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# ESR Studies on $\gamma$ -Irradiated Methanol Glasses Produced by Vapour Condensation Method

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## Abstract

Trapped electrons in  $\gamma$ -irradiated pure  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  glasses prepared by the vapour condensation method were studied by ESR and DTA. Differences of the ESR line width of trapped electrons in the pure methanol glasses and ones in methanol glasses and ones in methanol-water matrices prepared by rapid cooling were found.

## 1. Introduction

Trapped electrons ( $e_t$ ) have been investigated<sup>1,2)</sup> in various kinds of glassy matrices such as alkaline ices, alcohols, ethers, amines, alkenes and alkanes irradiated at 77 K. The nature of  $e_t$  has been mainly examined using ESR and optical spectroscopy. In the case of alkaline ices the yields of  $e_t$  are higher than in polycrystalline matrices (3 or 5 times). By contrast, significant yields of  $e_t$  have not been found in organic crystalline systems<sup>3)</sup>. However, the possibility of electron trapping in hydrocarbon crystals is still under discussion<sup>4)</sup>. Recently the mechanisms and dynamics of electron stabilization in glassy solid methanol has been studied in terms of presolvated and solvated electrons<sup>5-7)</sup>. The existence of presolvated electrons which are trapped shallowly and produce sharp singlets has been generally observed at 4.2 K or lower temperature in other glassy matrices. However, an annealed methanol-water matrix has recently been found to stabilize both presolvated and solvated electrons at 77 K. In that work, the samples containing 69 mol%  $\text{H}_2\text{O}$  were annealed for 5 min at 173 K. Annealed samples were somewhat polycrystalline and gray and evidently had different phase from unannealed ones.

For almost all organic solids, the detailed discussions on the phase effects have not been performed sufficiently because of the difficulty to regulate the phase of solids. Therefore, the investigations on  $e_t$  were confined to some liquids easy to freeze in a glassy state by a rapid cooling method or by adding some solutes. The realization of the glassy state of methanol has been unsuccessful using the usual rapid cooling method and most experiments have been made with methanols which contain a significant amount of solute to prevent crystallization<sup>8)</sup>.

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Recently, Haida, Suga and Seki have developed successfully the vapour condensation method<sup>9)</sup>. In the present paper, we report the application of the vapour condensation method to produce pure glassy methanol and the investigation on the ESR spectra of  $e_t$ .

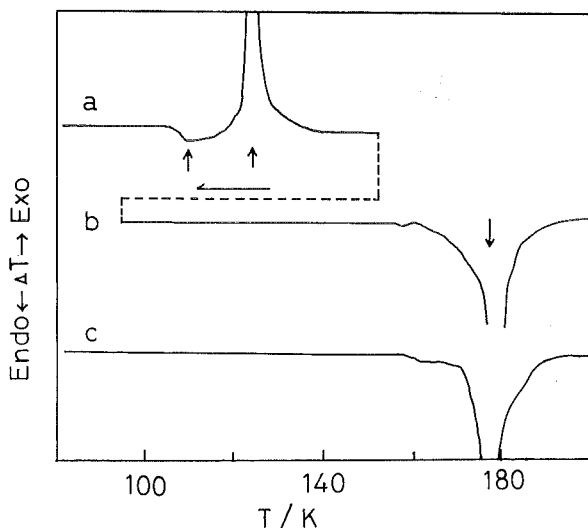
## 2. Experimental

Commercial extra pure methanol (Wako Junyaku Co. Ltd) was dried by magnesium metal and distilled.  $\text{CH}_3\text{OD}$  (>99.5%, Merck) was used without further purification. The samples were then deaired carefully under vacuum using freeze and thaw technique and were transferred into a sample storing vessel. The vapour condensation apparatus used was essentially similar to that has been described by Haida, Suga and Seki<sup>9)</sup>. Some modifications were added to make it possible to transfer samples from a Dewar vessel into liquid nitrogen. The sample vapour was passed through the variable leak valve and the sampling tube, and was deposited onto the surface of copper block which was cooled by liquid nitrogen in the Dewar vessel. The deposited samples removed into liquid nitrogen, were crushed in pieces, and were sealed off in an ESR sample tube under high vacuum. Irradiations were carried out with  $\gamma$ -ray of  $\text{Co}^{60}$  for 40 minutes with dose of  $3.3 \times 10^{19}$  eV/g. ESR measurements were made with a X-band apparatus built in our laboratory with magnetic field modulation of 100 KHz. All ESR spectra were observed at 77 K. Differential thermal analyses (DTA) were carried out with a Rigaku Denki low temperature DTA apparatus. Samples were put into a aluminum holder in liquid nitrogen and were set into the DTA apparatus. The heating rate was 10 K/min for all samples.

## 3. Results and discussion

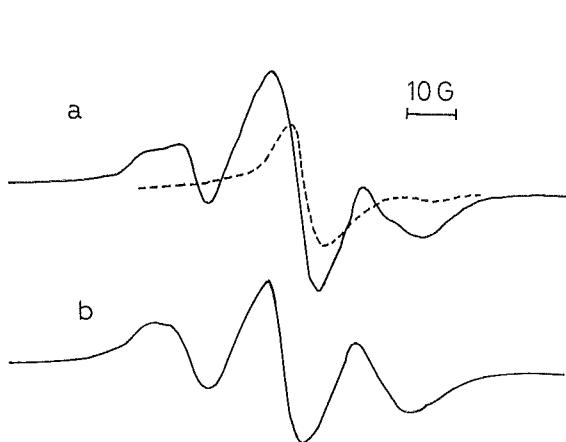
Fig. 1 shows the DTA curves of methanol prepared by vapour condensation at a rate of 0.05 g/h and by rapid cooling. A small endothermic anomaly began at 107 K and was followed by very sharp exothermic peak at 122 K (curve a). When the temperature cycling was carried out, after passing the anomaly at 122 K these two anomalies disappeared in the subsequent warm-up cycle (curve b). Such a phenomenon is a typical feature of glass transition and is an irreversible phase transition, *i. e.*, crystallization of supercooled liquid. Curve c shows no existence of evidence for glass transition in the case of rapid cooled methanol. A shoulder at about 170 K corresponds to the annealing temperature used in the work of references<sup>5-7)</sup>. The endothermic anomaly at 175 K coincides with the melting point of methanol.

The ESR spectrum of the deposited methanol gives a triplet spectrum due to  $\cdot\text{CH}_2\text{OH}$  radical superimposed on a singlet due to  $e_t$  (fig. 2a). Visible light photolysis of the irradiated sample excluded the singlet and generated a similar spectrum to polycrystalline methanol (fig. 2b). The subtraction of the spectrum b from the spectrum a gives a singlet with a line width of  $9 \pm 1$  G (fig. 2a dotted line) which is assigned to be due to  $e_t$ . The power saturation curve of this singlet indicates



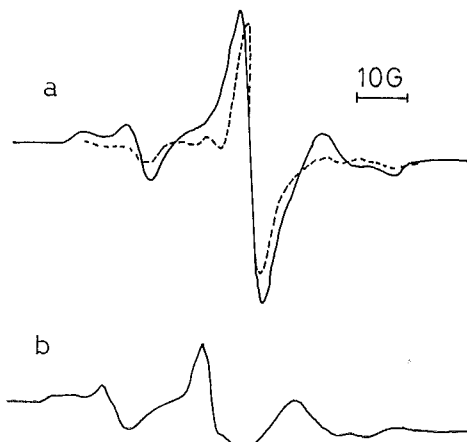
**Fig. 1.** DTA curves for methanol.

a and b : methanol deposited at the rate of deposition 0.05 g/h.  
 c : methanol cooled down rapidly.



**Fig. 2.** ESR spectra of  $\gamma$ -irradiated methanol prepared by the vapour condensation method.

a : after irradiation at 77 K.  
 b : after photobleaching with visible light.  
 (---) difference spectrum between a and b.



**Fig. 3.** ESR spectra of  $\gamma$ -irradiated methanol-OD prepared by the vapour condensation method.

a : after irradiation at 77 K.  
 b : after photobleaching with visible light.  
 (---) difference spectrum between a and b.

an intense saturation characteristic of  $e_t$  at the microwave power level higher than  $10^{-5}$  W. The ESR spectrum of the deposited  $\text{CH}_3\text{OD}$  contains a singlet due to  $e_t$ , the line width of which is 5.1 G (fig. 3), about a half of that in  $\text{CH}_3\text{OH}$ .

The amount of added water regulates the phase of methanol<sup>9)</sup>. The spectrum of glassy methanol with 5.2 mol% water content was observed for comparison with

that of pure methanol. Fig. 4 a shows the spectrum of irradiated sample at 77 K and fig. 4b is obtained after visible light photobleaching. The difference spectrum between a and b produces a singlet with a line width of about 18 G which is twice as large as that in pure methanol. The discrepancy of water contained methanol and pure methanol agrees with the reported values by other workers as follows. Kevan et al.<sup>10</sup> found the line width of  $e_t$  is 11 G in pure methanol drops, and Bennett et al.<sup>11</sup> reported 11.2 G for methanol condensed together with sodium. On the other hand, 14 G and 20 G of the line width about  $e_t$  are reported in 1 mol% isopropanol by Ekstrom et al.<sup>12</sup>, and in 5 mol% water by Chachaty et al.<sup>2</sup>, respectively.

The magnetic moment of  $e_t$  in methanol will interact with the magnetic moments of the surrounding nuclei. Kip, Kittel, Levy and Portis<sup>13</sup> previously carried out the theoretical treatment of the line widths of F centers in ionic crystals. They found that the line width is given by eq. (1), in which  $\Delta H_{rms}$  is the root mean square line width,  $\mu_i$  is the magnetic moment of nucleus  $i$ ,  $I_i$  is the spin of nucleus  $i$ , and  $|\psi_i|^2$  is the charge density at the  $i$ th nucleus.

$$(\Delta H_{rms})^2 = \frac{64\pi^2}{27} \sum \mu_i^2 \frac{(I_i + 1)}{I_i} |\psi_i|^4 \quad (1)$$

We assume that the line width arises from hyperfine interactions of  $e_t$  with surrounding protons of  $n$  methanol molecules equivalently ligated around  $e_t$ . The wavefunction of  $e_t$  is assumed to have the same density at each proton of hydroxyl group and also have the same density at each proton of methyl group. For Gaussian line, the line width at maximum slope equals 2.0 times the root-mean-square line width. The line widths at the maximum slope of 9.0 and 5.1 G for  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  were observed respectively. Using the above values and the ratio of  $\mu^2(I+1)/I$  ( $=\alpha$ ) for proton and deuteron,  $\alpha_D/\alpha_H=1/16$ , we have from eq. (1),

$$81 = W_H^2 + W_{\text{CH}_3}^2$$

$$26.4 = W_H^2/16 + W_{\text{CH}_3}^2,$$

where  $W_{\text{CH}_3}$  and  $W_H$  are contributions in gauss to the observed line width at the maximum slope from proton interaction and deuteron interaction. Values of  $W_{\text{CH}_3}$  and  $W_H$  of 4.8 and 7.6 G were calculated and a contribution,  $W_{\text{H-CH}_3}$ , from one

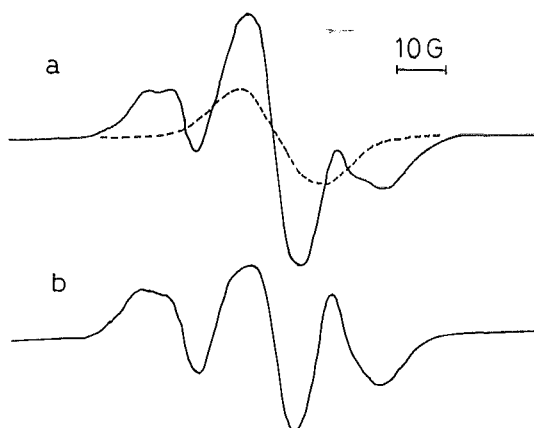


Fig. 4. ESR spectra of  $\gamma$ -irradiated methanol prepared by rapid cooling method.

a : after irradiated at 77K.

b : after photobleaching with visible light.

(---) difference spectrum between a and b.

TABLE 1. The charge densities calculated for reasonable number of methanol molecules surrounding  $e_i$ .

$n$	$ \phi_{\text{H-CH}_3} ^2$	$ \phi_{\text{H}} ^2 (\times 10^{24}/\text{cm}^3)$
4	0.0058	0.016
6	0.0047	0.013
8	0.0041	0.011

proton of methyl group of 2.75 G was also done similarly. From the values of  $W_{\text{H-CH}_3}$  and  $W_{\text{H}}$ , the charge densities at the proton were deduced and listed in the table for a reasonable number of methanol molecules surrounding  $e_i$ . Then  $n=4$  implies that four methanol molecules are solvated around  $e_i$ .  $N=6$ , and  $n=8$  have the same meaning as  $n=4$ . These values listed in the above table suggest that the charge density at the proton of hydroxyl group is nearly three times as large as that of the methyl group and a methanol molecule may not necessarily be directed toward  $e_i$  with its hydroxyl group regardless of the high electronegativity of the oxygen atom in OH group. The direction of electric dipole of methanol molecule may be considered to be along with a bisector between two axes of methyl and hydroxyl group. If the dipole is directed to  $e_i$ , both groups have about the same distances from  $e_i$  so as to produce similar values of charge density of the wave function.

In conclusion, we believe that the vapour condensation method seems a very powerful tool to investigate the phase effects in detail on radiolysis of solids which are difficult to regulate the phase with use of other methods.

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