Effect of the Spin Dephasing on the Photoconductivity-Detected Magnetic Resonance Spectra Observed in the Photolysis of Xanthone and *N*,*N*-Diethylaniline in 2-Propanol[†]

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The photoconductivity-detected magnetic resonance (PCDMR) spectrum observed in the photoinduced electron-transfer reaction of xanthone and *N*,*N*-diethylaniline in 2-propanol shows a peculiar spectral shape by microwave radiation with high power. The resonance center of the spectrum shows a spin-locking effect, and the wing portions show a broadened transition (pumping). When the lifetime of the radical-ion pair (RIP) becomes longer by controlling the solvent property, the wing portions become larger. We try to clarify the relation between the broadened wings and the lifetime of the radical-ion pair by the calculation employing the spin-dephasing effect. We conclude that the broadness appears under high microwave power conditions and the existence of effective triplet−triplet dephasing (TTD). TTD is the spin-phase relaxation between the triplet states of the radical-ion pair, and this relaxation may be mainly induced by the modulation of electron spin dipole−dipole interaction. The long lifetime of the present RIP system and its spin relaxation phenomena suggest the transient formation of a RIP confined strongly in a solvent cage or a structured RIP involving solvent molecule(s).

Introduction

Spin dynamics of a radical-ion pair (RIP) plays an important role in the photoinduced electron-transfer reaction because it controls the direction and efficiency of the photochemical reactions. Reaction-yield-detected magnetic resonance (RYDMR) methods[1−6] are used to investigate the reaction manifold and to control the reaction yield of the RIP. Photoconductivity-detected magnetic resonance (PCDMR)[7−10] is one of the RYDMR methods, which detects free ion radicals escaping from the RIP as photoconductivity. The intensity of the photoconductivity is proportional to the amount of free ion radicals, and its rise time almost reflects the decay rate of the RIP. In short, the lifetime of the RIP can be monitored by the rise time of the photoconductivity. The most important property of the PCDMR method is detection of only ion radicals, which have electric charges, and exclusion of the contribution of the neutral radicals, which may be generated by the hydrogen abstract reaction and so on.

Recently, we reported the PCDMR spectra and kinetics of the photoinduced electron-transfer reaction in the system of xanthone (Xn) and *N*,*N*-diethylaniline (DEA).[7] In the report, we showed an extraordinarily long lifetime of the RIP of this system in 2-propanol and the appearance of a broadened spectral shape under high microwave power conditions. The reaction scheme of this system[11] is as follows:

$$^3\mathrm{Xn}^* + \mathrm{DEA} \rightarrow {}^3\mathrm{RIP} \qquad \mathrm{(A)}$$

$$^3\mathrm{RIP} \xrightarrow{\mathrm{ISC}} {}^1\mathrm{RIP} \qquad \mathrm{(B)}$$

$$^1\mathrm{RIP} \xrightarrow{\mathrm{reaction}} \mathrm{products} \qquad \mathrm{(C)}$$

$$^{1,3}\mathrm{RIP} \xrightarrow{\mathrm{escape}} {\cdot}\mathrm{Xn}^+ + {\cdot}\mathrm{DEA}^- \qquad \mathrm{(D)}$$

$${\cdot}\mathrm{Xn}^+ + {\cdot}\mathrm{DEA}^- \xrightarrow{\mathrm{free\ pair}} {}^{1,3}\mathrm{RIP} \qquad \mathrm{(E)}$$

$${\cdot}\mathrm{Xn}^+ + {\cdot}\mathrm{DEA}^- \xrightarrow{\mathrm{quenching}} \mathrm{products} \qquad \mathrm{(F)}$$

where products in eq F may include neutral radicals.

When the microwave power was weak (10 W), photoconductivity decreased at the resonance center.[7] This phenomenon is easily explained by the acceleration of the reaction of the RIP by the microwave-induced transition between the triplet states followed by the $S-T_0$ mixing and is called a “pumping” effect. The PCDMR spectrum corresponds to the ordinary electron spin resonance (ESR) spectrum, which is composed of the hyperfine splitting of the cation and anion radicals. However, when the microwave power was strong (1 kW), the PCDMR spectrum was changed to a strange shape.[7] Photoconductivity increased at the resonance center because of the deceleration of the reaction by the prohibition of the $S-T_0$ mixing according to the strong coupling between the triplet states by the microwave field. This is called a “spin-locking” effect. This effect did not diminish even after 2 μs from its appearance. The pumping effect appears as wings at both sides of the spin-locking field. The broad wing structure of the pumping becomes gradually very intense under continuous microwave irradiation conditions. It is difficult to explain the broadness of this pumping by the ordinary ESR theory. This type of a broadened wing spectrum has been reported in the system of polymethylene-linked biradical,[1] which has a long lifetime. The lifetime of the present system is also long (about 200 ns).[7] The long lifetime of the present RIP in the homogeneous solution is another interesting problem that should be solved.

In this paper, we show the investigation of the strange line shape of the PCDMR spectra observed under high microwave power conditions using various solvents to control the lifetime

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of the RIP. The model calculation including the spin-phase relaxation is tried to analyze the peculiar spectral shape. An important contribution of the triplet−triplet dephasing (TTD) to the line shape is proposed. According to these results, the property of the present RIP is discussed.

Theory

To investigate the cause of the broadened spectral shape, a single-site exponential model of a modified Liouville equation including the microwave field and spin dephasing[12,13] was used for the theoretical calculation as follows:

$$\frac{\partial \rho_{\mathrm{RIP}}}{\partial t} = -\frac{i}{\hbar}[\hat{\boldsymbol{H}}, \rho_{\mathrm{RIP}}] - \hat{\hat{\boldsymbol{K}}}_{\mathrm{S}}\rho_{\mathrm{RIP}} - \hat{\hat{\boldsymbol{W}}}\rho_{\mathrm{RIP}} - k_{\mathrm{e}}\rho_{\mathrm{RIP}} + k_{\mathrm{f}}{\rho_{\mathrm{IR}}}^{2} \quad (1)$$

$$\frac{\partial \rho_{\mathrm{IR}}}{\partial t} = k_{\mathrm{e}}\rho_{\mathrm{RIP}} - k_{\mathrm{f}}{\rho_{\mathrm{IR}}}^{2} - k_{\mathrm{q}}{\rho_{\mathrm{IR}}}^{2} \quad (2)$$

where ρ_{RIP} and ρ_{IR} are the spin density of the RIP and that of the free ion radicals, respectively. The spin Hamiltonian is given as

$$\hat{\boldsymbol{H}} = \hat{\boldsymbol{H}}_{\mathrm{Z}} + \hat{\boldsymbol{H}}_{\mathrm{hyp}} + \hat{\boldsymbol{H}}_{\mathrm{ex}} + \hat{\boldsymbol{H}}_{\mathrm{rf}} \quad (3)$$

where $\hat{\boldsymbol{H}}_{\mathrm{Z}}$, $\hat{\boldsymbol{H}}_{\mathrm{hyp}}$, $\hat{\boldsymbol{H}}_{\mathrm{ex}}$ and $\hat{\boldsymbol{H}}_{\mathrm{rf}}$ are the Zeeman, hyperfine, exchange interaction, and microwave field terms, respectively.

$$\hat{\boldsymbol{H}}_{\mathrm{Z}} = (g_{\mathrm{a}}\mu_{\mathrm{B}}\hbar^{-1}\boldsymbol{B}_0 - \omega)\cdot\hat{\boldsymbol{S}}_{\mathrm{az}} + (g_{\mathrm{b}}\mu_{\mathrm{B}}\hbar^{-1}\boldsymbol{B}_0 - \omega)\cdot\hat{\boldsymbol{S}}_{\mathrm{bz}} \quad (3a)$$

$$\hat{\boldsymbol{H}}_{\mathrm{hyp}} = \sum_{n} A_{\mathrm{a},n}\hat{\boldsymbol{S}}_{\mathrm{a}}\cdot\hat{\boldsymbol{I}}_{\mathrm{a},n} + \sum_{m} A_{\mathrm{b},m}\hat{\boldsymbol{S}}_{\mathrm{b}}\cdot\hat{\boldsymbol{I}}_{\mathrm{b},m} \quad (3b)$$

$$\hat{\boldsymbol{H}}_{\mathrm{ex}} = J({}^{1}/_{2} + 2\hat{\boldsymbol{S}}_{\mathrm{a}}\cdot\hat{\boldsymbol{S}}_{\mathrm{b}}) \quad (3c)$$

$$\hat{\boldsymbol{H}}_{\mathrm{rf}} = g_{\mathrm{a}}\mu_{\mathrm{B}}\hbar^{-1}\boldsymbol{B}_1\cdot\hat{\boldsymbol{S}}_{\mathrm{ax}} + g_{\mathrm{b}}\mu_{\mathrm{B}}\hbar^{-1}\boldsymbol{B}_1\cdot\hat{\boldsymbol{S}}_{\mathrm{bx}} \quad (3d)$$

where the exchange interaction J is a function of the distance of two radicals in the RIP, and the averaged value of J is used here. $\hat{\hat{\boldsymbol{K}}}_{\mathrm{S}}$ is the reaction super operator from the singlet state, and k_{p} is the reaction rate constant of the singlet state.

$$\hat{\hat{\boldsymbol{K}}}_{\mathrm{S}}\rho_{\mathrm{RIP}} = \frac{k_{\mathrm{p}}}{2}[\hat{\boldsymbol{P}}_{\mathrm{S}}, \rho_{\mathrm{RIP}}] = \frac{k_{\mathrm{p}}}{2}(\hat{\boldsymbol{P}}_{\mathrm{S}}\rho_{\mathrm{RIP}} + \rho_{\mathrm{RIP}}\hat{\boldsymbol{P}}_{\mathrm{S}}),\ \ \hat{\boldsymbol{P}}_{\mathrm{S}} = |\mathrm{S}\rangle\langle\mathrm{S}| \quad (4)$$

$\hat{\hat{\boldsymbol{W}}}$ is the spin dephasing superoperator of the RIP, which includes both singlet−triplet dephasing (STD) and TTD.

$$\hat{\hat{\boldsymbol{W}}} = \hat{\hat{\boldsymbol{W}}}_{\mathrm{STD}} + \hat{\hat{\boldsymbol{W}}}_{\mathrm{TTD}} \quad (5)$$

$$\hat{\hat{\boldsymbol{W}}}_{\mathrm{STD}} = k_{\mathrm{STD}}\sum_{j=0,\pm1}(|\mathrm{ST}_j\rangle\langle\mathrm{ST}_j| + |\mathrm{T}_j\mathrm{S}\rangle\langle\mathrm{T}_j\mathrm{S}|) \quad (5a)$$

$$\hat{\hat{\boldsymbol{W}}}_{\mathrm{TTD}} = k_{\mathrm{TTD}}\sum_{i=\pm1}(|\mathrm{T}_i\mathrm{T}_0\rangle\langle\mathrm{T}_i\mathrm{T}_0| + |\mathrm{T}_0\mathrm{T}_i\rangle\langle\mathrm{T}_0\mathrm{T}_i|) \quad (5b)$$

k_{e} is the escape rate constant of the RIP. k_{f} is the free-pair-generating rate constant of free ion radicals. k_{q} is the bimolecular quenching rate constant of free ion radicals. In these calculations, no apparent contribution of k_{q} and k_{f} to the calculated spectral shape was recognized.

As for the spin dephasing, STD[12] is the phase relaxation between the singlet and triplet states and is thought to be due to the modulation of J and/or the anisotropy of the hyperfine coupling constant (A_{aniso}) and the g value (g_{aniso}). TTD is the phase relaxation between triplet states and may be induced by the modulation of the electron spin dipole−dipole (d−d) interaction or A_{aniso} and g_{aniso} or both. When the distance of the radicals changes rapidly, J is modulated intensively and the STD rate may increase. The tumbling motion of individual radicals may induce both STD and TTD by A_{aniso} and g_{aniso}. The tumbling motion of a whole radical pair may induce TTD by the d−d interaction. We did not include the d−d interaction in the Hamiltonian (eq 3) because the matrix elements of this interaction are traceless and no significant effect on the present system in the homogeneous solution is expected. However, the modulation of this d−d interaction by the random motion works as one of the causes of the spin phase relaxation (eq 5).

Experimental Section

The concentrations of Xn and DEA were 1.0×10^{-3} and 2.0×10^{-2} M (mol/dm^3), respectively, in all experiments. 2-Propanol, 1-propanol, and mixtures of cyclohexanol and acetonitrile were used as solvents. Mixing ratios of cyclohexanol/acetonitrile were 3:1 and 3:2. The sample solution, which was deoxygenated by bubbling with nitrogen gas, was excited by the third harmonic light of a Nd:YAG laser ($\lambda = 355$ nm) in an X-band electron spin resonance (ESR) cavity (TE$_{011}$ mode) at room temperature. Xn could be excited selectively by this laser under the present conditions. Photoconductivity was measured in a specially designed flat quartz-flow cell (light path of 0.6 mm) with platinum electrodes. The potential between electrodes was about 150 V/mm. Experimental setup was the same as that of the previous paper.[7] A 50 Ω resistance inserted in the observation circuit, which converted photocurrent to voltage, gave a time resolution of ca. 20 ns. A proton-resonance-type NMR gaussmeter was used for the PCDMR observation. The signal of the transient photoconductivity stored in a 10 bit digital oscilloscope (LeCroy 9430) was transferred to a microcomputer system for data processing. The observed data were converted to the “field effect”, which was the ratio of the photoconductivity intensity change as shown in eq 6.

$$\text{field effect} = \frac{I(\mathrm{MW_{on}}) - I(\mathrm{MW_{off}})}{I(\mathrm{MW_{off}})} \quad (6)$$

A traveling wave tube (TWT) amplifier (Litton) with a maximum power of 1 kW was used to boost the microwave pulse (duration of 10 μs). The microwave power was 1 kW ($B_1 \approx 3$ mT) for spin locking and 10 W ($B_1 \approx 0.3$ mT) for pumping. These B_1 values (microwave magnetic field) were estimated using a system showing a quantum oscillation by the microwave field.[4] The microwave pulse was switched on 2 μs before the laser pulse, and all of the experimental sequence was done in the duration of the microwave pulse.

Results and Discussion

Experimental Observation of the Solvent Effect on PCDMR Spectra. Figure 1 shows the PCDMR spectra observed at 1 kW microwave power radiation in different solvents. All spectra show the spin-locking effect at the resonance center and the pumping as wings. The rise time of photoconductivity, which might nearly reflect the lifetime of the RIP, became slower in the following order: mixed solvent of cyclohexanol and acetonitrile (fast) [3:2 > 3:1] > 1-propanol > 2-propanol (slow). The rise time in the different mixing solvents was not able to be distinguished because of an instrumental limitation, but the lifetime of the RIP in 3:2 cyclohexanol/acetonitrile could be shorter than that in the 3:1 mix because of the low viscosity and the high permittivity. It is apparent that the pumping wing

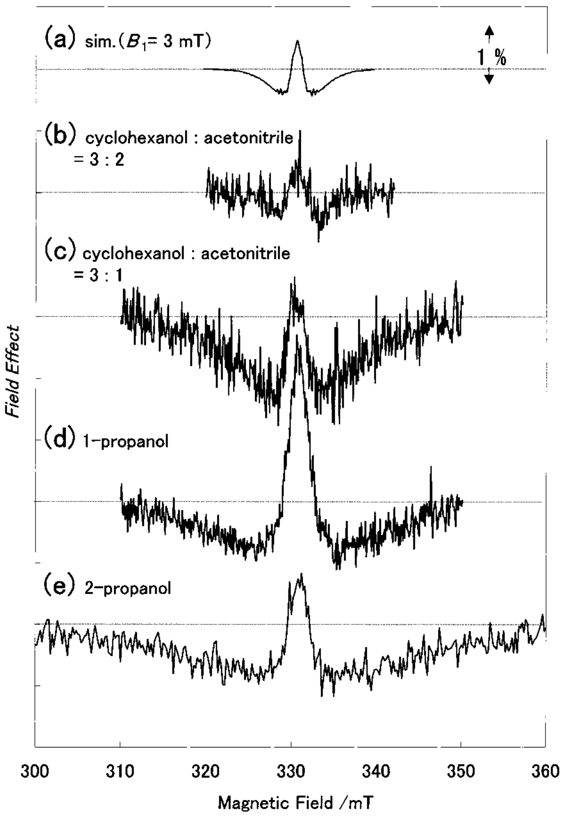

Figure 1. The solvent effect on the PCDMR spectrum observed at the radiation of high microwave power (1 kW) in which the data were time-integrated between 1.0 and 1.5 μs after excitation: (a) the calculation that takes account of only spin Hamiltonian (see text); PCDMR spectra observed (b) in a mixed solvent of cyclohexanol and acetonitrile of the ratio of 3:2, (c) in a mixed solvent of 3:1, (d) in 1-propanol, and (e) in 2-propanol. The straight horizontal lines show the baselines of the respective spectra.

structure becomes larger when the lifetime of the RIP is longer. Contrary to this observation, the line width of the spectral center showing the spin locking is not apparently changed. When the lifetime of the RIP is shorter, PCDMR spectrum is in good accordance with the simple calculation of the spin Hamiltonian without exchange interaction.[14] When the microwave power was weak (10 W), PCDMR spectra in these systems were almost identical (not shown here); that is, these systems did not show the solvent effect on the spectral shape. This result suggests that there is no strong relation between the lifetime and the spectral shape of the RIP in low microwave power conditions. The simple calculation using the spin Hamiltonian without J[14] nearly reproduced the observed spectrum.

Theoretical Calculation of the Effect of Exchange Interaction on the Spin-Locking. First of all, we examined the effect of the magnitude of the averaged exchange interaction, J, on the spectral shape. J is known as one-half of the energy separation between the S state and the T_0 state of the RIP. When the RIP feels a large J at the close encounter of radicals, S$-T_0$ mixing is suppressed. This behavior is similar to the spin-locking phenomenon, which separates the S and T_0 states. The contribution of J to the calculation is shown in Figure 2. Here, the rate parameters of the spin dephasing (k_{STD}, k_{TTD}) are assumed to be zero. As shown in Figure 2a, the finite J value affects the spectral center, namely, it enhances the spin-locking effect. When the J is zero, the spin locking appears only immediately after laser excitation and the field effect gradually decreases to "pumping" as shown in Figure 2b. However, the field effect showing the spin locking does not decrease and does not change, when the J is larger than 0.1 mT. Therefore, J works to enhance the effect of spin locking. This time-independent phenomenon under a finite J is similar to the experimentally observed results of time dependence of the PCDMR spectral center. Accordingly, the present RIP system has a finite J.

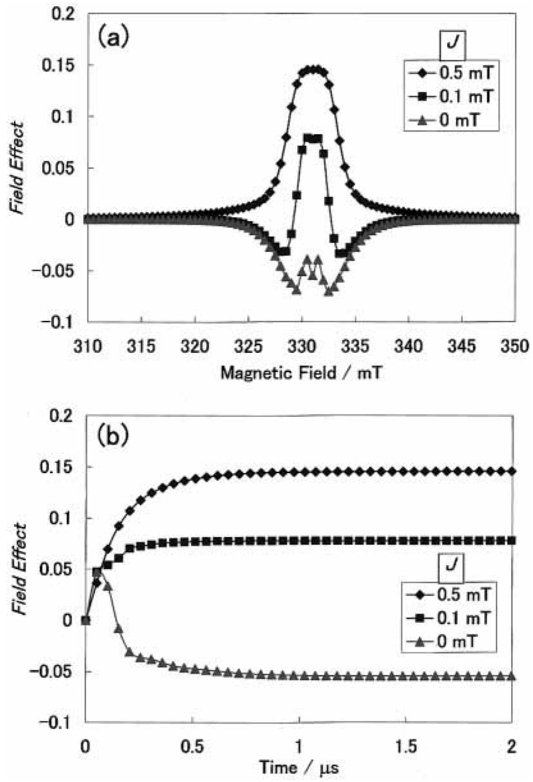

Figure 2. The effect of the exchange interaction J of 0, 0.1, and 0.5 mT (a) on a calculated PCDMR spectra (B_1 = 3 mT) at 1.5 μs after the RIP formation and (b) on the time profiles at the spectral center (331.0 mT).

Theoretical Calculation of the Effect of Spin Dephasing on the Spectral Shape. When we handle the spin relaxation of a radical pair, the concept of spin dephasing may be appropriate. There are two spin-dephasing mechanisms: STD (singlet$-$triplet dephasing, eq 5a) and TTD (triplet$-$triplet dephasing, eq 5b). STD was proposed by Shusin,[12] and we employed this concept to rationalize the spin dynamics observed in the system of a singlet-born radical pair in an SDS micelle.[15,16] The result of the model calculation is shown in Figure 3a. The effect of STD only appears at the resonance center where the spin locking works and does not appear at the wing portions (no broad wings). When the k_{STD} increases, the contribution of pumping becomes larger and the magnitude of field effect decreases by time. Consequently, STD works to spoil the spin-locking effect. Because the spin locking of the PCDMR spectra shown in Figure 1 did not decrease by time, the effect of STD did not apparently work in the present system.

In contrast, TTD works for the appearance of the wing portion as shown in Figure 3b. TTD has been proposed and applied to the analysis of the quantum beat phenomenon in a micellized radical pair.[17] When the rate constant of k_{TTD} increases, the wing portions gradually increase. Furthermore, it does not affect the spin-locking portion at the resonance center. When the microwave power is weak, the effect of TTD disappears dramatically in both the experimental spectrum and the calculated one. The appearance of the broad wings of the spectrum requires high microwave power and effective TTD.

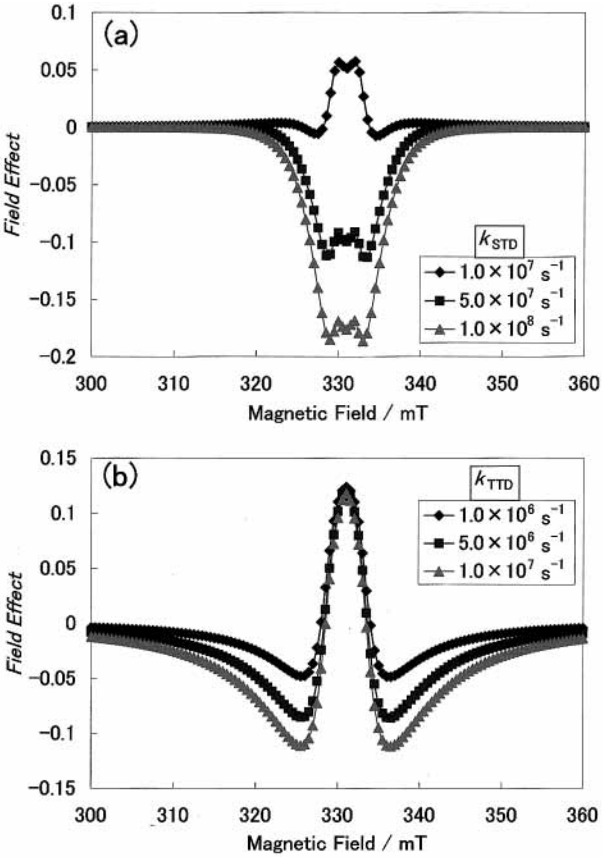

Figure 3. The effect of STD and TTD on the calculated spectral shape ($B_1 = 3$ mT, $J = 0.5$ mT) at 1.5 μs after the RIP formation: (a) the effect of STD where $k_{TTD} = 0$; (b) the effect of TTD where $k_{STD} = 0$.

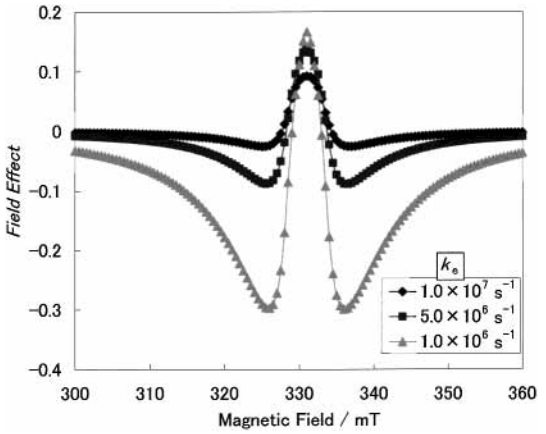

Figure 4. The effect of the lifetime of the RIP ($1/k_e$) on the spectral shape under the active TTD conditions ($k_{TTD} = 1.0 \times 10^7$ s^{-1}, $k_{STD} = 0$, $B_1 = 3$ mT, $J = 0.5$ mT) at 1.5 μs after the RIP formation.

The correlation between the appearance of the wing portions and the lifetime of the RIP is examined by the model calculation including TTD as shown in Figure 4. In the present system, the lifetime of the RIP is mainly controlled by the escape rate, k_e.[7] When k_e increases, the wing pumping part is gradually weakened and seems to be narrowed. This means that a long lifetime of the RIP along with the effective TTD and high power of microwave makes the wing parts of the spectrum more intense (apparent broadening).

Here, we consider the conventional concept of spin relaxation. Because the spin relaxation is induced by A_{aniso}, g_{aniso}, and d−d interaction, the spin dephasing phenomena, STD and TTD, are surely related to the concept of spin relaxation, especially to the spin−spin relaxation time, T_2. The calculation trial of the present model using the Redfield matrix[18,19] instead of the superoperator of STD and TTD shows that the spectral wings are gradually growing by decreasing T_2. However, the spectral center of the spin-locking portion also decreases as shown in Figure 5. This suggests that T_2 includes both contributions of STD and TTD together as we expected. Our experimental data cannot be explained only by T_2, and the spin-dephasing calculation suggests that the contribution of STD is weak compared with that of TTD in the present system. Consequently, it is concluded that the most important contribution to the spectral shape is TTD, which is mainly induced by the modulation of electron spin dipole−dipole interaction in the present system. The contribution of the anisotropy of the hyperfine coupling constants and g factor may be weak. This conclusion is in contrast with that reported in the system of polymethylene-linked biradical[1] in which the contribution of STD to the RYDMR data was proposed. Especially, the J modulation due to the fast fluctuation of the distance of two radicals was pointed out. Although this polymethylene-linked system should show much a stronger spin-locking effect at nearly the same B_1 field as the present report because of the narrower hyperfine distribution of the biradical, the spin-locking effect appeared weakly.[20] Contrary to this system, the spin-locking portion of the PCDMR spectrum is stronger in the present system. This may be due to the effective TTD induced by the tumbling motion of the electron spin dipole−dipole interaction of the RIP, and the distance fluctuation probably does not work effectively in the present system. Furthermore, the contribution of the degenerate electron hopping between DEA$^{\bullet+}$ radical and DEA, which may reduce T_2, was not apparently observed even upon changing the concentration of DEA in the present system. Because the long lifetime of the present RIP system is still mysterious, different aromatic amines were used instead of DEA to examine the contribution of the counter radical.

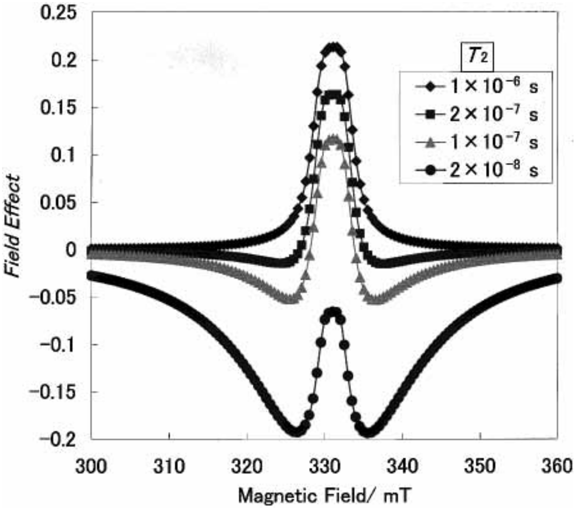

Figure 5. The effect of T_2 in the Redfield matrix used instead of TTD and STD on the spectral shape ($B_1 = 3$ mT, $J = 0.5$ mT, $T_1 = 1.0$ μs) at 1.5 μs after the RIP formation.

Experimental Observation of the Effect of Other Aromatic Amine-Reducing Reagents. There are several reports of radical pair systems with long lifetimes and showing magnetic field effects in 2-propanol.[7−9,11] Therefore, the cause of the long lifetime of the radical pair is thought to be 2-propanol as a special solvent. In the present report, all of the solvents other than 2-propanpl showed shorter lifetime. We examined several

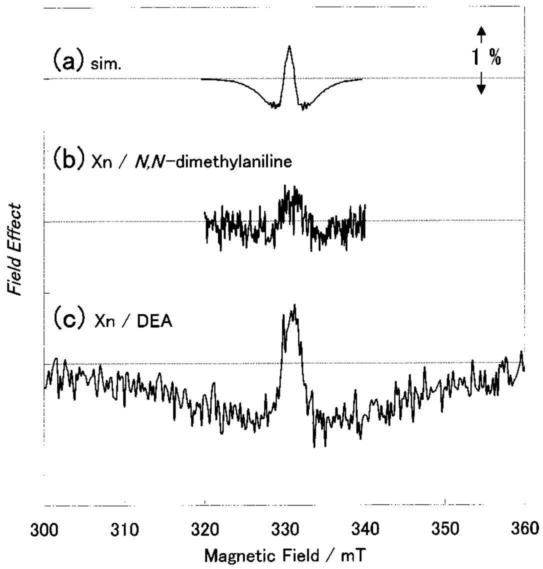

Figure 6. The PCDMR spectra in 2-propanol observed at the radiation of strong microwave power (1 kW) in which the data were time-integrated between 1.0 and 1.5 μs after laser excitation: (a) the calculated spectrum that takes account of only spin Hamiltonian; (b) the system of Xn and *N*,*N*-dimethylaniline; (c) the system of Xn and DEA. The straight horizontal lines show the baselines of the respective spectra.

combinations of Xn and the other aromatic amine systems in 2-propanol. In Figure 6, the PCDMR spectrum observed in the system of Xn and *N*,*N*-dimethylaniline is shown along with that of the present system. Even in 2-propanol, this system seems to show weak pumping. The fast rise of the photoconductivity observed in this system indicates that the lifetime of the RIP is much shorter than that of Xn/DEA in 2-propanol. The system of Xn and *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine also showed a shorter lifetime, and the spectrum did not show broadened wings (not shown here). Consequently, the use of 2-propanol is not the only cause of the long lifetime of the RIP. The combined system of Xn, DEA, and 2-propanol worked efficiently to prolong the lifetime of the RIP, so far. It is apparent that the Coulomb force in the RIP is not the main contribution in the present system. This is a natural situation because of the weak Coulomb force in highly polar solvents such as alcohols. According to the above results and discussion, we tentatively propose the transient formation of the RIP of Xn anion and DEA cation being confined in a solvent cage or having a local structure involving 2-propanol molecule(s). In this case, the fluctuation of the distance between the two radical ions is not the main cause of the spin relaxation. In other words, the contribution of the modulation of the exchange interaction is not significant. The tumbling motion of the electron spin dipole−dipole interaction induces the spin relaxation as discussed before. At this stage, the observation of this kind of RIP in solvent is not easy and a high-microwave-powered RYDMR technique can provide the information.

Conclusion

The photoinduced electron-transfer reaction of Xn and DEA was studied by the PCDMR method. These PCDMR spectra showed spin locking at the resonance center and broad-wing-like pumping at both sides of the spectral center. The appearance of the wing portions is related to the lifetime of the RIP. As the lifetime of the RIP becomes longer, the broad wings become more intense. The one-site exponential model of the Liouville equation including spin-dephasing operators is used for the simulation of the present system. The finite exchange interaction, which is due to two closely located radicals, enhances the spin locking. The pumping under high microwave power is enhanced by TTD together with the long lifetime of the RIP. The TTD may be mainly caused by the electron spin dipole−dipole interaction. The combination of Xn, DEA, and 2-propanol may make the RIP more stable under conditions in which the two radicals are confined in the short range.

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