

## LETTERS TO THE EDITOR

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## COMMUNICATIONS

### Observation of spin-correlated radical pairs via two-dimensional electron paramagnetic resonance nutation spectroscopy

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Two-dimensional (2D) Fourier-transform (FT) electron paramagnetic resonance (EPR) nutation experiments were done in order to verify anomalous flip-angle dependence of a FT-EPR spectrum of a photochemically generated spin-correlated radical pair (SCRP). It was demonstrated by both the experiment and theory that the signals of SCRPs have additionally higher and lower nutation frequencies than that of a free radical. This spectroscopy provides a direct spectroscopic evidence of spin-correlation within SCRPs, and enables one to partially separate SCRPs signals from free radical signals in the 2D EPR spectrum. © 1995 American Institute of Physics.

Fourier-transform electron paramagnetic resonance (FT-EPR) spectroscopy has been limelighted during the last decade owing to its outstanding frequency resolution and sensitivity.<sup>1</sup> An application in a multidimensional fashion is another important aspect of FT-EPR.<sup>2</sup> The excellent time resolution enables us to observe short-lived species.<sup>3</sup> For a case of a photochemically generated spin-correlated radical pair (SCRP),<sup>4-6</sup> the spin system can be considered as *AX* or *AB* system in terms of NMR, where an exchange interaction between the two radicals is analogous to a weak homonuclear spin-spin coupling. Furthermore, SCRPs, coming from a singlet or a triplet precursor, has a nonequilibrium population over the four eigenstates of the spin-Hamiltonian (spin-correlation). These peculiarities of SCRPs are expected to cause anomalous flip-angle dependence of the FT-EPR spectra, according to the theory proposed by Ernst and his associates.<sup>7</sup>

It has been proposed by Harashanori *et al.*<sup>8</sup> and Dinse and co-workers<sup>9</sup> that intensities of FT-EPR signals of SCRPs should be proportional to  $\sin(2\beta)$ , whereas those of free radicals to  $\sin \beta$ , in a case that both unpaired electron spins which constitute the SCRPs are simultaneously excited by a microwave (MW) pulse of a flip angle  $\beta$ . From their theory, nutation frequencies of SCRPs are expected to be twice those of free radicals. This phenomenon has been experimentally demonstrated by Harashanori *et al.*<sup>8</sup> by comparing intensities of FT-EPR spectra of SCRPs with those of a stable radical under a set of various microwave field strength at an on-resonance position.

In this communication, we report on a two-dimensional (2D) FT-EPR nutation experiment of SCRPs generated in the photoreduction of acetone with 2-propanol. It is well known<sup>6,10,11</sup> that SCRPs CIDEP (chemically induced dynamic electron polarization) signals of an acetone ketyl-radical pair show the faster rise and decay than those of free radical CIDEP of an acetone ketyl radical. We compare the nutation spectrum of SCRPs with that of the free radical by selecting

the time delay between the laser pulse and the MW pulse. A one-dimensional EPR measurement was carried out as usual. The temperature of the sample, 1 mol dm<sup>-3</sup> solution of acetone-*d*<sub>6</sub> in 2-propanol-*d*<sub>8</sub>, was maintained at -88 °C throughout the experiments. A MW pulse with a duration of about 10 ns follows a laser shot of the fourth harmonics of Nd:YAG laser (266 nm) and the quadrature free-induction-decay (FID) signals were recorded with a CYCLOPS phase cycle. A missing part of the FID due to the instrumental deadtime was extrapolated with a LPQRD method.<sup>12</sup> Phase of FT-spectra were corrected by assuming that the spectra at delay times from 25 μs to 30 μs do not contain any dispersive components. Remarkable patterns of antiphased doublets were observed in the center of the FT-spectra with the delay time of 100 ns to 3 μs. These signals are attributed to the SCRPs CIDEP signals as already reported.<sup>6,10,11</sup> The free-radical signals, due to the acetone ketyl radical, were also observed in a wider range of delay time. The SCRPs signals have almost the same line shapes as those observed by the continuous wave time-resolved EPR technique,<sup>6,10,11</sup> and showed a constant exchange integral  $|J|$  which is  $\leq 0.6$  MHz within the lifetime.

For a 2D nutation experiment, a one-pulse experiment was made as displayed in Fig. 1,<sup>13-15</sup> where a MW pulse with various durations of  $t_1$  was synchronized with the laser flash. Subsequent complex FID was sampled along  $t_2$ , giving a 2D complex FID as a function of both  $t_1$  and  $t_2$ . A two-dimensional nutation spectrum was obtained with a nutation frequency of  $\omega_1$  and an EPR frequency of  $\omega_2$ , after apodization, zero-filling, and 2D complex Fourier-transformation, successively. The two different delay times of 500 ns and 8 μs were employed because SCRPs signals were detected at the former time and no such signals at the latter time in the one-dimensional experiment. In Fig. 2, 2D nutation spectra with delay times of 500 ns and 8 μs are partly depicted in absolute-value representation. The contour plots are shown in Fig. 3. These plots are normalized to the

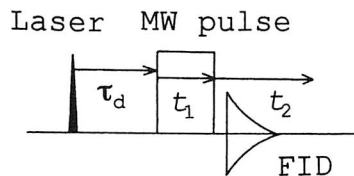


FIG. 1. Designed pulse sequence for the 2D nutation experiment  $\tau_d$  is a delay time between the laser pulse and the microwave pulse. One obtains a 2D FID as the function of  $t_1$  and  $t_2$ .

maximum intensities. Two important features should be pointed out from the figures. First, there exist peaks with the common EPR and nutation frequencies in both delay times. These peaks, which we refer to as group A, had relatively strong intensities in comparison with other groups. Second, in the spectrum of 500 ns, we see additional peaks which have the higher (group B) and the lower (group C) nutation frequencies than those of group A. The group A peaks in the nutation spectrum of 8  $\mu$ s are easily attributed to the free-radical signals, compared with the results obtained in the one-dimensional experiment. As the resonance offset increases, the nutation frequency of these peaks becomes higher. This observation is fully interpreted in terms of the Bloch equations. That is, for the case of free radicals, the  $z$ -magnetization is rotated around the effective MW field which becomes larger as the resonance offset becomes larger (off-resonance effect).<sup>16</sup>

The nutation spectrum with the delay time of 500 ns is not explained by the above treatment and a theory based on the density matrix formalism is required. Dinse's theory concerning a flip-angle dependence of SCRPs signals is adequate

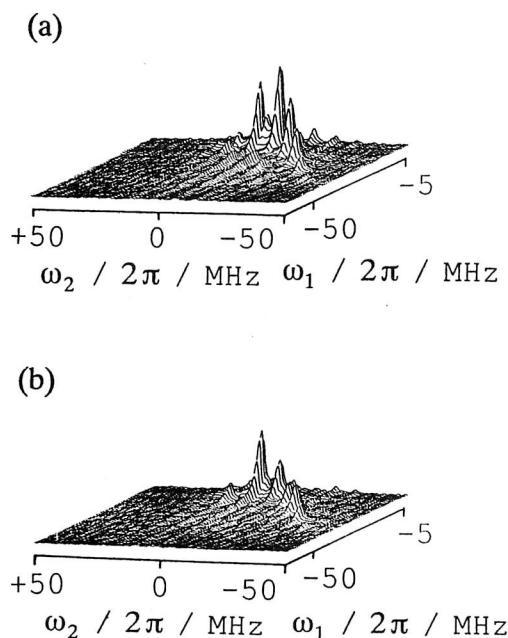


FIG. 2. 2D FT-EPR nutation spectra of acetone- $d_6$ /2-propanol- $d_8$  system at delay times of 500 ns (a) and 8  $\mu$ s (b).  $\omega_1$  and  $\omega_2$  are nutation frequency and EPR frequency, respectively, and only the parts with negative  $\omega_1$  are shown. The components with the higher and the lower nutation frequencies are newly detected in the spectra of 500 ns.

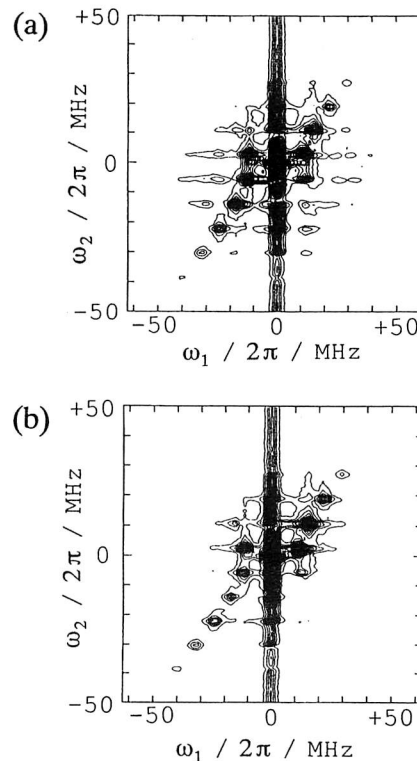


FIG. 3. Contour plots of Fig. 2 with both positive and negative nutation frequencies. Strong  $\omega_1=0$  components are due to an experimental artifact.

only when the off-resonance effect is negligible. We must take this effect into consideration in order to attain fundamental appreciation of the nutation spectrum of SCRPs. If the high-field approximation holds, the spin-Hamiltonian of SCRPs in a rotating frame is given by

$$H_0 = \Omega_a S_{az} + \Omega_b S_{bz} - J(2S_a \cdot S_b + \frac{1}{2}), \quad (1)$$

where  $J$  is an exchange interaction within the pair and  $\Omega_a$  and  $\Omega_b$  are the resonance offsets of electron spins  $a$  and  $b$ , respectively. Other symbols have usual meanings. The term that expresses an interaction between the spin system and the MW field is

$$H_p = -\gamma_a B_1 S_{ay} - \gamma_b B_1 S_{by}, \quad (2)$$

where  $B_1$  denotes the strength of the MW field that faces toward negative  $y$  axis. Time evolution of the spin system under the MW pulse is governed by  $H_0 + H_p$  if we neglect spin relaxations and developments of spin polarizations and assume a constant exchange interaction in time. The spin-density operator right after the MW pulse is then written by

$$\sigma_+ = e^{-i(H_0 + H_p)t_1} \sigma(0) e^{i(H_0 + H_p)t_1}, \quad (3)$$

where  $\sigma(0)$  is an initial density operator and  $t_1$  expresses the MW duration. By taking into consideration the present situation where  $\gamma_a B_1 = \gamma_b B_1 \approx 11 \text{ MHz} \gg |J|$ , the spin-Hamiltonian under the MW pulse,  $H_0 + H_p$ , almost equal to a sum of the Hamiltonian of two electron spins without the exchange interaction. Using the commutability of these terms, we can calculate the exponential operator  $e^{i(H_0 + H_p)t_1}$  as a tensor product of  $2 \times 2$  exponential operators, i.e.,  $\exp\{i(\Omega_a S_{az} - \gamma_a B_1 S_{ay})t_1\}$  and  $\exp\{i(\Omega_b S_{bz}$

TABLE I. Transverse magnetizations right after the MW pulse for spin-correlated radical pair coming from a triplet precursor. Meanings of the symbols are cited in the text.

EPR frequency	Transverse magnetization after the MW pulse
$\Omega_a + J$	$\frac{1}{12} \sin \theta_a [\cos^2 \theta_b \{ \sin \omega_a t_1 + i \cos \theta_a (1 - \cos \omega_a t_1) \}$ $+ \frac{1}{2} \sin^2 \theta_b \{ \sin(\omega_a - \omega_b) t_1 + i \cos \theta_b \{ \cos \omega_b t_1 - \cos(\omega_a - \omega_b) t_1 \}$ $+ \sin(\omega_a + \omega_b) t_1 + i \cos \theta_b \{ \cos \omega_b t_1 - \cos(\omega_a + \omega_b) t_1 \} \}$
$\Omega_a - J$	$- \frac{1}{12} \sin \theta_a [\cos^2 \theta_b \{ \sin \omega_a t_1 + i \cos \theta_a (1 - \cos \omega_a t_1) \}$ $+ \frac{1}{2} \sin^2 \theta_b \{ \sin(\omega_a - \omega_b) t_1 + i \cos \theta_b \{ \cos \omega_b t_1 - \cos(\omega_a - \omega_b) t_1 \}$ $+ \sin(\omega_a + \omega_b) t_1 + i \cos \theta_b \{ \cos \omega_b t_1 - \cos(\omega_a + \omega_b) t_1 \} \}$
$\Omega_b + J$	$\frac{1}{12} \sin \theta_b [\cos^2 \theta_a \{ \sin \omega_b t_1 + i \cos \theta_b (1 - \cos \omega_b t_1) \}$ $+ \frac{1}{2} \sin^2 \theta_a \{ \sin(\omega_b - \omega_a) t_1 + i \cos \theta_a \{ \cos \omega_a t_1 - \cos(\omega_b - \omega_a) t_1 \}$ $+ \sin(\omega_b + \omega_a) t_1 + i \cos \theta_a \{ \cos \omega_a t_1 - \cos(\omega_b + \omega_a) t_1 \} \}$
$\Omega_b - J$	$- \frac{1}{12} \sin \theta_b [\cos^2 \theta_a \{ \sin \omega_b t_1 + i \cos \theta_b (1 - \cos \omega_b t_1) \}$ $+ \frac{1}{2} \sin^2 \theta_a \{ \sin(\omega_b - \omega_a) t_1 + i \cos \theta_a \{ \cos \omega_a t_1 - \cos(\omega_b - \omega_a) t_1 \}$ $+ \sin(\omega_b + \omega_a) t_1 + i \cos \theta_a \{ \cos \omega_a t_1 - \cos(\omega_b + \omega_a) t_1 \} \}$

$-\gamma_b B_1 S_{by} t_1$ ), where these operators can be derived analytically. Since the  $J$  value is also much smaller than the hyperfine coupling constant,  $\sim 8.2$  MHz, all combinations of nuclear substates that practically contribute to the spectrum of the SCRPs have  $|\Omega_a - \Omega_b|$  which is much larger than  $|J|$ . This situation also allows us to assume that the eigenbases of  $H_0$  is not so far from the product bases (approximation of the AX system in terms of NMR) and the initial condition is taken to be

$$\sigma(0) = \begin{bmatrix} \alpha\alpha & \alpha\beta & \beta\alpha & \beta\beta \\ 1/3 & & & \\ & 1/6 & & \\ & & 1/6 & \\ & & & 1/3 \end{bmatrix}, \quad (4)$$

when the pair is created from a triplet precursor. Single quantum coherences associated with the EPR transitions immediately after the MW pulse are summarized in Table I. In this table,  $\omega_a$  and  $\omega_b$  are nutation frequencies of spins  $a$  and  $b$  observed when they are existing as free radicals, respectively, and these terms come from the following type of expression:

$$\tan \theta_a = \frac{\gamma_a B_1}{\Omega_a} = \frac{B_1}{\Delta B_{1a}}. \quad (5)$$

Here,  $\Delta B_{1a}$  is identical to the hypothetical residual field in the rotating frame and  $\theta_a$  denotes a deviation from the on-resonance position ( $\theta_a = \pi/2$  for on-resonance and  $\theta_a \rightarrow 0$  corresponds to the limit of off-resonance). What should be emphasized in the formulas listed in Table I is the existence of frequencies of  $\omega_a + \omega_b$  and  $\omega_a - \omega_b$  associated with each EPR transition. An origin of these nutation frequencies of the nonequilibrated spin-polarized SCRPs is "longitudinal two-spin order" which has a representation of  $S_{az} S_{bz}$  based

on the product-operator formalism.<sup>17</sup> The spin-polarization of free radicals can be represented by a linear combination of  $S_{az}$  and  $S_{bz}$  and includes no  $S_{az} S_{bz}$  term, even if the spin-Hamiltonian is the same as that of SCRPs in the limit of  $J=0$ . The  $S_{az}$  and  $S_{bz}$  terms cause ordinary flip-angle dependence, and  $S_{az} S_{bz}$  different one.

Relative-intensity ratios of these nutation components are determined by the resonance offset felt by the coupling partner spin. In Fig. 4, nutation frequencies of relatively strong components are collected in some combinations of resonance offsets. When both spins are close to the on-resonance position, nutation frequencies of  $\omega_a + \omega_b$  are detected. These components, thus, give higher nutation frequencies. The group B peaks, in the nutation spectrum at the delay of 500 ns, behave in this way, so we conclude that

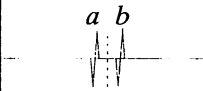



Combination of resonance offsets	Transition of spin $a$	Transition of spin $b$
	$\omega_a + \omega_b$ ( $\approx 2\omega$ )	$\omega_a + \omega_b$ ( $\approx 2\omega$ )
	$\omega_a$	$\omega_a$ $\omega_a + \omega_b$ $\omega_a - \omega_b$
	$\omega_a$	$\omega_b$
	$\omega_a$	$\omega_b$

FIG. 4. Nutation frequencies of peaks with relatively strong intensities in some combinations of resonance offsets, obtained by the formulas listed in Table I. Broken lines indicate on-resonance positions.

these group B peaks arise from the SCRPs with combinations of nuclear substates having small resonance offsets. On the contrary, lower nutation frequencies than that of free-radical signals and large offset frequencies are connected by group C peaks. These peaks come from the SCRPs with combinations where one electron spin (we refer to spin  $a$ ) is near the resonance condition and the other (spin  $b$ ) is far from it. In this case, for the EPR transition of spin  $a$ , we have nutation frequency of  $\omega_a$ , and for that of spin  $b$ , nutation frequencies of  $\omega_a$  (instead of  $\omega_b$ ),  $\omega_a + \omega_b$  and  $\omega_a - \omega_b$  are expected. Here, among the nutation frequencies of spin  $b$ ,  $\omega_a$  and  $\omega_a - \omega_b$  are lower than  $\omega_b$ , and  $\omega_a + \omega_b$  is higher than  $\omega_b$ . We therefore refer the former frequencies to "lower nutation frequencies" and the latter to "higher nutation frequencies." As nutation frequencies of  $\omega_a + \omega_b$  and  $\omega_a - \omega_b$  vary with the change of offsets of both  $a$  and  $b$ , these components tend to spread inhomogeneously in the spectrum. On the contrary, components with nutation frequencies of  $\omega_a$  show less tendency to spread out, so these peaks may survive in the nutation spectrum constituted from the contributions from many combinations of nuclear substates. We can therefore say that the lower nutation frequencies of group C peaks are coming from the EPR transitions of the coupling-partner spin locating close to on-resonance.

Consequently, it has turned out that this 2D EPR spectroscopy gives a direct spectroscopic evidence of spin-correlation existing within photochemically generated SCRPs; anomalous nutation frequencies of SCRPs signals verify the nonequilibrium population as well as the spin-Hamiltonian, although complete separation of SCRPs signals from free-radical signals could not be attained due to the off-resonance effect. The correlations of EPR frequencies and nutation frequencies observed in the nutation spectrum were simply interpreted in terms of the formulas derived under the assumptions of the small exchange coupling. The effect of large exchange interaction can be included when we carry out the

complete calculation of time evolution of the spin-density operator. Further studies including justification of the above assumptions are published elsewhere.

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- <sup>1</sup>M. K. Bowman, in *Modern Pulsed and Continuous Wave Electron Spin Resonance*, edited by L. Kevan and M. K. Bowman (Wiley, New York, 1990).
- <sup>2</sup>J. Gorcester, G. L. Millhauser, and J. H. Freed, in *Modern Pulsed and Continuous Wave Electron Spin Resonance*, edited by L. Kevan and M. K. Bowman (Wiley, New York, 1990).
- <sup>3</sup>H. van Willigen, P. R. Levstein, and M. H. Ebersole, *Chem. Rev.* **93**, 173 (1993).
- <sup>4</sup>M. C. Thurnauer, M. K. Bowman, and J. R. Norris, *FEBS Lett.* **100**, 309 (1979).
- <sup>5</sup>M. C. Thurnauer, A. W. Rutherford, and J. R. Norris, *Biochem. Biophys. Acta* **682**, 332 (1982).
- <sup>6</sup>C. D. Buckley, D. A. Hunter, P. J. Hore, and K. A. McLauchlan, *Chem. Phys. Lett.* **135**, 307 (1987).
- <sup>7</sup>S. Schäublin, A. Höhner, and R. R. Ernst, *J. Magn. Reson.* **13**, 196 (1974).
- <sup>8</sup>K. Harashanori, H. Levanon, J. Tang, M. K. Bowman, J. R. Norris, D. Gust, T. A. Moore, and A. L. Moore, *J. Am. Chem. Soc.* **112**, 6477 (1990).
- <sup>9</sup>G. Kroll, M. Plüschau, K.-P. Dinse, and H. van Willigen, *J. Chem. Phys.* **93**, 8709 (1990).
- <sup>10</sup>K. Tominaga, S. Yamauchi, and N. Hirota, *J. Chem. Phys.* **88**, 553 (1988).
- <sup>11</sup>K. Tominaga, S. Yamauchi, and N. Hirota, *J. Chem. Phys.* **92**, 5157 (1990).
- <sup>12</sup>J. Tang, C. P. Lin, and J. R. Norris, *J. Magn. Reson.* **62**, 167 (1985).
- <sup>13</sup>A. Samoson and E. Lippmaa, *Chem. Phys. Lett.* **100**, 205 (1983).
- <sup>14</sup>F. M. M. Geurts, A. P. K. Kentgens, and W. S. Veeman, *Chem. Phys. Lett.* **120**, 206 (1985).
- <sup>15</sup>A. P. M. Kentgens, J. J. Lemmens, F. M. M. Geurts, and W. S. Veeman, *J. Magn. Reson.* **71**, 62 (1987).
- <sup>16</sup>H. C. Torrey, *Phys. Rev.* **76**, 1059 (1949).
- <sup>17</sup>O. W. Sørensen, G. W. Eich, M. H. Levitt, G. Bodenhausen, and R. R. Ernst, *Prog. Nucl. Magn. Reson. Spectrosc.* **16**, 163 (1983).