frac{\gamma^2}{4} H_0^2 \overline{(g_{zz} - \overline{g_{zz}})^2} + m_I^2 \frac{\overline{((\vec{A} \cdot \vec{A}_0) - A_0^2)^2}}{A_0^2} + \right.$$

$$\left. + \gamma H_0 m_I \frac{\overline{(g_{zz} - \overline{g_{zz}})(\vec{A} \cdot \vec{A}_0 - A_0^2)}}{A_0} \right\} \tag{5}$$

with $\gamma = g_e \beta / \hbar$, where g_e is g-factor of free electron. The second term in (4) presents the nonadiabatic rate constant:

$$\frac{1}{T_2^{na}} = \tau_c \frac{1}{8(1 + \frac{1}{4} A_0^2 \tau_c^2)} \frac{\overline{A}^2 A_0^2 - \overline{(\vec{A} \cdot \vec{A}_0)^2}}{A_0^2} \tag{6}$$

In the absence of motion, hamiltonian (1) results in the following expression for the resonance line positions in EPR spectrum:

$$\omega_m(\theta,\varphi) = \frac{g_e\omega_0}{g_{zz}} - m_I A_0 \tag{7}$$

where ω_0 is the spectrometer angular frequency, θ and φ are the angles determining magnetic field direction in the molecular framework (where $\hat{g}$ and $\hat{A}$ tensor are diagonal). The dependence on θ and φ in (7) arises due to the g_{zz} and A_0 angular dependences. The explicit forms of these dependences are given by Libertini and Griffith (ref. 9) (including those for the vector $\vec{A}$ components). If we take into account the unresolved hfi with the neighbouring nuclei, the resulting EPR lineshape can be recorded as

$$E_0(\omega) = \sum_m \frac{1}{4\pi} \int \sin\theta d\theta d\varphi \ f_G(\omega-\omega_m(\theta,\varphi)) \tag{8}$$

Here we assume a Gaussian distribution $f_G(\Delta\omega)$ for the resonance line shifts $\Delta\omega$ due to unresolved hfi.

In our model the low-amplitude motion is supposed to have no effect on the nitroxide spectral line positions but to cause the echo signal decay due to magnetic relaxation. So for the echo-induced spectrum taken at 2τ instead of (8) we shall have

$$E_\tau(\omega) = \sum_m \frac{1}{4\pi} \int \sin\theta d\theta d\varphi \ \exp(-2\tau/T_2) \ f_G(\omega-\omega_m(\theta,\varphi)), \tag{9}$$

where T_2^{-1} is given by eqs. (4-6); it depends on θ and φ and on the concrete motional model.

For example, for rotation about the X' molecular axis by a small angle α the angles θ and φ change in a following way:

$$\Delta\theta = \alpha \sin\varphi \tag{10a}$$

$$\Delta\varphi = \alpha \ \text{ctg}\theta \ \cos\varphi \tag{10b}$$

The angle α could be considered to be a random value with the mean quantity equal to zero. One can expand the right-hand parts of eqs.(5,6) as a power series in α. For small angles α it is enough to conserve only the first expansion terms which are proportional to α^2. So the echo-induced spectral shape will depend on two parameters - the products 2τ $\overline{\alpha^2}\tau_c$ and $A_0\tau_c$.

Note that in (5) the first expansion term is equal to zero when $\theta = 0$ and when $\theta = \pi/2$. This means that these nitroxide orientations are less sensitive to the motionally-induced spectral diffusion than other ones.

Eqs. 4-6 are valid only for ^{15}N nitroxides. For ^{14}N nitroxides, when $m_I=0$, the relaxation rate cannot be presented in the simple form of eq. 4, as follows from the analysis of Redfield equations. Moreover, relaxa-

tion here is nonexponential. But this component ($m_I=0$ corresponds to the central component of the triplet EPR spectrum, see Fig. 1) is nearly isotropic, because its width, usually about 10 G, is comparable with unresolved line broadening, which is about 6 G peak-to-peak. Therefore this component is not interesting for the lineshape analysis. But for the analysis of other components, $m_I = \pm 1$, one can apply eqs. 4-6.

The comparison of theoretical and experimental spectra was performed for ^{15}N nitroxides dissolved in ethanol (ref. 6). This comparison shows the formulae (4-10) describe well the echo-induced spectra measured at 77 K. In the comparison, τ_c was assumed to exceed 10^{-8} s otherwise the agreement could not be achieved. This condition means that $A_0\tau_c>1$ so the non-adiabatic rate constant (eq.6) is negligibly small as compared with the adiabatic one (eq. 5) and spectra do not depend on $A_0\tau_c$.

DISCUSSION

The model of low-amplitude orientational motion near equilibrium position agrees with experimentally observed echo-induced EPR spectra. This agreement has not been reached for "classical" theoretical models of orientational motion - models of jump, Brownian and free angular diffusion (see Introduction).. This seems to be related with the unrestricted character of motion in these models.

The theory developed above is valid only for short $\tau_c<T_2$. Here T_2 refers to relaxation caused by librations. In organic matrixes it is possible to study relaxational processes with T_2 of the order of 10^{-6}s. Shorter T_2 leads to echo disappearence due to the dead time phenomenon, the longer T_2 cannot be measured because other relaxation mechanisms exist which result in signal decay. Therefore the condition for when the theory works can be rewritten as $\tau_c<10^{-6}$s. Note that recent investigations of supercooled organic liquids by inelastic light scattering (ref. 10) show that the temperature dependence for the lifetime of the vibrational excitions, extrapolated to 77 K, leads to the values about 10^{-9}s – 10^{-7}s at this temperature.

The transformation of echo-induced EPR spectra with increasing τ was observed early for spin probes in water-glycerol solutions (ref. 5), in dibutyl phthalate (refs. 11 and 12), and for spin labels in amorphous polymers (ref. 13). This transformation is of a same type as shown in Fig. 1 for glassy state.

The librations observed for nitroxide molecules seem to be characteristic for disordered media. In a crystalline state, they do not manifest themselves. There is now much evidence for the existence in amourphous materials of vibratious of some special type which are not present in crystalline state. These were obtained by studying specific heat and thermoconductivity (ref. 14), low-energy spectra of neutron (ref. 15) and Raman light (ref. 16) scattering and of infrared absorption (ref.

17) – see also refs. therein. Probably these vibrations are responsible also for echo-induced spectra transformation disscussed here. Note that in the above techniques nobody can distiguish between orientational vibrations and translational ones, and the echo-induced spectra are sensitive only to the formers. So their studies may provide a useful information about dynamical properties of disordered media.

Fig. 1 shows that echo-induced spectra give possibility of making a conclusion about the phase state of any system where the nitroxide probes are introduced. Probably this can have interesting application for biological systems. For a long time it is known that formation of a glassy state on cooling biological systems can have a cryoprotection action (ref. 18). The potential of the method based on echo-induced spectra is demonstrated by studying embryos and endosperm of wheat kernels and various models (ref. 19). It is shown that some parts of embryo cell change on cooling to a glass state and others to a crystalline one.

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