Anisotropic Intersystem Crossing from the Upper Excited Triplet States of Anthracenes: Two-laser Time-Resolved EPR Study

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A two-laser, two-color time-resolved EPR (TREPR) technique has been applied to the investigation of the electron spin polarization in the excited triplet states of anthracene and its halogen anthracene in rigid glassy matrixes. The one-laser excitation of anthracenes with 355 nm gave the triplet TREPR spectra of the lowest excited triplet (T_1) states with EEE/AAA polarization pattern. For 9-bromoanthracene and 9,10-dibromoanthracene, the reexcitation by a dye laser (442 nm) to the upper excited triplet (T_n: $n > 3$) states brought about the opposite phase polarization in the T_1 states. The phenomena were interpreted in terms of the sublevel selective reverse intersystem crossing (RISC) from the T_n ($n = 2$ or 3) state to the S_1 state. The time profiles of the polarization were analyzed taking into account the anisotropic RISC processes. On the other hand, for anthracene and 9,10-dichloroanthracene, little effect was observed on the electron spin polarization by two-step laser irradiation.

Introduction

The time-resolved EPR technique has been successfully applied to investigate the nature of short-lived excited triplet states.[1−4] Since electron spin polarization (ESP) reflects the relaxation pathway in the excited states, the phase of ESP as well as temporal behaviors provides the information on the excited-state dynamics. Almost all studies have been focused on the spin dynamics in the intersystem crossing (ISC) process between the lowest excited singlet (S_1) and triplet (T_1) states. However, the technique is widely applicable to clarify the photophysical pathway where the spin angular momentum changes through the magnetic interactions. During the relaxation processes from the highly excited states, reverse intersystem crossing (RISC) processes are expected to create ESP in the triplet EPR spectra. To confirm the above possibility, we investigated the behavior in the excited triplet states of anthracene and its derivatives.

The relaxation processes from the excited states in anthracene and its derivatives have been under investigation more than three decades because of the large energy difference between the T_2 and T_1 states. Various experimental results, such as the buildup rates of the T−T absorption and the temperature dependence of the fluorescence yields as well as lifetimes, indicate the participation of the T_n ($n = 2$ or 3) states in the $S_1 \rightarrow T_1$ ISC process.[5−12] It has been clarified, furthermore, that the rates of the RISC ($T_2 \rightarrow S_1$) and $T_2 \rightarrow T_1$ internal conversion (IC) are comparable.[10,13−16] The effects of temperature and heavy atoms on the quantum yield (Φ_{TS}) of the RISC were also studied by the stepwise two-photon excitation technique. The results were well interpreted in terms of the relative energy levels of the S_1 and T_2 levels and the spin−orbit coupling (SOC).

In this paper we report on the ESP in the T_1 states of anthracene and *meso*-substituted halogen derivatives followed by the reexcitation to the T_n ($n > 3$) state. The molecular structures examined in the present investigation and their principal axis systems are shown in Figure 1. A two-laser, two-color excitation technique was employed to create the T_n states. One-laser experiments gave the polarized EPR spectra of their T_1 states. The polarization patterns were well explained by the symmetry selection rules. The second laser pulse irradiation with the wavelength corresponding to the T−T transition of bromoanthracenes induces the opposite phase polarization in the T_1 states. The changes of the ESP were analyzed quantitatively taking into account the sublevel selective relaxation in the RISC process.

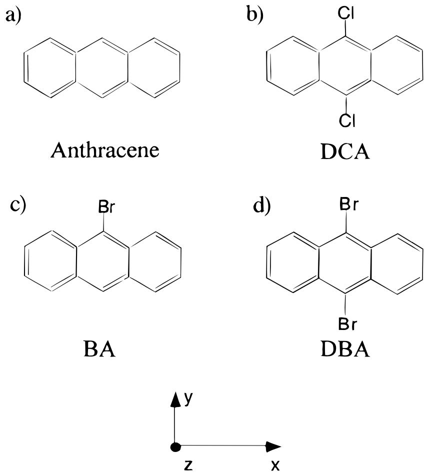

Figure 1. Molecular structures and principal axes systems of anthracene and its halogen derivatives.

Experimental Section

Two separate laser systems have been used for the two-step excitation TREPR experiments. Triplet generation was carried out by excitation with the 355 nm pulse from a Nd:YAG laser (Quanta-Ray GCR-14, third harmonics). The triplets were, in turn, reexcited with pulses from a Lumonics HD 300 Dye laser, normally tuned at 442 nm. The delay time of the second laser pulse from the first one was controlled by a delay generator (Stanford DG 535). The detection system of TREPR signals

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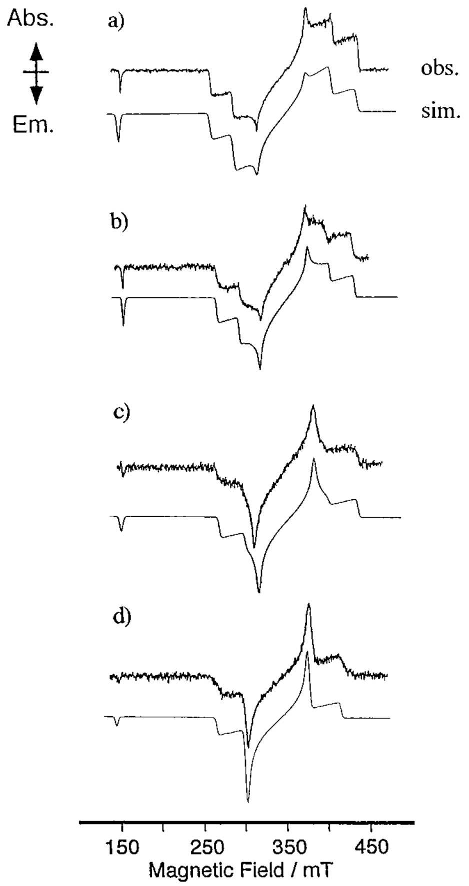


Figure 2. TREPR spectra of (a) anthracene, (b) DCA, (c) BA, and (d) DBA observed at 500 ns after the laser pulse (355 nm) at 50K in a toluene matrix.

was described elsewhere.[17] Measurements at cryogenic temperatures were performed using an Oxford ESR 900 helium flow cryosystem.

Anthracene and 9-bromoanthracene (BA, Tokyo Kasei) were recrystallized twice from ethanol before use. 9,10-Dichloroanthracene (DCA, Nacalai Tesque) was purified by repeated recrystallization from ethanol. Purified 9,10-dibromoanthracene (DBA) was kindly provided by Prof. Takahashi. The solvent toluene (Nacalai Tesque, Spectrograde) was purified by column chromatography on aluminum oxide. Methylcyclohexane and 2-methylbutane (Aldrich, Spectrograde) were degassed and stored on molecular sieves 4 A under vacuum. The sample solutions ($\sim$1.0 × 10^{-2} M) were deaerated by a vacuum line technique.

Results

Figure 2 shows the TREPR spectra obtained from the excitation of anthracene and its halogen derivatives in a toluene glassy matrix observed at 0.5 μs after the laser excitation with 355 nm at 50 K. The emissive signal at 0.15 T corresponds to the $|\Delta M_S| = 2$ transitions. The $|\Delta M_S| = 1$ transitions show the spin polarization pattern of EEE/AAA, where E and A are emission and enhanced absorption of microwave radiation, respectively. The zero field splitting (ZFS) parameters determined by computer simulation are summarized in Table 1. The results indicate that both $|D|$ and $|E|$ values are decreased by the substitution of heavy atoms of the *meso*-positions.

The energy order of the triplet sublevels of anthracene has been assigned as $T_x > T_y > 0 > T_z$ by experimental and theoretical studies, where the principal axis system is shown in Figure 1.[18] The D and E values are related to the principal values ($-X$, $-Y$, and $-Z$) by $D = -3Z/2$ and $E = (Y - X)/2$. In contrast to anthracene, there have been no data on the ZFS parameters for the halogen derivatives. It is reasonable to assume that the spin−orbit interaction due to the halogens enhances the ISC from the S_1 state to the T_1 state of the halogen substituted anthracenes. Therefore, the sublevel selective ISC into the T_y sublevel would increase with increasing atomic number of the *meso*-substituted halogens. On the basis of the populations in the triplet sublevels, we conclude that the order of the triplet sublevels in DCA and BA is the same as that of anthracene. On the other hand, for DBA the population differences among the sublevels were not determined by computer simulations, since the T_x and T_y sublevels are nearly degenerate ($E \sim 0$) in the T_1 state.

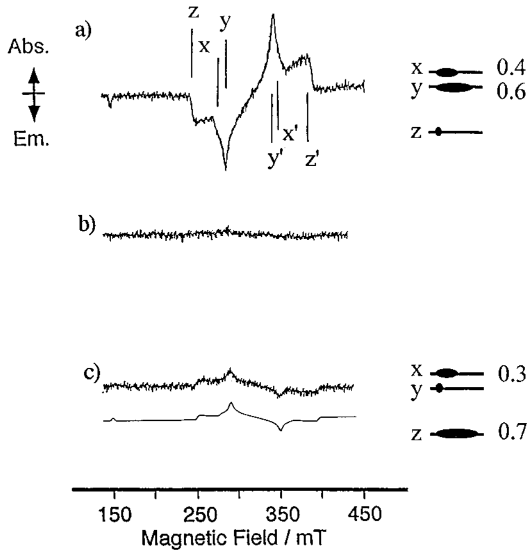


Figure 3. TREPR spectra of BA observed by (a and b) one-laser and (c) two-laser excitations in a toluene matrix at 50 K. The observed spectra were taken at (a) 0.5 μs and (b) 15.5 μs after the Nd:YAG laser pulse, respectively. The spectrum (c) was measured at 0.5 μs after the second laser pulse (442 nm) following the Nd:YAG laser flash (355 nm) with a delay time of 15 μs.

TABLE 1: Zero-Field Splitting Parameters (D^a and E^b) and Relative Population Differences of Anthracenes in a Toluene Glassy Matrix at 50 K

molecule	D/cm^{-1}	E/cm^{-1}	P_x-P_z:P_y-P_z
anthracene	+0.0712	−0.0080	0.55:0.45
9,10-dichloroanthracene	+0.0680	−0.0070	0.48:0.52
9-bromoanthracene	+0.0678	−0.0045	0.40:0.60
9,10-dibromoanthracene	+0.0610	±0.0010	

[a] $D = -3Z/2$. [b] $E = (Y - X)/2$.

Figure 3 depicts the TREPR spectra of BA observed in one and two-laser experiments. When the second dye laser pulse (442 nm) was not used, the ESP completely disappeared at 15 μs after the laser pulse irradiation (Figure 3b). However, the polarized EPR spectrum was clearly created by the re-excitation of the T_1 state to the T_n states of BA at 15 μs after the first laser pulse as shown in Figure 3c. The polarization pattern of AAA/EEE was observed. The pattern was completely opposite to that of the spectrum observed by the one-laser experiment. The spectrum was well reproduced by the same ZFS parameters of T_1 state BA, while the lowest sublevel was preferentially populated; the relative population differences of P_x-P_y:P_z-P_y = 0.3:0.7. The facts indicate that a spin selective pathway contributes to the reproduction of the T_1 state from the T_n state,

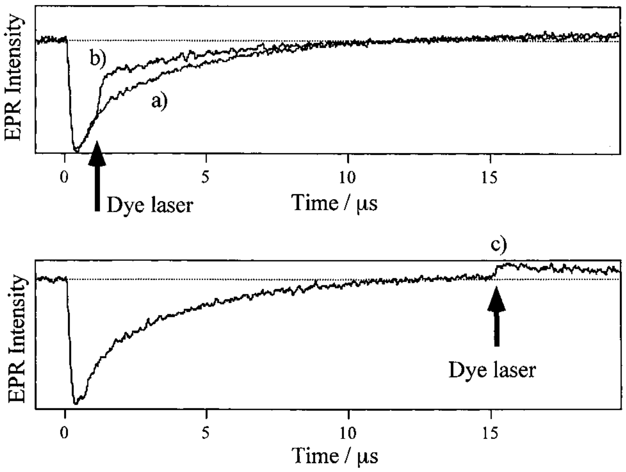


Figure 4. Time profiles of the TREPR signals observed at low field part of *y* canonical orientations for T_1 state BA at 50 K in a toluene matrix observed by (a) one-laser and (b and c) two-laser excitation.

which induces the preferential population into the lowest out-of-plane sublevel.

Figure 4 shows the temporal behaviors of the ESP in the T_1 state of BA under conditions of one- and two-laser excitation at 50 K. To remove the background contribution, which was independent of the applied field, the signals at off-resonance positions were subtracted from those at the resonance positions. The time profile was observed at the low field position corresponding to the *y* canonical orientation of the spectrum. The behavior at the high field part was identical to that observed at the low field except the phase in response to the laser pulse irradiation. In the other canonical orientations, similar time-profiles were observed, though they showed relatively poor signal-to-noise ratio (S/N).

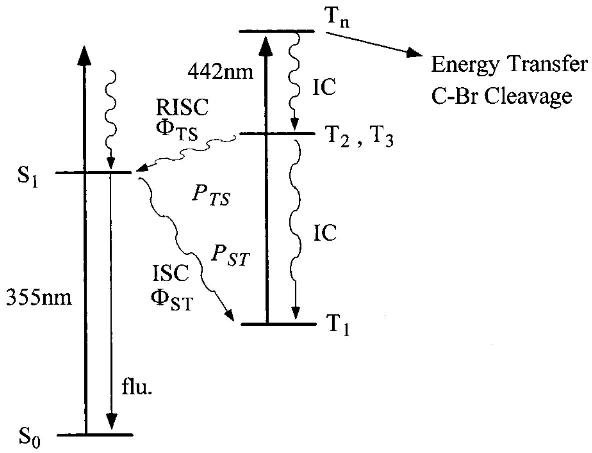
The lifetime of the T_1 state of BA was determined to be ~110 μs at 50 K from the decay of the thermally populated EPR signal intensity. On the other hand, the relaxation time of the ESP in the T_1 state of BA was ~2 μs in a toluene glassy matrix. The relaxation time was twice shorter in BA than in anthracene. Since the unpaired electrons in the T_1 state of anthracene distribute considerably on the *meso*-positions,[19,20] the acceleration of the relaxation results from the SOC due to the heavy atom substituent.

Figure 4, time profiles b and c, show the time profiles of the ESP in the T_1 state of BA following two-laser (355 nm followed by 442 nm) excitation. The second laser pulse reexcites the triplet states of BA which are in thermally nonequilibrium (delay time, 1 μs) and in equilibrium (15 μs) with respect to the sublevel populations, respectively. No depletion of the samples was observed during the experiments, indicating the contribution from the C−Br bond cleavage to be negligible at very low temperatures.

As shown in the time profile b in Figure 4, the excitation to the T_n state from the polarized triplet state induces the reduction of the ESP in the T_1 state. On the other hand, the opposite phase polarization was created by the second laser pulse following relaxation of the T_1 state ESP (Figure 4, time profile c). The ESP produced by the second laser irradiation decayed with the inherent relaxation time to give the thermally equilibrated states. The change of the ESP is considered to be due to the sublevel selective photophysical processes opened by the excitation to the T_n states.

McGimpsey and Scaiano pointed out that the T_n state in DBA had sufficiently long lifetime to participate in intermolecular energy transfer to the solvent (benzene).[15] Therefore, the T_n quenching by the solvent molecules could occur in the present system, because the T_1 state of toluene has comparable energy with that of benzene.[21] Thus, we also examined the matrix effects on the ESP in the two-step laser excitation. Similar effects on the ESP were observed in methylcyclohexane and 3-methylbutane matrixes. The results of the quantitative analysis are discussed later.

SCHEME 1



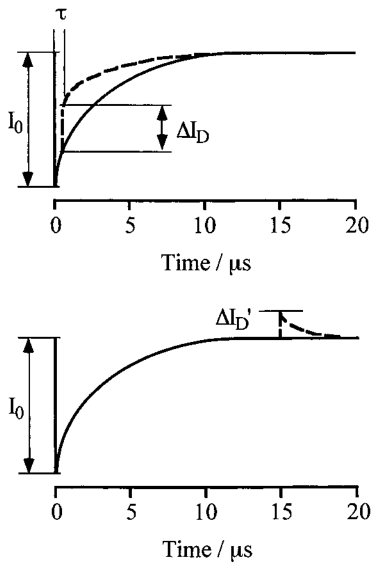
We also carried out the two-step laser excitation experiments on anthracene, DCA and DBA. For DBA, similar changes in the ESP were induced by the reexcitation of the T_1 state by the second laser pulse in a toluene glassy matrix. In a methylcyclohexane matrix, however, the intensity of the ESP was gradually decreased by the repeated excitation, suggesting that photochemical reactions occur from the T_n state in this matrix. On the other hand, for anthracene and DCA the stepwise excitation showed little effect on the TREPR spectra, indicating that the change of polarization is negligibly small. These facts suggest that the heavy atom induces the sublevel selective relaxation to create the ESP with the AAA/EEE pattern.

Discussion

We observed the ESP with opposite phase when the T_1 states of BA and DBA were irradiated by the second laser pulse. The creation of new polarization was not explained in terms of sublevel nonselective photochemical processes such as the T_n quenching by the energy transfer to solvent molecules (toluene) or debromination.[22] Scheme 1 describes the relaxation processes from the T_n state produced by two-step excitation. It can be considered that the RISC ($T_2 \rightarrow S_1$) process plays an important role in creating the new ESP in the bromine substituted anthracenes by the present two step excitation, because the SOC interaction governs the process. In contrast, the $T_2 \rightarrow T_1$ IC process is well-known to conserve the spin angular momentum quantum number. When the RISC rate is comparable to that of the IC rate, its sublevel selectivity may produce the spin polarized T_2 state. If the depopulation rates from the highest and middle sublevels are faster than that from the lowest one, the IC process from the T_2 state yields the T_1 state having preferential population of the lowest triplet sublevel.

Hamanoue et al.[12] pointed out that the direct $S_1 \rightarrow T_1$ ISC is very important in BA and DBA at low temperatures, because the temperature independent rates of fluorescence and ISC are comparable. Since the direct $S_1 \rightarrow T_1$ ISC process gives the preferential population into the middle and highest sublevels, the combination process involving the RISC followed by ISC diminishes the ESP generated by the IC process from the

SCHEME 2



polarized T_2 state. Therefore, these competing paths can be considered to result in the ESP observed in the present stepwise photolysis experiments.

We attempted the quantitative analysis of the time evolution of the ESP to estimate the quantum yield of the RISC process (Φ_{TS}). The initial TREPR signal intensity I_0 is proportional to the triplet concentration as well as the population difference between two sublevels in the T_1 state. When the T_n quenching by solvent molecules is negligibly small, the triplet concentration is constant during the time course in the ESP relaxation. In Scheme 2, we schematically depict the changes in signal intensities, ΔI_D and $\Delta I'_D$ generated by the excitation of the T_1 states in nonequilibrium (experiment b in Figure 4) and in equilibrium (experiment c) with respect to the sublevel populations, respectively. The initial signal intensity generated by one-laser irradiation is denoted as I_0, which is proportional to the initial polarization, $P_{ST(0)}$, produced by the $S_1 \rightarrow T_1$ ISC. The $T_2 \rightarrow S_1$ RISC process creates new polarization $-P_{TS}$ in the T_2 state. Then the ESP is transferred to the T_1 state via the IC process, where the negative polarization is derived from the phase observed in the present stepwise excitation experiments. On the other hand, the ISC process from the S_1 state, which is generated by the RISC process, creates the ESP with $P_{ST(0)}$ in the T_1 state. So the total change of ESP in the T_1 state is proportional to $(P_{ST(0)}\ \Phi_{ST} - P_{TS})\Phi_{TS}$, where Φ_{ST} is the $S_1 \rightarrow T_1$ ISC yield. Furthermore, in experiment b, where the reexcitation from the T_1 state was carried out before the ESP relaxation, we have to take into account the reduction of the T_1 state ESP induced by the $T_2 \rightarrow S_1$ RISC process. The contribution from this process is proportional to $P_{ST(\tau)}\ \Phi_{TS}$, where $P_{ST(\tau)}$ is the polarization at the delay time of τ after the first pulse. Assuming that all molecules in the T_1 state are reexcited by the dye-laser pulses, we can express the ratios between the signal intensities due to the ESP generated by one and two laser excitation as follows;

experiment b:

$$\frac{\Delta I_D}{I_0} = \frac{(P_{ST(0)}\Phi_{ST} - P_{TS})\Phi_{TS}}{P_{ST(0)}} - \frac{P_{ST(\tau)}\Phi_{TS}}{P_{ST(0)}}$$

experiment c:

$$\frac{\Delta I'_D}{I_0} = \frac{(P_{ST(0)}\Phi_{ST} - P_{TS})\Phi_{TS}}{P_{ST(0)}}$$

From these equations, Φ_{TS} is easily described as follows:

$$\Phi_{TS} = \frac{P_{ST(0)}}{P_{ST(\tau)}}\left(\frac{\Delta I'_D - \Delta I_D}{I_0}\right)$$

The validity of the present assumption was verified by the experiments on the excitation power dependence of the $\Delta I'_D/I_0$ value. The Φ_{TS} values were estimated at the laser power region where the $\Delta I'_D/I_0$ values were independent of the photon number. For BA, the Φ_{TS} values estimated from the present analysis were 0.26 in toluene, 0.17 in methylcyclohexane, and 0.17 in 3-methylbutane at 50K, respectively. The relatively large Φ_{TS} value obtained in toluene seems to be due to the neglect of the energy transfer from the T_n state to the matrix molecules. The same procedure was adopted to analyze the time profiles of the ESP for DBA. The quantum yield of the RISC process obtained was 0.20 in a toluene glassy matrix at 50 K. However, a reliable Φ_{TS} value was not obtained in methylcyclohexane and 3-methylbutane matrixes, because the ESP signals decreased gradually during the measurements. This is probably due to the C−Br bond breaking in the highly excited states of DBA. The present Φ_{TS} value for DBA is larger than that (0.09) determined in benzene solution at room temperature.[14,15]

For anthracene and DCA, we observed little change in the ESP by two-step laser photolysis. In anthracene, the RISC process is endothermic and inefficient even at ambient temperature.[14] Therefore, the Φ_{TS} would be negligibly small at low temperatures. Consequently, no polarization was observed by the excitation to the T_n state by the second pulse. DCA has a relatively small RISC yield of 0.015, while the yield of the $S_1 \rightarrow T_1$ ISC is comparable to that of the radiation.[14] Therefore, the ESP created by the RISC process may be too small to be detected by the TREPR technique, even if the RISC occurs anisotropically.

Conclusion

Two-color, two-laser TREPR measurements were carried out to investigate the spin dynamics in the upper excited triplet states of anthracene and its halogen derivatives in glassy matrixes. One laser excitation to their excited singlet states gave polarized EPR spectra due to the T_1 states. In BA and DBA, reexcitations to the T_n states produce the new polarization with an opposite phase compared to one-laser excitation experiments in their T_1 states. On the other hand, for anthracene and DCA, few effects were observed. We conclude that the sublevel selective RISC process is a key process in the polarization mechanism. The quantum yields of RISC were estimated from the analysis of the time profiles. The present method may be expected to play an important role in the investigation of relaxation processes in highly excited molecules.

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References and Notes

(1) Obi, K.; Imamura, T. *Rev. Chem. Intermed.* **1986**, *7*, 225.
(2) Hirota, N.; Yamauchi, S.; Terazima, M. *Rev. Chem. Intermed.* **1987**, *8*, 189.

(3) Akiyama, K.; Ikegami, Y.; Tero-Kubota, S. *J. Am. Chem. Soc.* **1987**, *107*, 2538.

(4) Ikoma, T.; Akiyama, K.; Tero-Kubota, S.; Ikegami, Y. *J. Phys. Chem. A* **1998**, *102*, 446.

(5) Lim, E. C.; Laposa, J. D.; Yu, J. M. H. *J. Mol. Spectrosc.* **1966**, *19*, 412.

(6) Liu, R. S. H.; Kellog, R. E. *J. Am. Chem. Soc.* **1969**, *91*, 250.

(7) Robert, J. P.; Dixon, R. S. *J. Phys. Chem.* **1971**, *75*, 845.

(8) Widman, R. P.; Robert, H. J. *J. Phys. Chem.* **1972**, *76*, 1524.

(9) Wu, K.-C.; Ware, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 5906.

(10) Wilson, T.; Halpern, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7272.

(11) Tanaka, M.; Tanaka, I.; Tai, S.; Hamanoue, K.; Sumitani, M.; Yoshihara, K. *J. Phys. Chem.* **1983**, *87*, 813.

(12) Hamanoue, K.; Nakayama, T.; Ikenaga, K.; Ibuki, K. *J. Photochem. Photobiol.* **1993**, *74A*, 147.

(13) Schmidt, R.; Brauer, H.-D.; Kelm, H. *J. Photochem.* **1978**, *8*, 217.

(14) Fukumura, H.; Kikuchi, K.; Kokubun, H. *J. Photochem. Photobiol. A* **1988**, *42*, 283.

(15) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 335.

(16) Bohne, C.; Kennedy, S. R.; Boch, R.; Negri, F.; Orlandi, G.; Siebrand, W.; Scaiano, J. C. *J. Phys. Chem.* **1991**, *95*, 10300.

(17) Akiyama, K.; Tero-Kubota, S.; Ikoma, T.; Ikegami, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5324.

(18) van der Waals, J. H.; ter Maten, G. *Mol. Phys.* **1964**, *8*, 301.

(19) Clarke, J. R.; Hutchison, C. A., Jr. *J. Chem. Phys.* **1971**, *54*, 2962.

(20) Yu, H.-L.; Sloop, D. J.; Weissman, S. I.; Lin, T.-S.; Norris, J. R.; Bowman, M. K. *J. Phys. Chem.* **1982**, *86*, 4287.

(21) Marchetti, A. P.; Kearns, D. R *J. Am. Chem. Soc.* **1967**, *89*, 768

(22) The referee has suggested the possibility of the spin-selective mechanism such as efficient radical pair recombination following halogen bond homolysis from the highly excited states. However, the debromination yield estimated from the two-step excitation experiments is on the order of 10^{-3} even at ambient temperature.[15] So we excluded this contribution from our analysis.