

Fast molecular dynamics: Novel effects studied by 3 cm and 2 mm band EPR

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Abstract - Motional characteristics were calculated for new type of free radicals starting from the anisotropic parameters obtained with the high resolution 2 mm band EPR. The general approach for deriving parameters of molecular tumbling and chemical exchange in the same experiment is discussed. A rather strong correlation between molecular and chemical dynamics of free radicals has been observed.

INTRODUCTION

Spin relaxation rates are the important source of information on molecular dynamics. To relate spin relaxation rates T_1^{-1} or T_2^{-1} with molecular frequencies, one usually needs values of the angular anisotropy of resonant frequency (or magnetic field) which are determined from the solid state spectra [1]. The latter anisotropy for organic free radicals is small and in most cases hardly determinable from conventional EPR spectra, except for some special cases like nitroxide radicals. High field (2 mm band) EPR essentially increases number of cases where parameters of anisotropy can be evaluated [2]. After it has been made parameters of molecular dynamics, spin and chemical exchange become available from both 2 mm and 3 cm band EPR.

EXPERIMENTAL AND CALCULATIONAL PROCEDURES

In spite of impressive development of modern pulsed EPR technique, the fastest spin relaxation processes are still detectable by continuous wave (CW) EPR. If, indeed, the spin relaxation rate T_2^{-1} (or T_1^{-1}) determines the observed linewidth ΔH_{p-p} of the order of magnitude from 1 to 10^3 G, it corresponds to $T_2 \approx (\gamma \Delta H_{p-p})^{-1} = 10^{-7} + 10^{-10}$ s. For free radicals in solution the relaxation linewidth is mostly determined by motional averaging of anisotropic interactions or by averaging of local magnetic fields by spin exchange or chemical exchange.

In the first case the well-developed theory predicts for the relaxation linewidth originating from averaging of anisotropic Zeeman

interaction the following expression (when $\omega_0 \tau_c \gg 1$) [1]:

$$T_2^{-1} = A_0 + A + Bm_1 + Cm_1^2, \quad (1)$$

with A_0 being the motion-independent residual linewidth, and other factors equal to

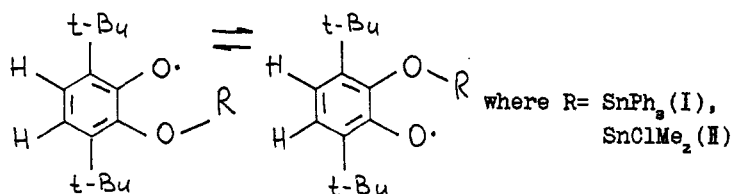
$$A = \frac{2(\Delta g : \Delta g) \beta^2 H_0^2}{15h^2} \tau_c, \quad B = \frac{7(\Delta g : \Delta T) \beta H_0}{15h^2} \tau_c, \quad C = \frac{2(\Delta T : \Delta T)}{15h^2} \tau_c. \quad (1')$$

where $(\Delta g : \Delta g)$, $(\Delta g : \Delta T)$ and $(\Delta T : \Delta T)$ are the inner products for the anisotropic parts of g - and hyperfine T -tensors, τ_c is the correlation time of molecular rotation, ω_0 and H_0 are values of resonant frequency and magnetic field, respectively ($\omega_0 = \gamma H_0$).

It is seen that g - and T -tensors should be known in order to find τ_c from experimental values of ΔH_{p-p} . This was probably the main reason why experiments on molecular dynamics were performed almost exclusively for nitroxide stable radicals for which Δg_i and T_i elements are relatively large and can be determined from the spectra in frozen solution.

After the high frequency version of EPR has been introduced to regular experiments [2], a possibility appeared to find Δg - and T -tensors for more number of free radicals and to expand experiments on molecular dynamics for larger variety of species. We shall review here such kind of experiments with phenoxide- and quinone-type free radicals. For that kind of radicals the possibility was discovered to observe chemical exchange (sometimes, spin exchange) reactions together with molecular rotations. It resulted in finding rather unexpected strong influence of viscosity on internal molecular processes [3-5].

As the typical example we consider molecular rotation and internal chemical conversion in tin-containing substituted oxyphenoxide radicals:



EPR spectra of vitrified toluene solutions (at 145 K) of radical I are presented in Fig. 1a for the conventional X band ($\lambda = 3\text{cm}$) and for the very high frequency F band ($\lambda = 2\text{mm}$). The X band spectrum can hardly be used to find any principal values of g - and T -tensors, while 2mm band spectrum exhibits quite clearly 3 principal positions for g_x , g_y , g_z and T_y -splitting for hyperfine tensor. Two other values T_x and T_z were estimated from the single parameter line shape simulation (note that isotropic splitting value $a = (T_x + T_y + T_z)/3$ was known from the liquid spectra [4,5]). Hence, it was found for anisotropic values of g - and T -tensors:

$$\begin{aligned} \Delta g_x &= 1.88 \cdot 10^{-3}, & \Delta g_y &= 0.44 \cdot 10^{-3}, & \Delta g_z &= -2.32 \cdot 10^{-3} \\ \Delta T_x &= 2.6 \text{ G}, & \Delta T_y &= -2.6 \text{ G}, & \Delta T_z &= 0.0 \text{ G}. \end{aligned} \quad (2)$$

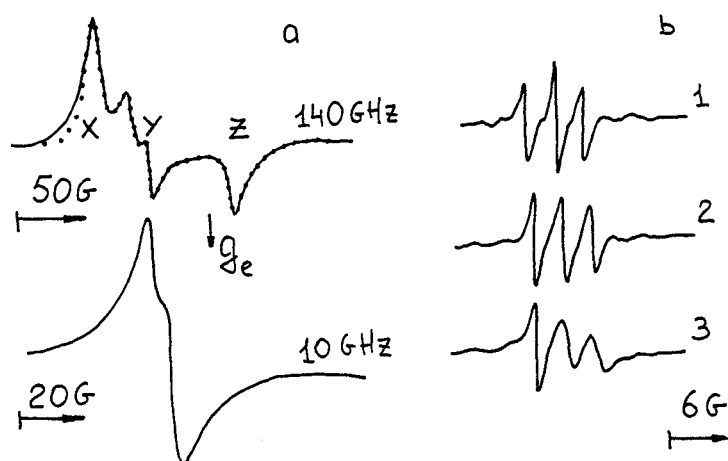


Fig.1. a. EPR spectra of radical I in vitrified toluene solution in 2 mm band (140 GHz) and X band (10 GHz). The 2 mm band spectrum calculated with parameters (2) is shown by dots.
 b. X band EPR spectra of radical I at 293 K in mixture of hexane with vaseline oil 1:2 (1), 1:10(2) and in vaseline oil (3). Satellite lines are due to tin isotopes Sn^{117} and Sn^{119} .

Hyperfine constants are known from the liquid spectrum ($a_1 = -5.1$ G, $a_2 = -2.1$ G), and experimental results allowed to determine the b-tensor introduced in Appendix ($b_{ii} = T_{ii}/a$):

$$b_{x'x'} \approx -0.5, \quad b_{y'y'} \approx 0.5, \quad b_{z'z'} \approx 0.0,$$

where x' axis is along C-H bond, z' axis is perpendicular to the phenyl plane, and y' axis is chosen to make right-handed coordinate system. In designations introduced in Appendix we can write for values of all inner products needed for equations (A3):

$$(\Delta g : b_p) = -0.72; \quad (\Delta g : b_m) = 0.36; \quad (b_1 : b_2) = -0.25.$$

Now let us turn to solution spectra, shown in Fig.1b for different viscosities. Triplet spectrum is determined by the hyperfine splitting at the two ring protons which are almost equivalent due to the fast transitions of SnPh_3 -fragment in I between two oxygen atoms [4]. The total nuclear spin quantum numbers for these lines are $m = -1, 0, +1$ (linewidth $\Gamma_1, \Gamma_2, \Gamma_3$, respectively), so that one can write down

$$\begin{aligned} \Gamma_1 &= (2/3)^{1/2} \left\{ (2/15) \gamma \tau_c \sum_{x,y,z} [(\Delta g_x H_o / g_o) - T_i]^2 \right\} + \Gamma_o \\ \Gamma_2 &= (2/3)^{1/2} \left\{ (2/15) \gamma \tau_c \sum_{x,y,z} [(\Delta g_x H_o / g_o)]^2 \right\} + \Gamma_o \\ \Gamma_3 &= (2/3)^{1/2} \left\{ (2/15) \gamma \tau_c \sum_{x,y,z} [(\Delta g_x H_o / g_o) + T_i]^2 \right\} + \Gamma_o \end{aligned} \quad (3)$$

where Γ_o is residual motion-independent linewidth (we remind that for

the first derivative Lorentzian lineshape recorded experimentally the linewidth between the points of maximal slope $\Gamma = (2/3^{1/2})(\gamma T_2)^{-1}$.

The estimations show quickly that the 'm=0' line is broadened more than predicted by (3), and this happens due to the chemical exchange effects [4]: if the difference of isotropic splittings is $\Delta a = a_H(\text{para}) - a_H(\text{meta})$ and transfer of SnPh₃-group occurs with a frequency τ_{ex}^{-1} , the 'exchange' relaxation linewidth Γ_{ex} should be added only to Γ_2 :

$$\Gamma_2 = (2/3^{1/2})(2/15)\gamma\tau_c \sum_{x,y,z} [(\Delta g_x H_0 / g_0)]^2 + \Gamma_0 + \Gamma_{ex},$$

$$\text{where } \Gamma_{ex} = (2/3^{1/2})\gamma \cdot (\Delta a)^2 / 8.$$

The problem we encountered was the existence of two ring protons and exchange between them, which made impossible using the well known formulas (1). By this reason we needed to derive some more complex expressions in the way shown in Appendix. Using all needed values of inner products the equations (A3) can be simplified in the following manner:

$$\begin{aligned} \Gamma_3 - \Gamma_1 &= 1.47\gamma\tau_c \\ \Gamma_2 - \Gamma_1 &= 1.16\gamma\tau_c + 1.39\gamma\tau_{ex} \end{aligned} \quad (4)$$

It was rather amusing that the previous rough equations turned out to be valid except for the only corrections: the factor 1.47 appeared in first equation of the system (4) instead of previous factor 4.62 [4].

In addition, the relationship

$$2I_1\Gamma_1^2 = I_2\Gamma_2^2 = 2I_3\Gamma_3^2$$

allowed to express easily linewidths Γ_2 and Γ_3 in terms of the narrowest linewidth Γ_1 , and line intensities I_1 , I_2 , I_3 :

$$\Gamma_3 = \Gamma_1 \cdot (I_1/I_3)^{1/2}, \quad \Gamma_2 = \Gamma_1 \cdot (2I_1/I_2)^{1/2}$$

Using formulas (4) we recalculated parameters τ_{ex} and τ_c for radical I in vaseline in temperature interval 273-323 K. Fig.2a and Fig.2b show correlation between τ_{ex} and τ_c obtained earlier [4] and derived from Eq.(4), respectively. It should be noted that linear correlation between τ_{ex} and τ_c remains valid but proportionality factor α ($\tau_{ex} = \alpha \cdot \tau_c$) changes from value of (3+4) to (0.5+1.0), i.e becomes 3+4 times smaller.

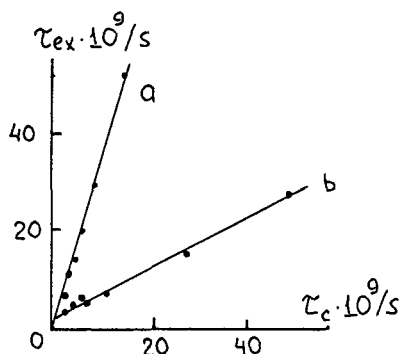


Fig.2. The dependence τ_{ex} vs τ_c for radical I obtained earlier in [4] (a), and with using 2 mm EPR data (b). The value of τ_c was varied by temperature variations (273-323 K) in vaseline oil.

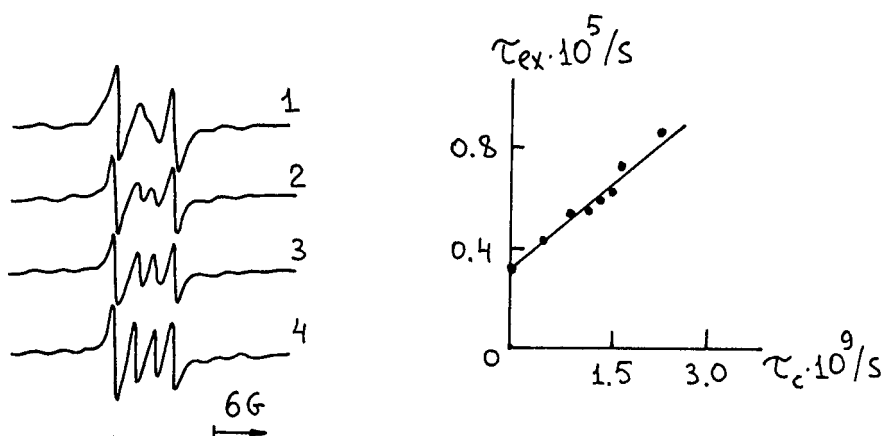


Fig.3. Left: EPR spectra of radical II at 303 K in hexane (1), mixture of hexane with vaseline oil 1:1 (2), 1:10 (3) and in vaseline oil (4). Right: The dependence of τ_{ex} vs τ_c for radical II. The value of τ_c is varied by viscosity and temperature (293-303 K).

Actually the conditions of validity of Equations (4) become incorrect for $\tau_{ex} \leq \tau_c$ which is the case for the given example. This appearing situation is very tedious and we only sketched its solution in the approximation of rigid radical (see Appendix).

Another pattern (Fig.3) was registered for radical II [5]: in the same conditions (temperature, viscosity) the frequency of chemical exchange of SnMe₂Cl-group is 3-4 order smaller. It brings about the registration of its spectra in condition of slow exchange when two central components of the quadruplet spectrum are exchange broadened. In [5] the following expression for the exchange time was obtained:

$$\tau_{ex} \approx \tau_f + 8900 \cdot \tau_c$$

where $\tau_f = 3 \cdot 10^{-8}$ s is the chemical exchange time in non-viscous limit ($\tau_c \rightarrow 0$) and the value of τ_{ex} was determined from exchange broadening of the two central lines. After corrections of τ_c by applications of Equations (4) we obtained (Fig.3)

$$\tau_{ex} \approx \tau_f + 2400 \cdot \tau_c.$$

It should be underlined that the observed correlation for radical II can not be explained any way, by the direct influence of the chemical exchange on the anisotropic broadening of the outer lines ($m=-1,+1$) because the exchange time scale is 3 orders of magnitude greater than the motional time scale. A different situation takes place for radical I, where the chemical exchange appears much faster and the spectral pattern corresponds to the fast exchange situation. As we have seen above, $\tau_{ex} \leq \tau_c$ for radical I and a direct influence of chemical transfer on the value of τ_c can not be definitely excluded.

The results of these experiments demonstrate that the progress in high resolution EPR techniques has initiated a new field of kinetic studies. The possibility to obtain high resolution spectra of organic radicals provides values of magnetic resonance parameters which can be used to calculate molecular dynamics and fast chemical exchange parameters. The observed correlation between molecular dynamics and chemical reactivity establishes a new approach to the investigation of the specific mechanism of elementary processes in liquids and disordered solids.

APPENDIX: SOME GENERAL EXPRESSIONS FOR RELAXATION RATES

In this appendix we obtain the expressions for the relaxation rates for substituted oxyphenoxyl radical when substituent fragment R can be chemically exchanged between two oxygen atoms in addition to the random rotational motion of the radical as a whole. We assume the following Hamiltonian (in angular frequency units):

$$\begin{aligned} \hat{\mathcal{H}} &= (g_0 \beta / \hbar) \left[g_0^{-1} \cdot \hat{H}_0 \cdot \hat{g} \cdot \hat{S} + \hat{I}_1 \cdot \hat{A}_1 \cdot \hat{S} + \hat{I}_2 \cdot \hat{A}_2 \cdot \hat{S} \right] = \hat{\gamma} \\ &= \gamma \left[g_0^{-1} \cdot \hat{H}_0 \cdot \hat{g} \cdot \hat{S} + \hat{I}_1 \cdot \hat{A}_1 \cdot \hat{S} + \hat{I}_2 \cdot \hat{A}_2 \cdot \hat{S} \right], \end{aligned} \quad (A1)$$

where $g_0 = \text{Tr}(g)$ and $\gamma = g_0 \beta / \hbar$ denotes hypermagnetic ratio for radical and hyperfine tensor A is expressed in magnetic field units (G).

If the radical is reoriented randomly, anisotropic part of Hamiltonian (A1) can be considered as a perturbation $\hat{V}(t)$ which determines relaxation rates [1]:

$$T_1^{-1} = 2 \cdot \overline{|V_{\alpha\beta}|^2} \cdot \frac{2\tau_c}{1 + \omega_0^2 \tau_c^2}, \quad T_2^{-1} = T_1^{-1} / 2 + (T_2^0)^{-1}, \quad (A2)$$

where $(T_2^0)^{-1} = (1/2) \cdot \overline{|V_{\alpha\alpha} - V_{\beta\beta}|^2} \cdot 2\tau_c$.

In our range of correlation times ($\tau_c > 10^{-9}$ s) the condition $\omega_0 \tau_c \gg 1$ holds, so that $T_1^{-1} \ll (T_2^0)^{-1}$ and $T_2^{-1} = (T_2^0)^{-1}$.

To include the chemical exchange we need introducing several spin-Hamiltonians $\mathcal{H}(I)$, $\mathcal{H}(II)$ for radicals I and II chemically exchanging with each other:

$$\begin{aligned} \hat{\mathcal{H}}(I) &= \gamma \left[g_0^{-1} \cdot \hat{H}_0 \cdot \hat{g}(I) \cdot \hat{S} + \hat{I}_1 \cdot \hat{A}_1(I) \cdot \hat{S} + \hat{I}_2 \cdot \hat{A}_2(I) \cdot \hat{S} \right] \\ \hat{\mathcal{H}}(II) &= \gamma \left[g_0^{-1} \cdot \hat{H}_0 \cdot \hat{g}(II) \cdot \hat{S} + \hat{I}_1 \cdot \hat{A}_1(II) \cdot \hat{S} + \hat{I}_2 \cdot \hat{A}_2(II) \cdot \hat{S} \right]. \end{aligned} \quad (A1')$$

Before extracting anisotropic parts of these Hamiltonians it is worth to make some additional remarks concerning the g - and A - tensors for this kind of radicals. First, it should be noted that radicals I and II are identical and they are characterized by the same tensors but variously oriented. In addition, we suppose that anisotropic part of HFI

tensor is proportional to its isotropic value (that is quite natural because both isotropic and anisotropic parts of HFI are proportional to the value of spin density ρ_{π} on adjacent carbon atom). It allows to simplify the final expressions:

$$\hat{I}_{1,2} \cdot A_{1,2}(I, II) \cdot \hat{S} = a_{1,2}(I, II) \cdot \hat{I}_{1,2} \cdot \left[1 + b_{1,2}(I, II) \right] \cdot \hat{S}$$

where we used notations $a_{1,2}(I, II)$ and $a_{1,2}(I, II) \cdot b_{1,2}(I, II)$ for isotropic and anisotropic HFI respectively for nuclei \hat{I}_1, \hat{I}_2 in radicals I and II, 1 for unity matrix. As a result we have

$$\begin{aligned} \hat{H}(I) = & \gamma \left[H_0 + a_1(I) \cdot \hat{I}_1 + a_2(I) \cdot \hat{I}_2 \right] \cdot \hat{S} + \\ & + \gamma \left[H_0 \cdot \Delta g(I) / g_0 + a_1(I) \cdot \hat{I}_1 \cdot b_1(I) + a_2(I) \cdot \hat{I}_2 \cdot b_2(I) \right] \cdot \hat{S} = \hat{H}_0(I) + \hat{V}(I); \quad (A1'') \\ \hat{H}(II) = & \gamma \left[H_0 + a_1(II) \cdot \hat{I}_1 + a_2(II) \cdot \hat{I}_2 \right] \cdot \hat{S} + \\ & + \gamma \left[H_0 \cdot \Delta g(II) / g_0 + a_1(II) \cdot \hat{I}_1 \cdot b_1(II) + a_2(II) \cdot \hat{I}_2 \cdot b_2(II) \right] \cdot \hat{S} = \hat{H}_0(II) + \hat{V}(II). \end{aligned}$$

The perturbation $\hat{V}(t)$ can be written as a sum

$$\hat{V}(t) = f_x(t) S_x + f_y(t) S_y + f_z(t) S_z,$$

and taking into account (A2) we conclude that the values of T_2^{-1} and linewidth will be determined only by the term f_z :

$$(T_2)^{-1} = \overline{|f_{zz}(t)|^2} \cdot \tau_c.$$

The HFI constants with *para*- and *meta*-protons are equal to

$$a_1(I) = a_2(II) = a_p; \quad a_2(I) = a_1(II) = a_m.$$

We will take nuclei spins quantum numbers along z axis to be equal m_1 and m_2 for nuclei \hat{I}_1, \hat{I}_2 ; $(m_1, m_2) = (+, -)$. The spectral field position $H_0(m_1, m_2)$ of the lines with nuclei quantum number (m_1, m_2) determined by isotropic parts of Hamiltonians are:

$$H_0(m_1, m_2) = H_0^0 - m_1 \cdot a_1 - m_2 \cdot a_2$$

The following consideration depends on the relative rates of the molecular tumbling and the chemical exchange.

1. Fast molecular motion and slower chemical exchange

In this case the anisotropic part of Hamiltonian is averaged effectively by molecular rotation with residual linewidth:

$$\Gamma(m_1, m_2) = (2/\sqrt{3}) (\gamma \cdot T_2(m_1, m_2))^{-1},$$

where $(T_2(m_1, m_2))^{-1} = \overline{\gamma^2 \tau_c (H_0 \Delta g_{zz} / g_0 + a_1 m_1 b_{1zz} + a_2 m_2 b_{2zz})^2}$

It is known that for tensors **A** and **B** with zero traces the rotational averaging gives [1]:

$$\overline{A_{zz} B_{zz}} = (2/15) \cdot (\mathbf{A}:\mathbf{B}),$$

where $(\mathbf{A}:\mathbf{B})$ denotes the inner product of two tensors

$$(\mathbf{A}:\mathbf{B}) = \sum_{i,k} A_{ik} \cdot B_{ki}$$

As a result we obtain

$$\begin{aligned} T_2^{-1} = & (2/15) \gamma^2 \tau_c \left\{ \left[(H_o/g_o)^2 (\Delta g:\Delta g) + a_1^2 m_1^2 (b_1:b_1) + a_2^2 m_2^2 (b_2:b_2) \right] + \right. \\ & \left. + \left[2a_1 m_1 (H_o/g_o) (\Delta g:b_1) + 2a_2 m_2 (H_o/g_o) (\Delta g:b_2) + 2a_1 a_2 m_1 m_2 (b_1:b_2) \right] \right\} = \\ = & (2/15) \gamma^2 \tau_c \left\{ \left[(H_o/g_o)^2 (\Delta g:\Delta g) + (b_1:b_1) \cdot (a_1^2 m_1^2 + a_2^2 m_2^2) \right] + \right. \\ & \left. + \left[2a_1 m_1 (H_o/g_o) (\Delta g:b_p) + 2a_2 m_2 (H_o/g_o) (\Delta g:b_m) + 2a_1 a_2 m_1 m_2 (b_1:b_2) \right] \right\} \end{aligned}$$

Because of the symmetry of radicals I and II we have relationships between inner products:

$$\begin{aligned} (\Delta g(\text{II}):\Delta g(\text{II})) &= (\Delta g(\text{I}):\Delta g(\text{I})) = (\Delta g:\Delta g), \quad (b_2:b_2) = (b_1:b_1), \\ (\Delta g(\text{I}):b_1(\text{I})) &= (\Delta g(\text{II}):b_2(\text{II})) = (\Delta g:b_p) \quad - \text{for } \textit{para}\text{-protons}, \\ (\Delta g(\text{I}):b_2(\text{I})) &= (\Delta g(\text{II}):b_1(\text{II})) = (\Delta g:b_m) \quad - \text{for } \textit{meta}\text{-protons}. \end{aligned}$$

Chemical exchange has no influence on the components (++) and (--):

$$\begin{aligned} T_2^{-1} \begin{pmatrix} ++ \\ -- \end{pmatrix} = & (2/15) \gamma^2 \tau_c \left\{ \left[(H_o/g_o)^2 (\Delta g:\Delta g) + (b_1:b_1) \cdot (a_1^2 + a_2^2) / 4 \right] + \right. \\ & \left. a_1 a_2 (b_1:b_2) / 2 \pm \left[a_1 (H_o/g_o) (\Delta g:b_p) + a_2 (H_o/g_o) (\Delta g:b_m) \right] \right\}, \end{aligned}$$

but it results in spectral exchange between components (+-) and (-+). Very slow exchange ($\tau_{ex} \gg \gamma \cdot |a_1 - a_2|$) will cause only addition of τ_{ex}^{-1} to T_2^{-1} value for lines (+-) and (-+):

$$\begin{aligned} T_2^{-1} \begin{pmatrix} +- \\ -+ \end{pmatrix} = & (2/15) \gamma^2 \tau_c \left\{ \left[(H_o/g_o)^2 (\Delta g:\Delta g) + (b_1:b_1) \cdot (a_1^2 + a_2^2) / 4 \right] - \right. \\ & \left. a_1 a_2 (b_1:b_2) / 2 \pm \left[a_1 (H_o/g_o) (\Delta g:b_p) - a_2 (H_o/g_o) (\Delta g:b_m) \right] \right\} + \tau_{ex}^{-1}, \end{aligned}$$

meanwhile the fast chemical exchange ($\tau_{ex} \ll \gamma \cdot |a_1 - a_2|$) results in exchange narrowing of the lines (+-) and (-+) and triplet spectrum is observed with values of T_2^{-1} :

$$\begin{aligned} T_2^{-1} \begin{pmatrix} +- \\ -+ \end{pmatrix} = & (2/15) \gamma^2 \tau_c \left\{ \left[(H_o/g_o)^2 (\Delta g:\Delta g) + (b_1:b_1) \cdot (a_1^2 + a_2^2) / 4 \right] - \right. \\ & \left. a_1 a_2 (b_1:b_2) / 2 \right\} + \gamma^2 \cdot (a_1 - a_2)^2 \tau_{ex} / 8. \end{aligned}$$

Using above expressions for Δg - and b -tensors we obtain:

$$\begin{aligned} \Gamma_3 - \Gamma_1 &= (4/15\sqrt{3}) \gamma \tau_c \cdot \left[a_1 (\Delta g:b_p) + a_2 (\Delta g:b_m) \right] (H_o/g_o) \\ \Gamma_2 - \Gamma_1 &= (2/\sqrt{3}) \gamma \tau_{ex} \cdot (a_1 - a_2)^2 / 8 + \\ & (4/15\sqrt{3}) \gamma \tau_c \cdot \left[-a_1 a_2 (b_1:b_2) + \left[a_1 (\Delta g:b_p) + a_2 (\Delta g:b_m) \right] (H_o/g_o) \right] \end{aligned} \quad (\text{A3})$$

The substitution of all needed inner products in equations (A3) transforms them into (4) which were used in the text.

2. Fast molecular motion and very fast chemical exchange

The problem in this case is immensely complicated because the averaging by the process of chemical exchange (more effective mechanism) should be considered ahead of the molecular tumbling effects. Therefore 'exchange' terms appear in the expressions for linewidth of lines (++) and (--), because the orientational anisotropy for these lines has not yet been averaged by the molecular rotation and their spectral positions for radicals I and II are different. So the difference $\mathcal{H}(I) - \mathcal{H}(II)$ between spin-Hamiltonians of exchanging radicals is averaged by chemical exchange giving

$$T_2^{-1}(ex, \vec{n}) = (\mathcal{H}(I, \vec{n}) - \mathcal{H}(II, \vec{n}))^2 \tau_{ex} / 8$$

with line position $\omega_p(\vec{n}) = (\mathcal{H}(I, \vec{n}) + \mathcal{H}(II, \vec{n})) / 2$, where ' \vec{n} ' designates that all these values depend on orientation of radicals. Then fast rotations average the orientation dependent values $T_2^{-1}(ex, \vec{n})$ and $\omega_p(\vec{n})$ giving as a result the T_2^{-1} value:

$$T_2^{-1} = \overline{T_2^{-1}(ex, \vec{n})} + \left[\overline{T_2^{-1}(ex, \vec{n})} - \overline{T_2^{-1}(ex, \vec{n})} \right]^2 \tau_c + (\overline{\omega_p(\vec{n})} - \overline{\omega_p(\vec{n})})^2 \tau_c,$$

where $\overline{\omega_p} = \overline{\omega_p(\vec{n})}$. In the last formula the first term corresponds to the average 'exchange' width when two others give residual linewidth arising from averaging of both anisotropic 'exchange' linewidth $T_2^{-1}(ex, \vec{n})$ and position of the line $\omega_p(\vec{n})$.

Unfortunately, the practical realization of this formula has not been fulfilled and it remains unknown whether the influence of the chemical exchange on the registered value of τ_c appears essential. The solution of this problem needs additional experiments and hopefully will be achieved in near future.

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