J. Phys. Chem. A **2004,** *108,* 754−757

Viscosity Dependence of the Magnetic Field Effect Due to the Δ*g* Mechanism

Yasutaka Kitahama, Masanobu Wakasa,[†] and Yoshio Sakaguchi*

RIKEN (The Institute of Physical and Chemical Research), 351-0198 Wako, Saitama, Japan

Received: June 18, 2003; In Final Form: October 21, 2003

We investigated the magnetic field effect on the yields of the escaping radicals formed by the hydrogen abstraction reaction of excited triplet 4-methoxybenzophenone with 4-chlorothiophenol in mixtures of 2-propanol and cyclohexanol. The yields of the escaping radicals decreased with increasing external magnetic field owing to the Δg mechanism. The relative yield of the escaping radicals to that in the absence of the external magnetic field in 2-propanol was 0.9 at 1.4 T. The magnetic field effects in a nonviscous solution such as 2-propanol were proportional to the square root of the external magnetic field and the solvent viscosity, $(B\eta)^{1/2}$. However, the deviation from this relationship, the decrease in the exponent, was observed by increasing the solvent viscosity, up to 60 cP. The relative yield in cyclohexanol was 0.88 at 0.8 T and roughly constant up to 1.4 T.

Introduction

Magnetic field effects (MFEs) on chemical reactions via radical pairs (RPs) in solution have been investigated extensively.[1,2] One of the important mechanisms to induce MFEs is the Δg mechanism. This is caused by the magnetic field dependence of the singlet−triplet ($S-T_0$, where T_0 is the middle triplet sublevel) mixing due to the difference between the g values, namely the Larmor frequencies, of the component radicals of the RP. Here we consider the following case. The triplet precursor produces the initial triplet RP. The $S-T_0$ mixing takes place in the presence of magnetic field, and then the singlet RP recombines. The probability of the recombination is proportional to $Q^2(Q^2 + J^2)^{-3/4}$.[3] Here J is the exchange interaction between the RP, and Q is half of the difference between the resonance frequencies of the component radicals of the RP and is given by

$$Q = \frac{\Delta g \mu_B B}{2\hbar} + \frac{1}{2}\left(\sum_i A_{1,i} M^{a}_{1,i} - \sum_j A_{2,j} M^{b}_{2,j}\right) \qquad (1)$$

where $\Delta g = g_a - g_b$, B is the external magnetic field, $A_{1,i}$ is the hyperfine coupling constant (hfc) of radical 1 due to ith nuclei, $M^{a}_{1,i}$ is the nuclear magnetic quantum number of radical 1 due to ith nuclei, which exists in the overall nuclear spin states a, and the other symbols have their usual meanings. The first term of eq 1 is ascribed to the Δg mechanism. If we neglect J and the hfcs of the radicals, the probability of recombination is proportional to $Q^{1/2}$ and accordingly to $B^{1/2}$. This $B^{1/2}$ relationship has been confirmed by many experimental results.[4−8]

In chemically induced dynamic electron polarization (CIDEP) studies,[9,10] a similar mechanism to the Δg mechanism has been known, which produces large electron spin polarization of transient radicals. It is the $S-T_0$ mixing radical pair mechanism (ST_0M-RPM).[11] When J approaches zero with an increase of the inter-radical distance, the $S-T_0$ mixing occurs via Q, which is mainly caused by the difference between the hfcs and/or the nuclear magnetic quantum numbers of the component radicals of the RP. Then the RP feels J due to the re-encounter, and ST_0M-RPM polarization is produced. This re-encounter model predicts that the magnitude of the ST_0M-RPM polarization is proportional to $Q^{1/2}$ and has been commonly used to analyze CIDEP spectra. However, several groups have discussed the deviation from the $Q^{1/2}$ relationship in the case of slow diffusion.[12−16]

In this paper, we investigated the external magnetic field (B) and solvent viscosity (η) dependence of the MFE due to the Δg mechanism on the yields of the escaping radicals formed by the hydrogen abstraction reaction of excited triplet 4-methoxybenzophenone (MBP) with 4-chlorothiophenol (ClPhSH) in the mixtures of 2-propanol (2-PrOH) and cyclohexanol (c-HexOH), namely in the case of viscous solution, up to 60 cP.

Experimental Section

4-Methoxybenzophenone (Cica-Merck) and 4-chlorothiophenol (Tokyo Kasei) were recrystallized from ethanol and a mixture of ethanol and water, respectively. 2-Propanol (Junsei Chemical) and cyclohexanol (Cica-Merck) of guaranteed grade were used as obtained. The sample solutions were degassed under N_2 atomosphere and flowed into a quarts tube at room temperature. The concentration of MBP and ClPhSH was 0.02 and 0.12 mol dm^{-3}, respectively. The viscosities of mixtures of 2-PrOH and c-HexOH were measured by a viscometer (VM-1G-L, Yamaichi). The third harmonic, 355 nm, of an Nd:YAG laser (Quanta Ray GCR-3, Spectra-Physics) was used as an exciting light source. We observed the time profiles of the transient absorptions due to MBP ketyl radical (MBPH$^\bullet$) and 4-chlorophenylthiyl radical (ClPhS$^\bullet$) at 550 nm[17,18] and 510 nm,[19] respectively. The measurement system was based on an X-band pulsed ESR spectrometer (RSV2000, JEOL) without using microwave and the apparatus for the nanosecond time-resolved optical absorption measurements, which was similar to that described elsewhere.[20]

Results and Discussion

The hydrogen abstraction reaction of excited triplet MBP with ClPhSH, which is similar to the system investigated by Wakasa

---

* Address correspondence to this author. Phone: +81-48-467-9395 Fax: +81-48-462-4664. E-mail: ysakaguc@postman.riken.go.jp

[†] Present address: Department of Chemistry, Faculty of Science, Saitama University, 338-8570 Saitama, Saitama, Japan.

10.1021/jp030779+ CCC: $27.50

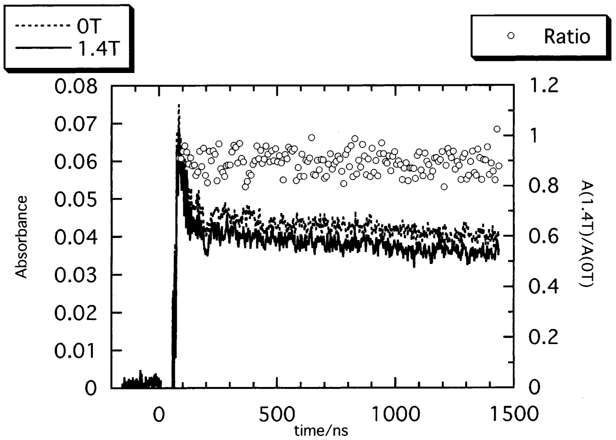

Figure 1. Time profiles of transient absorptions due to 4-methoxybenzophenone ketyl radical in cyclohexanol, which was observed at 550 nm, and the ratio of the transient absorption at 1.4 T to that at 0 T.

et al.,[8] was confirmed by the quenching of the transient absorption of the excited triplet MBP at 680 nm[17,18] in the presence of ClPhSH. The reaction scheme is represented as follows:

$$^{3}\text{MBP} + \text{ClPhSH} \rightarrow {}^{3}(\text{MBPH}^{\bullet}\ \ \text{ClPhS}^{\bullet}) \tag{2}$$

$$^{3}(\text{MBPH}^{\bullet}\ \ \text{ClPhS}^{\bullet}) \leftrightarrow {}^{1}(\text{MBPH}^{\bullet}\ \ \text{ClPhS}^{\bullet}) \tag{3}$$

$$^{3,1}(\text{MBPH}^{\bullet}\ \ \text{ClPhS}^{\bullet}) \rightarrow \text{MBPH}^{\bullet} + \text{ClPhS}^{\bullet} \tag{4}$$

$$^{1}(\text{MBPH}^{\bullet}\ \ \text{ClPhS}^{\bullet}) \rightarrow \text{recombination products} \tag{5}$$

In the presence of magnetic fields, eq 3 describes the $S-T_0$ mixing because the other singlet–triplet ($S-T_\pm$, where $T_\pm$ are top and bottom triplet sublevels) conversions are inhibited by Zeeman splitting. The $S-T_0$ mixing due to the Δg accelerates with an increase in the magnetic field. Thus the recombination products and the escaping radicals become larger and smaller at higher magnetic field, respectively. The g value of $\text{MBPH}^{\bullet}$ has been observed to be 2.0027.[8] It is thought that the g value of $\text{ClPhS}^{\bullet}$ is similar to that of phenylthiyl radical ($\text{PhS}^{\bullet}$), 2.0082, based on the broad and unsymmetrical signal at 77 K.[21] The fast electron spin relaxation of $\text{ClPhS}^{\bullet}$ may occur in the same way as that of the thiyl radical.

Figure 1 exhibits the time profiles of transient absorption due to $\text{MBPH}^{\bullet}$ in c-HexOH and the ratio of the transient absorption at 1.4 T to that at 0 T. The ratio in this viscous solvent is independent of the delay time after the laser irradiation (80 ns $< t <$ 1440 ns). The MFE due to the longitudinal relaxation mechanism,[22] which causes the escaping radicals to become larger at higher magnetic field, rises more slowly than the MFE due to the Δg mechanism. The stationary ratio indicates that the MFE is not influenced by the longitudinal relaxation mechanism.

Figure 2 shows $Y(B) = A(B)/A(0)$, which were averaged from 820 to 1440 ns after the laser irradiation. We regard this value as the magnetic field dependence of the relative yields of the escaping radicals to that in the absence of the external magnetic field in 2-PrOH (η = 1.63 cP) and c-HexOH (η = 53.3 cP). In 2-PrOH, the relative yield decreases smoothly as B becomes larger and was approximately proportional to $B^{1/2}$ in the region of 0.11–1.4 T. On the other hand, the MFE observed in c-HexOH seems to saturate above 1 T. Under ultrahigh magnetic fields above 20 T,[8] the relative yields in 2-methyl-1-propanol have saturated and achieved the limiting value, $^{2}/_{3}$, because a complete $S-T_0$ mixing due to the Δg mechanism with an extremely fast recombination of the singlet RPs causes the T_0 state RPs, namely $^{1}/_{3}$ of the triplet RPs, vanish. However, the phenomenon in c-HexOH cannot be interpreted by the complete $S-T_0$ mixing, because the relative yields in c-HexOH were larger than those in middle viscosity solvents (see Figure 4), to say nothing of $^{2}/_{3}$. Therefore this can be caused by the deviation from the $B^{1/2}$ relationship for the MFE due to the Δg mechanism in the case of slow diffusion.

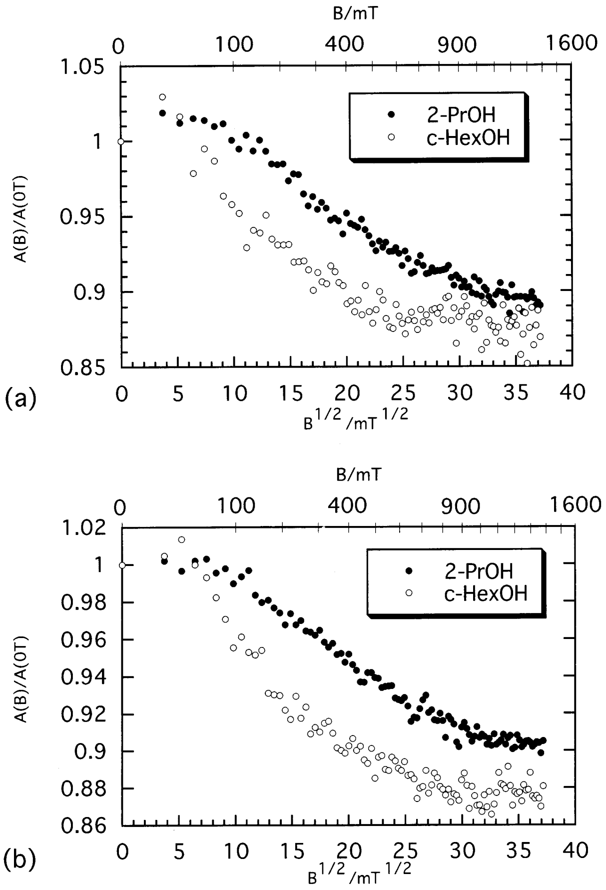

Figure 2. Magnetic field dependence of the yields of the escaping (a) 4-methoxybenzophenone ketyl and (b) 4-chlorophenylthiyl radicals, which were averaged from 820 to 1440 ns after the laser irradiation.

In the simple model where J and hfcs are neglected, the theoretical expression of the relative yields of the escaping radicals to that in the absence of the external magnetic field due to the Δg mechanism is given by[2]

$$R(B) = 1 - \sqrt{\frac{\pi}{2}}\frac{m}{p}(\Delta g \mu_{\text{B}} B)^{1/2} \tag{6}$$

where m is the square root of the average time between diffusive steps, and p is the total probability that the component radicals can re-encounter. To elucidate the relationship between the relative yields and the magnetic fields at various solvent viscosities, we tried to fit the results shown in Figure 2 with the following equation,

$$R(B) = 1 - aB^{x} \tag{7}$$

Here eq 7 originated from eq 6, a is a proportionality constant, and x is a variable exponent that can deviate from $^{1}/_{2}$. In the present study, we cannot eliminate the contribution of the hyperfine coupling mechanism[23] from $Y(B)$ at low magnetic

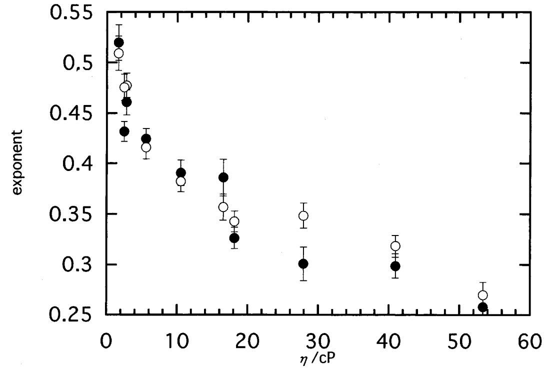

Figure 3. Solvent viscosity dependence of the exponent in the relationship of the magnetic field effect due to the Δg mechanism: $Y(B) = 1 - a(B - b)^x$. The solid and open circles show the results of 4-methoxybenzophenone ketyl and 4-chlorophenylthiyl radicals, respectively.

field. Therefore we excluded the data at the magnetic field below b, where b is the magnetic field under the condition for $Y(b) = 1$ and $b \neq 0$. We fitted the data using the corrective magnetic field, $B - b$, to fulfill the condition of $Y(B) \leq 1$ as follows,

$$Y(B) = 1 - a(B - b)^x \tag{8}$$

Figure 3 shows that the values of the exponents, x, decrease as η becomes larger.

There may be another possible explanation that the decrease in the obtained exponents is caused by the saturation of the MFE due to the Δg mechanism rather than the deviation from the $B^{1/2}$ relationship. The experimental results, which have been observed with the saturation of the MFE due to the Δg mechanism, of the RP consist of MBPH$^\bullet$ and PhS$^\bullet$ at $B = 0-30$ T and $\eta \leq 3.33$ cP have been well reproduced by the following equation,[8]

$$Y(B) = 1 - \left(\frac{1}{3} - p_B\frac{\mathscr{D}_{zfs}}{B}\right)\Lambda\frac{\frac{\sqrt{q}}{2}\left\{1 + \frac{1}{2}\ln\left(1 + \frac{\sqrt{q}}{2}\right)\right\}}{1 + \frac{\sqrt{q}}{2}\left\{1 + \frac{1}{2}\ln\left(1 + \frac{\sqrt{q}}{2}\right)\right\}} \tag{9}$$

$$q = Qd^2/D \cong \Delta g \mu_B B d^2/2\hbar D \tag{10}$$

Here $\mathscr{D}_{zfs}$ is (3/2)-fold of the zero-field splitting constant of the Z-axis, p_B is a polarization factor, Λ is a constant for the degree of diffusion-controlled reaction, d is the distance of closest approach, and D is the mutual diffusion constant, which is given by the Stokes−Einstein−Debye equation:

$$D = 2k_BT/3\pi\eta R \tag{11}$$

where R is the molecular diameter. Equation 9 is applicable for triplet precursor at $B > |\mathscr{D}_{zfs}|$ and the continuous free diffusion model.[8,9,24] This analytical form reproduces well the elaborated numerical calculation results in a large region of $q = Qd^2/D$. We tried to fit the "experimental curve" derived from eq 9 for this experimental system, namely, excited triplet MBP, $\mathscr{D}_{zfs} = 2.7$ GHz,[8] $p_B = 0.38$,[8] $q = 0.11-1.5$, corresponding to $B = 0.1-1.4$ T at $\eta = 60$ cP assuming that $d = R = 0.4$ nm, using eq 8. The obtained exponent was 0.48, larger than the values, 0.26 and 0.27, at 53.3 cP as shown in Figure 3. Therefore we concluded that the decrease in the exponents with the increase in η is caused by the deviation from the $B^{1/2}$ relationship for the MFE due to the Δg mechanism in the case of slow diffusion. This result may imply that the solvent structure and molecular interaction strongly affect the MFE due to the Δg mechanism like the CIDEP due to the ST$_0$M-RPM.[16]

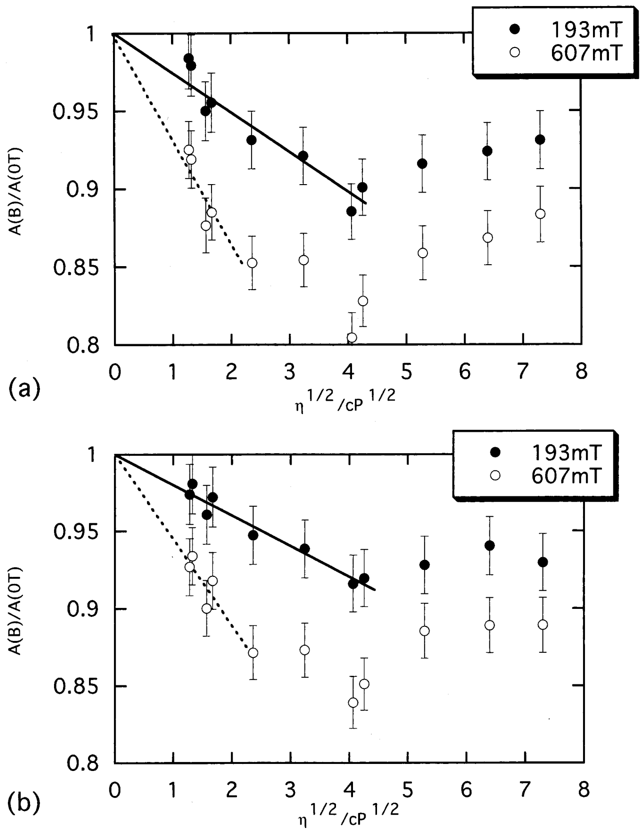

Figure 4. Solvent viscosity dependence of the magnetic field effects of the yields of the escaping (a) 4-methoxybenzophenone ketyl, which was observed at 550 nm, and (b) 4-chlorophenylthiyl radicals, which was observed at 510 nm.

Figure 4 shows that the relative yield decreases and then increases with the increase in the solvent viscosity. The yields at 0 T were independent of the solvent viscosities within experimental errors. The behavior of the relative yield can be explained qualitatively in the following way.[25] Component radicals of initial triplet RPs separate to a distance where the S−T$_0$ mixing occurs effectively. Then they approach each other and recombine from singlet RPs. The increase in the viscosity enhances the re-encounter and the geminate recombination due to the restriction of the escaping process. In the high-viscosity region, however, the increase in the viscosity suppresses the spin conversion owing to the repression of separation for the S−T$_0$ mixing. Thus the recombination probability from singlet RPs is enhanced and then suppressed by an increase in the solvent viscosity.

There are linear relationships between the relative yields and $\eta^{1/2}$ up to about 18 cP at 193 mT and 6 cP at 607 mT. The products of B and η have similar values (18 × 193 and 6 × 607), which indicates that the application of eq 10, $q = Qd^2/D$ (which is approximately proportional to $B\eta$), for analysis of the MFE is reasonable. The MFE due to the Δg mechanism in the system of benzophenone ketyl radical (BPH$^\bullet$) and PhS$^\bullet$ is approximately proportional to $\eta^{1/2}$ for small $B\eta$, ≤ 1.7 T × 3.33 cP.[6] On the other hand, the ST$_0$M-RPM polarization is approximately proportional to $(Qd^2/D)^{1/2}$ for $Qd^2/D \leq 0.016$, but the value of the exponent decreases as Qd^2/D becomes larger.[13] In this MFE due to the Δg mechanism in the system of MBPH$^\bullet$ and ClPhS$^\bullet$, the deviation from the $\eta^{1/2}$ relationship also takes place as $B\eta$ becomes larger than 3.6 T cP. There are linear relationships between the relative yields and $\eta^{1/2}$ for about $Qd^2/D \leq 0.06$, assuming that $d = R = 0.4$ nm.

Here we consider the $S-T_0$ mixing in the fast transverse relaxation spin system. The spin−spin relaxation time is given by [26]

$$T_2^{-1} = \frac{B_{\text{loc}}^{\ 2}}{4}\tau_c\left(1 + \frac{1}{1 + \omega^2\tau_c^{\ 2}}\right) \tag{12}$$

where B_{loc} is the local magnetic field, ω is the energy separation of two spin states, and τ_c is the rotational correlation time that is given by the Stokes−Einstein−Debye equation:

$$\tau_c = 4\pi\eta R^3/3k_BT \tag{13}$$

The transverse relaxation between S and T_0 states ($\omega = 0$), which enhances the recombination probability due to acceleration of the $S-T_0$ conversion,[27] is independent of the external magnetic field and is proportional to the solvent viscosity. Thus another possible model which explains that the exponents approach zero with an increase in η may be the effect due to the transverse relaxation. This model predicts that the relative yields of the escaping radical decrease as η becomes larger due to the relation of $T_2^{-1} \propto \eta$ in the high-viscosity region. However, the experimental relative yields increase as η becomes larger in the high-viscosity region as shown in Figure 4. Therefore the effect due to the transverse relaxation does not cause the viscosity dependence of the exponent in this system.

Conclusion

We investigated the external magnetic field and solvent viscosity dependence of the MFE due to the Δg mechanism in the case of slow diffusion. In viscous solution, deviation from the linear relationship of the MFE and $(B\eta)^{1/2}$ takes place, because this relationship is influenced by the re-encounter process between the separated RP that produces the $S-T_0$ mixing and also the contact RP that recombines from the singlet RP. On the other hand, a similar relationship has been examined in the studies of the ST_0M-RPM polarization in CIDEP. If the deviations from $(B\eta)^{1/2}$, namely $(Q/D)^{1/2}$ relationships in the MFE due to the Δg mechanism and that in the ST_0M-RPM polarization, are compared in the same system, further information on the dynamics of the RPs may be expected.

Acknowledgment. This work has been carried out under the Special Postdoctoral Researchers Program and the MR Science Project of RIKEN. The authors are greatly indebted to Dr. Hisaharu Hayashi, Head of the Molecular Photochemistry Laboratory in RIKEN, for his continuing encouragement.

References and Notes

(1) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.

(2) Hayashi, H. *Photochemistry and Photophysics*; CRC Press: Boca Raton, FL, 1990; Vol. 1, p 59.

(3) Kaptein, R. *J. Am. Chem. Soc.* **1972**, *94*, 6251.

(4) Tanimoto, Y.; Hayashi, H.; Nagakura, S.; Tokumaru, K. *Chem. Phys. Lett.* **1976**, *41*, 267.

(5) Wakasa, M.; Nakamura, Y.; Sakaguchi, Y.; Hayashi, H. *Chem. Phys. Lett.* **1993**, *215*, 631.

(6) Wakasa, M.; Hayashi, H. *J. Phys. Chem.* **1996**, *100*, 15640.

(7) Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem.* **1997**, *101*, 549.

(8) Wakasa, M.; Nishizawa, K.; Abe, H.; Kido, G.; Hayashi, H. *J. Am. Chem. Soc.* **1999**, *121*, 9191.

(9) Muus, L. M.; Atkins, P. W.; McLauchlan, K. A.; Pedersen, J. B. *Chemically Induced Magnetic Polarization*; Reidel: Dordrecht, The Netherlands, 1977.

(10) Murai, H.; Hayashi, H. *Radiation Curing in Polymer Science and Technology*; Elsevier Applied Science: London and New York, 1993; Vol. 2, p 63.

(11) Adrian, F. J. *J. Chem. Phys.* **1971**, *54*, 3918.

(12) Pedersen, J. B.; Freed, J. H. *J. Chem. Phys.* **1973**, *58*, 2746.

(13) Freed, J. H.; Pedersen, J. B. *Adv. Magn. Reson.* **1976**, *8*, 1.

(14) McLauchlan, K. A.; Stevens, D. G. *J. Magn. Reson.* **1985**, *63*, 473.

(15) Shushin, A. I. *Chem. Phys. Lett.* **1990**, *170*, 78.

(16) Kitahama, Y.; Kimura, Y.; Hirota, N. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 851.

(17) Shizuka, H.; Obuchi, H. *J. Phys. Chem.* **1982**, *86*, 1297.

(18) Baral-Tosh, S.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, *88*, 1404.

(19) Jeschke, G.; Wakasa, M.; Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem.* **1994**, *98*, 4069.

(20) Grant, A. I.; McLauchlan, K. A.; Nattrass, S. R. *Mol. Phys.* **1985**, *55*, 557.

(21) Morle, W.; Jezierski, A.; Singer, H. *Z. Chem.* **1979**, *19*, 147.

(22) Hayashi, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 322.

(23) Werner, H. J.; Staerk, H.; Weller, A. *J. Chem. Phys.* **1978**, *68*, 2419.

(24) Pedersen, J. B. *J. Chem. Phys.* **1977**, *67*, 4097.

(25) Aizawa, T.; Sakata, T.; Itoh, S.; Maeda, K.; Azumi, T. *Chem. Phys. Lett.* **1992**, *195*, 16.

(26) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper International: New York, 1967.

(27) Hansen, M. J.; Neufeld, A. A.; Pedersen, J. B. *Chem. Phys. Lett.* **2000**, *260*, 125.