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A Laser Flash Photolysis Study of Electron Transfer Processes of $[Ru(bpy)_3]^{2+}$ in High Magnetic Field

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Synopsis. The effect of high magnetic fields ($\leqslant$13 T) on the charge transfer reaction between Ru(II) tris(2,2′-bipyridine) and methylviologen is studied by laser flash photolysis in a pulse magnet. The initial yield of the methylviologen radical *decreases* by about 20% at 13 T and the second order decay rate constant of the escaped radicals *increases* as the magnetic field increases. These effects of high magnetic field are interpreted in terms of the Δg mechanism with strong spin-orbit coupling proposed by Steiner et al.

In many years, studies of magnetic field effects (MFEs) on reactions such as hydrogen abstraction and electron transfer reactions have been reported.[1—4] They are mainly carried out in low magnetic field ($\lesssim$1 T) and the mechanisms of MFEs on radical pairs and biradicals have been mostly established in low magnetic field. Very recently, the effects of high magnetic field (>1 T) upon electron transfer[5—8] and hydrogen abstraction reactions[9,10] have been reported.

The electron transfer processes of Ru(II) complexes have been studied in a magnetic field up to 5 T by Steiner's group,[5,11,12] and Ferraudi and Arguello.[7] In $[Ru(bpy)_3]^{2+}$ and methylviologen (MV^{2+}) system Steiner et al. observed the yield of the methylviologen radical ($^2MV^+$) produced by electron transfer reaction from $[Ru(bpy)_3]^{2+}$ complex in a magnetic field up to 3.5 T. As the magnetic field increases from zero to 3.5 T, the yield of $^2MV^+$ decreases. They explained this MFE by the Δg mechanism with strong spin-orbit coupling (SOC). The singlet and triplet states of the radical pair of $^2[Ru(bpy)_3]^{3+}$ and $^2MV^+$ are mixed considerably due to the strong SOC at the Ru center. Since $^2[Ru(bpy)_3)]^{3+}$ has an electron *g*-value much larger than that of usual organic radicals, difference of *g*-values in two radicals (Δg) induces fast transitions among singlet and triplet states of the pair by applying a magnetic field.

In a previous paper,[10] we examined the effect of high magnetic field (<14 T) on chain-linked triplet biradicals. In that study, a new type of MFE, which can not be detected in low magnetic field, emerges into the photoprocess in high magnetic field. The purpose of this paper is to examine whether the Δg mechanism, proposed by Steiner for interpretation of the MFE on the correlated radical pair generated by the electron transfer reaction of $[Ru(bpy)_3]^{2+}$ and MV^{2+} system at relatively low field (<5 T), is applicable to the effects on the correlated and uncorrelated pairs caused by high magnetic field (5—13 T). Further, we consider the spin-lattice relaxation induced by anisotropic *g*-value which becomes important in the decay of organic biradicals in high magnetic field as reported in a previous paper.[10]

Experimental

Materials. $Ru^{II}(2,2'\text{-bipyridine})_3Cl_2\cdot 6H_2O$ ($[Ru(bpy)_3]^{2+}$) and methylviologen (MV^{2+}) were purchased from Aldrich Chem. Co. Solvent used was deionized water. Concentrations of $[Ru(bpy)_3]^{2+}$ and MV^{2+} were about 4×10^{-5} M and 10^{-2} M (1 M=1 mol dm^{-3}), respectively. The ionic strength of the solutions was adjusted to 0.2 M by adding suitable amounts of NaCl. The solutions were deaerated by several freeze-pump-thaw cycles.

Apparatus. The transient absorption signals in high magnetic fields were measured with a pulsed-magnetic-field laser flash photolysis system which was reported in a previous paper.[9] A pulsed high magnetic field (<20 T, 2 ms) was generated by supplying an intense pulsed current from a capacitor bank (Nichicon, 5 kV, 50 kJ) to a homemade solenoid (9.7 mH, 0.7 Ω). The pump light source was the third harmonics (355 nm, fwhm 8 ns, 110 mJ/pulse) of an Nd:YAG laser (Spectra-Physics, GCR-11-1). The probe light source was an Xe arc lamp (Ushio, 150 W). The probe light was led to a 20-cm monochromator (Ritsu, MC-20L)–photomultiplier (Hamamatsu, R928)–digital oscilloscope (Tektronix, 2440)–microcomputer (NEC, PC-9801) system through a 3-m quartz optical fibre bundle (Fujikura, FBB-5-3M-A).

Results and Discussion

The reaction scheme between $[Ru(bpy)_3]^{2+}$ and MV^{2+} is expressed as follows: [5,12]

$$[Ru(bpy)_3]^{2+} \xrightarrow{h\nu} {}^1[Ru(bpy)_3]^{2+} \tag{1}$$

$$^1[Ru(bpy)_3]^{2+} \longrightarrow {}^3[Ru(bpy)_3]^{2+} \tag{2}$$

$$^3[Ru(bpy)_3]^{2+} + MV^{2+} \longrightarrow {}^3[Ru(bpy)_3{}^{3+}\cdots MV^+] \tag{3}$$

$$^3[Ru(bpy)_3{}^{3+}\cdots MV^+] \longrightarrow {}^2[Ru(bpy)_3]^{3+} + {}^2MV^+ \tag{4}$$

$$^3[Ru(bpy)_3{}^{3+}\cdots MV^+] \longrightarrow [Ru(bpy)_3]^{2+} + MV^{2+} \tag{5}$$

By photoexcitation and fast intersystem crossing, the lowest excited triplet state of an $[Ru(bpy)_3]^{2+}$ complex, $^3[Ru(bpy)_3]^{2+}$, is generated ((1) and (2)). Then charge transfer reaction occurs between $^3[Ru(bpy)_3]^{2+}$ and MV^{2+}, yielding the primary redox pair $^3[Ru(bpy)_3{}^{3+}\cdots MV^+]$ (3). From $^3[Ru(bpy)_3{}^{3+}\cdots MV^+]$ pair, solvent cage escape (4) and back electron transfer (5) processes occur.

In the transient absorption spectra of an $[Ru(bpy)_3]^{2+}$ and MV^{2+} system after 355 nm laser excitation, the absorption bands of the $^2MV^+$ radical are observed at about 395 nm and 500—600 nm region.[13] We examined the absorption intensity and time profile of transient absorption signal of $^2MV^+$ in high magnetic fields. Figure 1 shows the transient absorption signals observed at 550 nm in magnetic fields. As applied magnetic fields increase, the intensity of the transient absorption signal decreases. The absorbance immediately after laser excitation is attributable to the $^2MV^+$ radical escaped from a correlated radical pair $[Ru(bpy)_3^{3+}\cdots MV^+]$, whereas the intensity decrease occuring in the several tens μs time region is due to the reaction in the uncorrelated radical pair, generated by the collision of escaped $^2[Ru(bpy)_3]^{3+}$ and $^2MV^+$.

Magnetic Field Effects on the Correlated Pair. Firstly we examined the effects on the correlated pair. The relative yield, $\phi(H_{ex})$, of the escaped $^2MV^+$ radical from the correlated pair at a magnetic field H_{ex} is estimated from the absorbance immediately after laser excitation. The ratio $\phi(H_{ex})/\phi(0)$ of the yield in the presence and absence of a magnetic field H_{ex} is shown in Fig. 2. The ratio decreases significantly with increasing a magnetic field from zero to about 6 T and then becomes almost a constant value (ca. 0.8). The dependence of the ratio on the magnetic field up to 3.2 T is in good agreement with Steiner's results.[5,11,12]

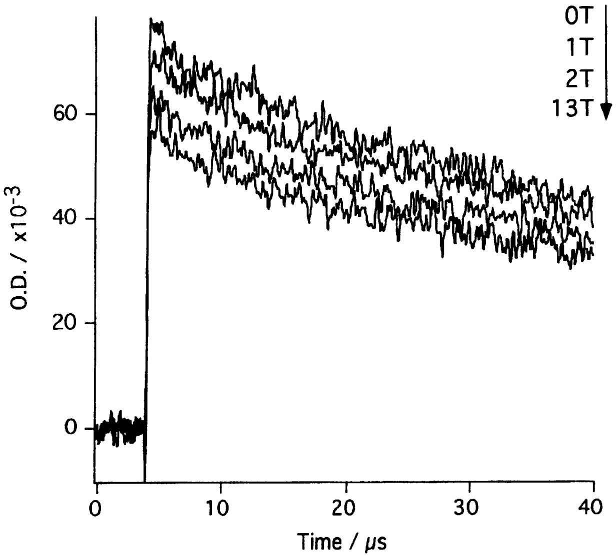


Fig. 1. Magnetic field effect on the decay of $^2MV^+$. The transient absorption signals were observed at 550 nm.

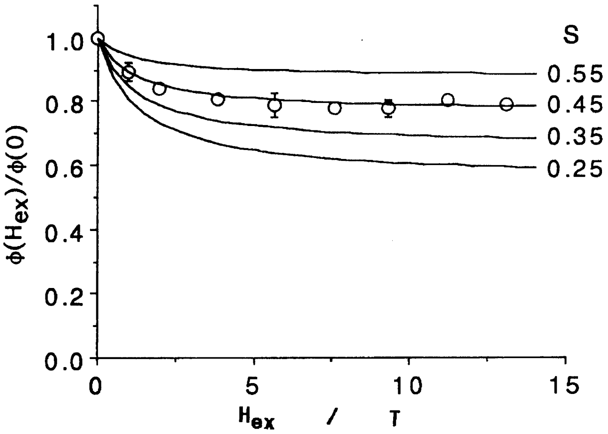
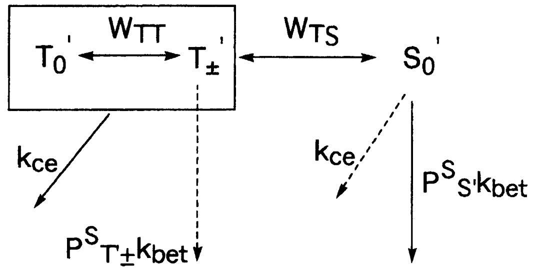


Fig. 2. The magnetic field dependence of the ratio $\phi(H_{ex})/\phi(0)$ of the yield of the escaped $^2MV^+$ radical in the presence and absence of a magnetic field H_{ex}. Error bars represent the standard deviation for five separate experiments. Lines are calculated using Eqs. 8, 9, 10, and 11 for various initial s' population. $D_r=12.5$ ns^{-1} and $k_{ce}=5$ ns^{-1} were kept constant. k_{bet} was adjusted that the yield is constant without magnetic field according to Steiner's method. The following values of k_{bet} (in the order of increasing s') had to be employed: 152, 127, 107, and 92 ns^{-1}.



Scheme 1. Reaction scheme. Taken from Ref. 12.

The model calculation of the absorption intensity of $^2MV^+$ in high magnetic field was attempted by applying the kinetic treatment given by Steiner and Bürßner.[12] The reaction scheme and parameters used are shown in Scheme 1. S′ and T'_0, $T'_\pm$ are singlet and triplet sublevels of a redox radical pair, respectively. T'_0 is pure triplet state but S′ and $T'_\pm$ are the mixed states between singlet and triplet states due to the strong SOC of Ru(III) complex. $^2MV^+$ radicals escape from all spin substates of radical pair with the rate constant k_{ce} and undergo back electron transfer from S′ and $T'_\pm$ states. Since the back electron transfer is much faster for S′ than $T'_\pm$, the effective back electron transfer rate constants are expressed as $P^s_{S'}k_{bet}$ and $P^s_{T'_\pm}k_{bet}$ for S′ and $T'_\pm$ states, respectively and $P^s_{S'}k_{bet} : P^s_{T'_\pm}k_{bet}=10:1$.[12] The relaxation between T′ states occur at a rate of W_{TT} and T′ states equilibrate with S′ at a rate constant of W_{TS}. W_{TT} and W_{TS} are expressed as follows:

$$W_{TT} = a_{TT}D_r + b_{TT}H_{ex} \tag{6}$$

$$W_{TS} = a_{TS}D_r + b_{TS}H_{ex} \tag{7}$$

where D_r is the diffusion constant and H_{ex} is the applied magnetic field. The following values are assumed:[12] $a_{TT}=10$, $a_{TS}=1$, $b_{TT}=100$ ns^{-1}T^{-1}, and $b_{TS}=20$ ns^{-1}T^{-1}. The kinetic rate equations of this system are expressed as follows:

$$\frac{d}{dt}[T'_0] = -(k_{ce}+2W_{TT})[T'_0] + W_{TT}([T'_+]+[T'_-]) \tag{8}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{T}'_+] = -(k_{\mathrm{ce}} + W_{\mathrm{TT}} + W_{\mathrm{TS}} + P^{\mathrm{S}}_{\mathrm{T}'_+} k_{\mathrm{bet}})[\mathrm{T}'_+] + W_{\mathrm{TT}}[\mathrm{T}'_0] + W_{\mathrm{TS}}[\mathrm{S}'_0] \tag{9}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{T}'_-] = -(k_{\mathrm{ce}} + W_{\mathrm{TT}} + W_{\mathrm{TS}} + P^{\mathrm{S}}_{\mathrm{T}'_-} k_{\mathrm{bet}})[\mathrm{T}'_-] + W_{\mathrm{TT}}[\mathrm{T}'_0] + W_{\mathrm{TS}}[\mathrm{S}'_0] \tag{10}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{S}'_0] = -(k_{\mathrm{ce}} + 2W_{\mathrm{TS}} + P^{\mathrm{S}}_{\mathrm{S}'} k_{\mathrm{bet}})[\mathrm{S}'_0] + W_{\mathrm{TS}}([\mathrm{T}'_+] + [\mathrm{T}'_-]) \tag{11}$$

The yield of the $^2\mathrm{MV}^+$ radical escaped from the correlated pair is calculated by integrating the value of $k_{\mathrm{ce}}([\mathrm{T}'_0]+[\mathrm{T}'_+]+[\mathrm{T}'_-]+[\mathrm{S}'_0])$ at 800 time points for 0.2 ns. Lines in Fig. 2 show the magnetic field dependence of the escaped radical yield with several initial populations of S′ state, s'. From Fig. 2, the best fitting parameters are obtained to be $s'=0.45$, $D_{\mathrm{r}}=12.5\ \mathrm{ns}^{-1}$ and $k_{\mathrm{bet}}=107\ \mathrm{ns}^{-1}$. These values are in good agreement with the results of Steiner and Bürßner.[12)]

In high magnetic field, spin-lattice relaxation induced by the g-anisotropy becomes important in the case of organic biradicals.[10)] This term, however, seems not to be given in Eqs. 6 and 7 as its usual form. Thus, the relaxation rate constant induced by the g-anisotropy is estimated separately. This constant is given as follows:

$$W_{\delta g} = \frac{\frac{1}{5}\left(\frac{\beta}{\hbar}\right)^2 \overline{\delta g^2}\tau_{\mathrm{R}} H_{\mathrm{ex}}^2}{1+\gamma^2\tau_{\mathrm{R}}^2 H_{\mathrm{ex}}^2} \tag{12}$$

where γ is the magnetogyric ratio of the electron, β is the Bohr magneton, $\hbar$ is the Planck's constant, $\overline{\delta g^2}=\sum_i(g_i-g_{\mathrm{av}})^2$, and τ_{R} is the correlation time. g_1, g_2, and g_3 are the g-values for the principal axes of g-tensor of a radical and $g_{\mathrm{av}}=\sum_i g_i/3$. τ_{R} is expressed by using of D_{r} as $\tau_{\mathrm{R}}=1/6D_{\mathrm{r}}$. In this system the g-anisotropy arises from Ru(III) complex and the experimental g-tensor components are $g_{\parallel}=1.14$ and $g_{\perp}=2.64$.[14)] So $W_{\delta g}$ is expressed as follows:

$$W_{\delta g} = \frac{387.5H_{\mathrm{ex}}^2}{D_{\mathrm{r}} + 861H_{\mathrm{ex}}^2/D_{\mathrm{r}}} \tag{13}$$

The values of $W_{\delta g}$ using $D_{\mathrm{r}}=12.5\ \mathrm{ns}^{-1}$ are estimated to be 4.76 and 5.62 ns^{-1} for 1 and 10 T, respectively. In consideration of $b_{\mathrm{TT}}=100\ \mathrm{ns}^{-1}\,\mathrm{T}^{-1}$, for example, it is clear that contribution of $W_{\delta g}$ to W_{TT} and W_{TS} is rather small in this case. Therefore in high magnetic field (3.5—14 T) the MFE of the signal intensity is explained solely by the Δg mechanism with strong SOC system.

Magnetic Field Effects on the Uncorrelated Pair. In Fig. 1 the decay of the signal of the $^2\mathrm{MV}^+$ radical lasting for 40 μs is considered as a bimolecular reaction shown below:

$$^2[\mathrm{Ru(bpy)_3}]^{3+} + {}^2\mathrm{MV}^+ \rightarrow {}^{1,3}[\mathrm{Ru(bpy)_3}^{3+}\cdots\mathrm{MV}^+] \rightarrow [\mathrm{Ru(bpy)_3}]^{2+} + \mathrm{MV}^{2+} \tag{14}$$

We examined the MFE on this reaction, since uncorrelated pairs generated from escaped radicals are involved as short-lived intermediates. Thus, the decay curves shown in Fig. 1 were analysed by assuming the second order decay kinetics. The signal intensity, $I(t)$, at time t is expressed as follows:

$$1/I(t) - 1/I(0) = (k_{\mathrm{app}}/\varepsilon l)t \tag{15}$$

where $I(0)$ is the signal intensity immediately after laser excitation, k_{app} is the rate constant of the apparent bimolecular reaction, ε is the molar extinction coefficient of $^2\mathrm{MV}^+$ and l is the path length of the cell. The magnetic field dependence of the ratio $k_{\mathrm{app}}(H_{\mathrm{ex}})/k_{\mathrm{app}}(0)$ of k_{app} in the presence and absence of a magnetic field H_{ex} is shown in Fig. 3. Since k_{app}'s were deterimined from the plots of the reciprocal of the signal intensities of $^2\mathrm{MV}^+$, which are very weak (Fig. 1), errors associated with k_{app} are quite large compared to the values shown in Fig. 2. Nevertheless, Fig. 3 indicates that k_{app} *increases* by 10—20% in the presence of high magnetic fields.

In the case of the bimolecular reaction shown in Eq. 14, the rate equation of the $^2\mathrm{MV}^+$ radical is given as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}[^2\mathrm{MV}^+] = -k_{\mathrm{bi}}[^2\mathrm{MV}^+][^2[\mathrm{Ru(bpy)_3}]^{3+}] + k_{\mathrm{ce}}([\mathrm{T}'_0] + [\mathrm{T}'_+] + [\mathrm{T}'_-] + [\mathrm{S}'_0]) \tag{16}$$

where k_{bi} is the bimolecular rate constant for generation of uncorrelated pairs. The rate equations of the uncorrelated pairs are obtained by simply adding a term, $k_{\mathrm{bi}}[^2\mathrm{MV}^+][^2[\mathrm{Ru(bpy)_3}]^{3+}]$, to the right-hand side of Eqs. 8, 9, 10, and 11 and therefore they are not given here. Kinetic parameters used for calculation of the escaped radical yield from the correlated pair indicates

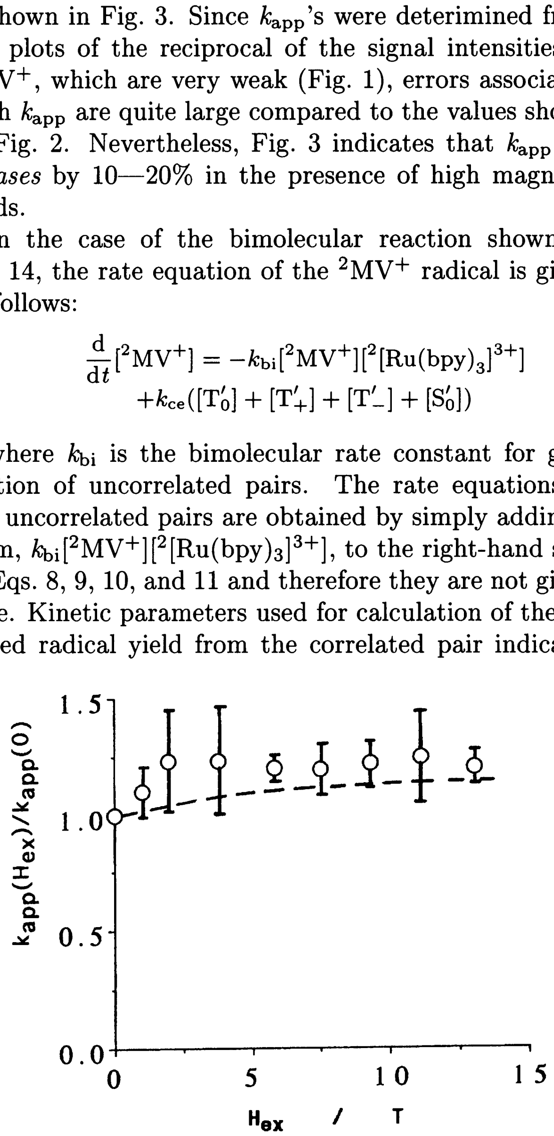


Fig. 3. The magnetic field dependence of the ratio $k_{\mathrm{app}}(H_{\mathrm{ex}})/k_{\mathrm{app}}(0)$ of k_{app} in the presence and absence of a magnetic field H_{ex}. Error bars represent the standard deviation for five separate experiments. The broken line is the calculated ratio, $\phi_{\mathrm{r}}(H_{\mathrm{ex}})/\phi_{\mathrm{r}}(0)$, in the presence and absence of a magnetic field H_{ex}. See text.

that the dynamic equilibrium in uncorrelated pairs occurs within a very short time compared to its generation time. Thus the rate equations for uncorrelated pairs mentioned above were solved under the steady-state condition to evaluate the steady-state concentrations of uncorrelated pairs, leading to the following equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}[{}^2\mathrm{MV}^+] = -k_{\mathrm{bi}}\phi_{\mathrm{r}}[{}^2\mathrm{MV}^+][{}^2[\mathrm{Ru(bpy)}_3]^{3+}] \tag{17}$$

ϕ_r is a complex function of kinetic parameters, k_ce, W_TT, W_TS, k_bet, $P^\mathrm{s}_{\mathrm{s}'}$ and $P^\mathrm{s}_{\mathrm{T}'_\pm}$ and its explicit form is not given here for simplicity. ϕ_r is considered to represent the yield of in-cage reaction in the uncorrelated pairs. Therefore the apparent bimolecular rate constant, k_app, determined experimentally corresponds to the value, $k_\mathrm{bi}\phi_\mathrm{r}$, derived from the rate equations proposed.

We calculated numerically ϕ_r at several magnetic fields using the kinetic parameters appeared in the previous subsection. $\phi_\mathrm{r}(0)$ at zero magnetic field is 0.798 and increases with increasing a magnetic field (0.901 at 13 T). The ratio, $\phi_\mathrm{r}(H_\mathrm{ex})/\phi_\mathrm{r}(0)$, in the presence and absence of a magnetic field H_ex, is obtained as shown in Fig. 3. The magnetic field dependence of the calculated ratio $\phi_\mathrm{r}(H_\mathrm{ex})/\phi_\mathrm{r}(0)$ is in reasonable agreement with that of the observed one $k_\mathrm{app}(H_\mathrm{ex})/k_\mathrm{app}(0)$, though errors in the latter are not small. By applying a magnetic field, the net yield of back electron transfer reaction in the uncorrelated pair is enhanced because of the Zeeman mixing of spin states as the case of the correlated pair described in the previous subsection. This enhancement of the yield results in the increase in the apparent bimolecular rate constant, k_app. Thus it is concluded that even in the case of MFE on uncorrelated pairs, observed MFE can be explained by the model proposed by Steiner.

The MFE on an uncorrelated pair generated by the re-encounter of free radicals is hardly observed in the typical radical reaction composed of organic radicals in fluid solution. Because the cage escape rate constant (>1 ns^{-1}) in fluid solution is much larger than the spin converion rate constant in organic radical pairs (for example, the rate constant for the hyperfine-induced intersystem crossing is typically 0.1 ns^{-1}), the MFE on the uncorrelated pair of organic free radicals is quite small. On the contrary, in the case of Ru complex system, the rate constants associated with the heavy atom effect are larger than the cage escape rate constant. Therefore this MFE is able to be observed in the uncorrelated radical pair containing heavy atoms.

Finally, we examined the MFE (0—13 T) on the decay rate constant of $^3[\mathrm{Ru(bpy)}_3]^{2+}$ emission (610—620 nm) in the absence of the MV^{2+} quencher in deaerated aqueous solution (pH=2—3). The rate constant is ca. 1.7×10^6 s^{-1} at zero field and no appreciable effect was detected, though it was reported that it was ca. 1.9×10^6 s^{-1} at zero field and ca. 2.5×10^6 s^{-1} at 5 T.$^{7)}$

In conclusion, the effect of high magnetic field (5—13 T) on the correlated and uncorrelated pairs of the present reaction is well interpreted in terms of the Δg mechanism proposed by Steiner to explain the effects on the correlated pair in relatively low fields (<5 T). The spin-lattice relaxation of the radical pair induced by the g-anisotropy is unimportant in the case of radical pairs containing a heavy atom in high magnetic field.

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