

# Radical species and their thermal stability in gamma-irradiated methane hydrate

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Synthetic methane hydrate irradiated by gamma-rays at 77 K has been measured by electron spin resonance (ESR). Three signals were observed. The quartet signal at  $g = 2.0029$  with the intensity ratio of approximately 1:3:3:1 and the hyperfine coupling constant  $A = 2.3$  mT was identified as the methyl radical ( $\text{CH}_3$ ). Doublet signal at  $g = 2.0021$  with the hyperfine coupling constant  $A = 50.8$  mT was identified as the hydrogen atom. The unidentified isotropic signal at  $g = 2.0014$  was observed. Dose response for the signal intensities of the methyl radical showed that the radicals were formed linearly up to 10 kGy with the formation efficiency per 100 eV (16 aJ), G value of 0.052. According to annealing experiments, it became unstable over 200 K where thermal dissociation of the hydrate had already started, though very weak signal was detectable up to 270 K. The methyl radical thermally decayed following second-order kinetics with activation energy of 0.26 eV (42 zJ). Existence of the signal at 270 K would be related to the extremely slow dissociation called the self-preservation effect of gas hydrate.

In addition, methyl radical ( $g = 2.0024$ ,  $A = 2.3$  mT) and unidentified signal ( $g = 2.0010$ ) were observed in natural methane hydrate after gamma-ray irradiation. The parameters and the thermal stability of methyl radical were very similar to those in a synthetic sample. The signal intensity was about one eightieth of that in synthetic one because methane hydrate had partially changed to ice. ESR signal intensity of the methyl radical after gamma-ray irradiation is used to estimate the amount of methane hydrate in a sample mixed with ice.