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A Further ESR Study of Irradiated D_2O Ice. On the Nature of the Species Appeared at $g=2.08$

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For D_2O ice warmed at *ca.* 120 K after the irradiation at 77 K, "$g=2.08$ line" was isolatedly detected at 4 K. The intensity of the line increased for the sample containing an electron scavenger. Photobleaching of solvated electrons caused no change in the intensity of the line. In D_2O single crystal, angular dependency of the line was not observed. The overall results were not accomodated to the hypothesis that "$g=2.08$ line" was due to O^- radical, but rather indicated the possibility that the species is a sort of positive ion or trapped hole.

Among numerous electron spin resonance (ESR) studies on irradiated ices, a few reports[1,2] described an asymmetric singlet line at $g=2.08$. However, the line was neither studied in detail nor identified until its thermal reversibility was firstly reported by Johnson and Moulton in 1978.[3] They found that in polycrystalline H_2O or D_2O ice irradiated at 4 or 77 K, "$g=2.08$ line" was observed only when ESR measurements were made at temperatures lower than 24 K. They proposed that "$g=2.08$ line" was probably due to H_2O^+ radical in irradiated H_2O ice, and D_2O^+ radical in irradiated D_2O ice.

Recently, however, Symons[4,5] has claimed that O^- radical is possibly responsible for "$g=2.08$ line". The experimental evidences on which the O^- hypothesis stands were: (i) the interconversion between OH radical and the species amounted to 50% for H_2O and 80% for D_2O ice[4] and (ii) when $D_2{}^{17}O$ ice was irradiated, a new line was observed in the $g=2.16$ region which was tentatively assigned to one of $g_{/\!/}$ components of $^{17}O^-$ radical, although 6 $g_\perp$ components of $^{17}O^-$ radical could not be visible.[5] By analogy with NH_2^+ radical, Symons speculated that the H_2O^+ hypothesis must be rejected on the following reasons: (i) proton coupling of an order of 25 G† should be expected for H_2O^+; (ii) g-value should be close to 2.00 for H_2O^+. It was also stressed by Symons that ESR spectrum of the species was similar in profile to that for O^- in alkaline ice.

The argument by Symons for identification of the species is not completely convincing for us, since (i) the argument partly stands on the analogy with other radicals; (ii) there are scarecely any positive evidences which support the O^- hypothesis; (iii) direct observation of 6 hyperfine lines due to $^{17}O^-$ radical failed except for a new line at $g=2.16$ which might be attributed to $g_{/\!/}$ component of $^{17}O^-$ radical.

Under these circumstances, it is worthwhile to study the nature of the species corresponding to "$g=2.08$ line" in order to further shed light on its identification.

In the present work, we have studied the effects of thermal annealing, addition of solute which is known as electron scavenger and photobleaching of solvated electrons(e^-_{sol}) on the "$g=2.08$ line" in polycrystalline D_2O ice containing NaOD. We have also studied the angular dependency of "$g=2.08$ line" in D_2O single crystal. Based on the results, we will discuss on the entity of "$g=2.08$ line".

Experimental

D_2O(99.75%) and NaOD(40% in D_2O) were obtained from MSD (Japan) and used without further purification. Reagent grade $AgNO_3$ were used. Polycrystalline samples were made in suprasil quartz ESR tubes by immersing the liquid samples into liquid nitrogen. Single crystals of D_2O were made as described previously.[6] Samples were irradiated by ^{60}Co gamma rays at 77 and 4 K at a dose of 2.2 Mrad/h. ESR measurements were carried out with a Varian E-9 spectrometer at 77 and 4 K.

Results and Discussion

Figure 1 shows ESR spectra of polycrystalline D_2O ice irradiated at 77 K. Figure 1(A) presents the spectrum recorded at 4 K and shows an asymmetric singlet line at $g=2.08$ in addition to the lines due to OD radical in the $g=2.00$ region. Yields of species corresponding to "$g=2.08$ line" and OD radical increased linearly with gamma dose upto at least 20 Mrads. When ESR spectrum was recorded at 77 K, "$g=2.08$ line" was no longer visible. This spectral change is the same as reported firstly by Johnson and Moulton.[3] After the sample was warmed at *ca.* 120 K, ESR spectrum was recorded at 4 K. The spectrum is shown in Fig. 1(B). It is noted in Fig. 1(B) that "$g=2.08$ line" is still visible, although its intensity is reduced. The weak signal remaining in the $g=2.00$ region is

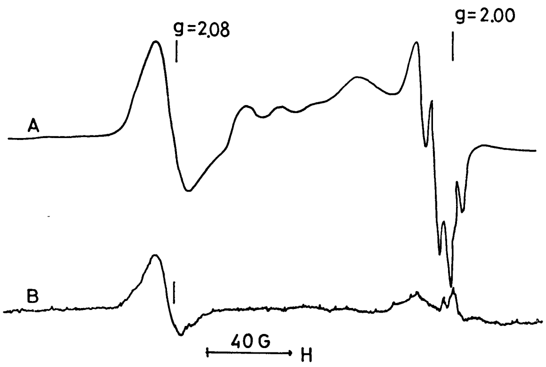

Fig. 1. ESR spectra of polycrystalline D_2O ice irradiated at 77 K. ESR spectrum at 4 K, (B) ESR spectrum at 4 K after warming to *ca.* 120 K. The ESR sensitivity for spectrum (B) was 5 times as large as that for spectrum (A).

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† $1\ G=10^{-4}\ T$.

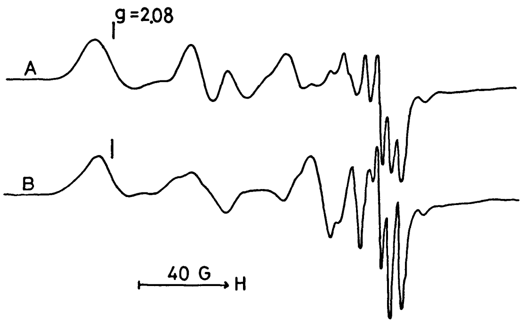

Fig. 2. ESR spectra of D_2O single crystal irradiated at 77 K. (A) ESR spectrum at 4 K, (B) ESR spectrum at 4 K after the cylindrical sample was rotated about 50°. The intensity of "$g=2.08$ line" remained nearly unchanged with any rotation angles.

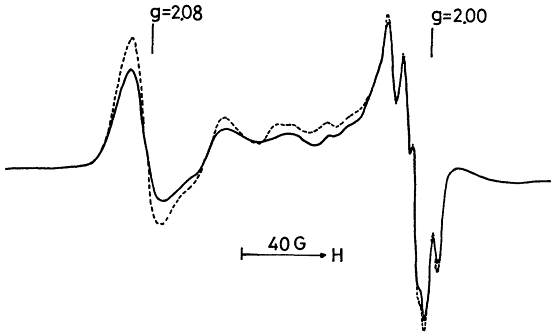

Fig. 3. ESR spectra of polycrystalline D_2O ice containing 0.1 M (solid line) and 0.5 M (dotted line) $AgNO_3$ which was irradiated at 77 K. ESR spectra were recorded at 4 K.

different from the signal due to either OD radical or $g_{//}$ component of O^- radical.

O^- radical is often reported for irradiated alkaline ices.7,8) It is known that the $g_{//}$ component of O^- radical in the $g=2.00$ region provides a featureless broad line with ESR intensity comparable to that of the $g_\perp$ component in the $g=2.07$ region. Thus the signal remaining in the $g=2.00$ region in Fig. 1(B) is unlikely O^- radical.

The "$g=2.08$ line" was also observed in D_2O single crystal irradiated at 77 K. The relative intensities of the ESR lines due to OD radical changed remarkably with rotation of the cylindrical samples, while the intensity of "$g=2.08$ line" remained almost unchanged. This is illustrated in Fig. 2. The luck of the angular dependency for the "$g=2.08$ line" suggests that the line may be broadened partly by an unresolved hyperfine interactions with surrounding nuclei similar to those for trapped electrons in alkaline ices. This may also contrast to the result that ESR spectrum of bromine atom having an unpaired electron orbital like O^- radical showed a prominent angular dependency due to a large proton superhyperfine coupling in *N*-bromosuccinimide single crystal.9)

When polycrystalline D_2O ice was irradiated at 4 K and ESR measurements were made at 4 K, the spectrum obtained was the same as that reported by Johnson and Moulton and showed "$g=2.08$ line" together with lines due to OD radical, trapped D atom and H atom.

Polycrystalline D_2O ices containing 0.1 or 0.5 M[††] $AgNO_3$ were irradiated at 77 K. The "$g=2.08$ line" was observed in the ESR spectra recorded at 4 K. The intensity of "$g=2.08$ line" increased with concentration of $AgNO_3$, being 1.4 and 2.1 times for 0.1 and 0.5 M $AgNO_3$ solutions, respectively, as large as that for the solute-free D_2O ice. This is illustrated in Fig. 3. Since $AgNO_3$ is an electron scavenger, the observed effect of $AgNO_3$ in D_2O ice is consistent with the hypothesis that "$g=2.08$ line" is ascribed to a positive ion or hole, *e.g.* D_2O^+. O^- radical is also a cation-like species, but may not be a candidate for "$g=2.08$ line" in consideration of the previous result7) that O^- yield was not affected by electron scavengers in alkaline ices at 77 K.

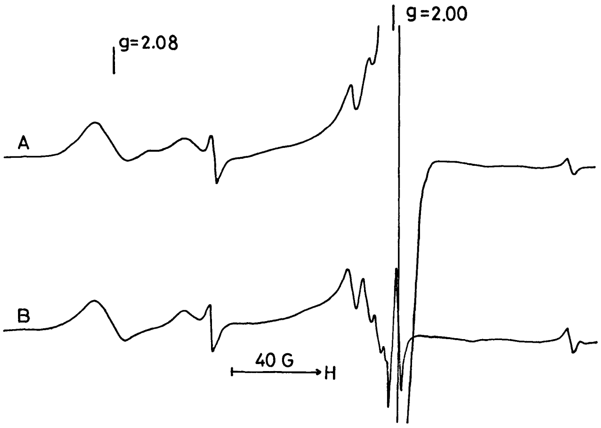

Fig. 4. ESR spectra of polycrystalline D_2O ice containing 1 M NaOD which was irradiated at 4 K. (A) ESR spectrum at 4 K, (B) ESR spectrum at 4 K after photobleaching the sample with the visible light at 4 K.

In polycrystalline D_2O ice containing 0.1 or 1.0 M NaOD, "$g=2.08$ line" was observed at 4 K. The intensity of the line was not affected by concentration of NaOD and remained nearly the same in both matrices. This result is in a remarkable contrast to the previous report7) that O^- yield increased with concentration of NaOH. An intense singlet line due to e_{sol}^- was observed in the $g=2.00$ region in 1.0 M NaOD solution. Photobleaching of e_{sol}^- at 4 K caused little changes in the intensity of "$g=2.08$ line". That this is the case is shown in Fig. 4. It is previously reported7) that complete photobleaching of e_{sol}^- in alkaline ices resulted in a decrease of about 70% of concentration of O^- radicals and that the decrease was attributed to the reaction of photodetached electrons with O^- radicals. Thus if "$g=2.08$ line" was attributed to O^- radicals, complete photobleaching of e_{sol}^- would reduce the intensity of "$g=2.08$ line". We infer that O^- radical must be produced in 1.0 M NaOD solution and that a broad ESR signal due to O^- radicals is probably masked in the apparent ESR spectrum. We also suppose that photodetached electrons in 1.0 M NaOD solution undergo a reaction

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[††] 1 M=1 mol dm^{-3}.

with O^- radicals more dominantly than another reaction with positive ion or hole. Thus the observed effects of NaOD in D_2O ice would be another evidence that "$g=2.08$ line" is not attributed to O^- radical.

In conclusion, we could not obtain any positive evidences for the hypothesis that "$g=2.08$ line" is ascribed to O^- radical.

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