



# DFT and direct ab-initio MD study on hyperfine coupling constants of methyl radicals adsorbed on model surface of silica gel

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## ABSTRACT

Methyl radicals interacting with silica gel surfaces have been investigated by means of DFT and direct ab-initio molecular dynamics (MD) methods using cluster models. Four typical binding sites of CH<sub>3</sub> on the cluster models were found in the geometry optimization from several initial geometries of CH<sub>3</sub> around the silica gel clusters. These were two silanol Si–OH sites and two siloxane Si–O–Si sites. In both sites, magnitude of hyperfine coupling constants of the methyl radical ( $a_H$ ) was smaller than that of free CH<sub>3</sub> ( $a_H = 23.04$  G). Temperature effects on  $a_H$  of the methyl radical were investigated by means of the direct ab-initio MD method. The hyperfine coupling constant of CH<sub>3</sub> interacting with the SiOH group decreased with increasing temperature. The methyl radical interacting with alkali metal supported silica gel was also investigated for comparison. The electronic states of methyl radicals on silica gel were discussed on the basis of theoretical results.

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## 1. Introduction

Neutral and ion radicals of organic molecules on the solid surface are important intermediates in catalytic reactions, electrochemical reactions, and plasma-induced reactions [1–3]. Therefore, detection of the radical adsorbed on the surface has been carried out mainly by electron spin resonance (ESR) spectroscopy. In particular, since the organic radical is an intermediate in the carbon–carbon (C–C), carbon–hydrogen (C–H), and carbon–halogen (C–X, where X=F and Cl) cleavage reactions of alkanes, the detection of the organic radicals on the solid surface is important in elucidating the reaction mechanism. ESR spectroscopy is a powerful tool to know the structure and electronic states of the paramagnetic radical on the surface.

The methyl radical is the simplest organic radical, which is often observed as an intermediate in the catalytic reactions of organic compounds on the solid surface [1–3]. The electronic states of the methyl radical interacting with solid surfaces are much different from those in gas phase and in inert gas solid phase. The ESR spectrum of free CH<sub>3</sub> shows an isotropic quartet lines with 1:3:3:1 intensity ratio and hydrogen-hyperfine coupling constant (hfcc) of 23.04 G [4]. On the other hand, the methyl radical interacting with solid surfaces shows significantly smaller hfccs (16.0–23.0 G) [5–12].

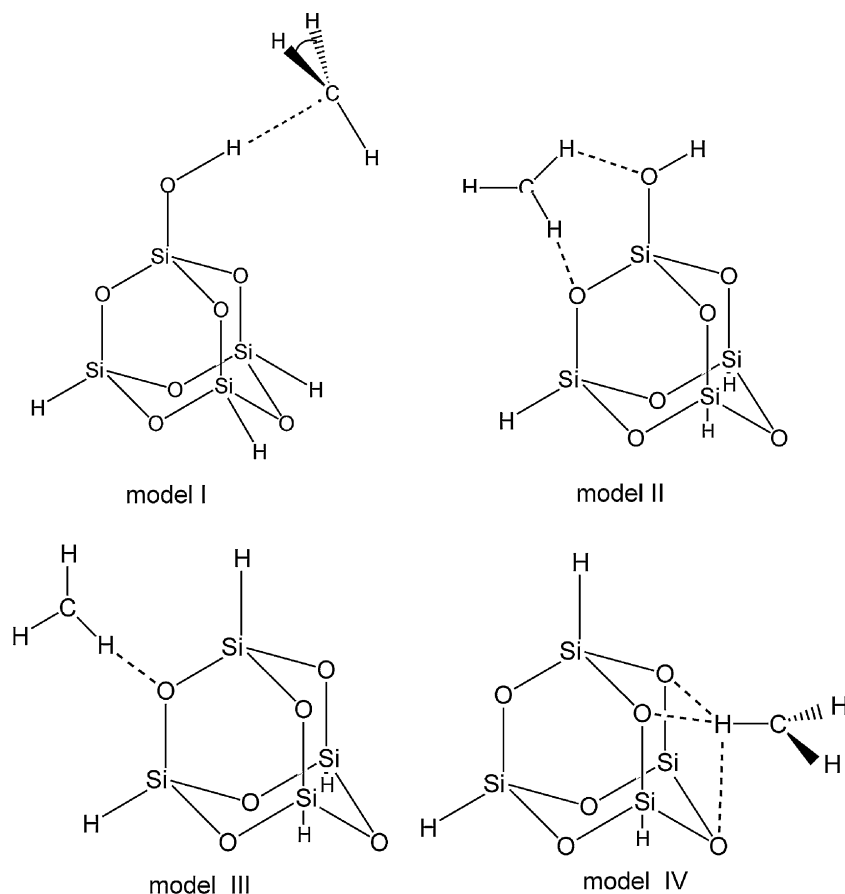
Garbutt and Gesser [5] measured hfccs of the methyl radical adsorbed on the porous Vycor glass. They showed that hfcc of CH<sub>3</sub> is 19.3 G. Kubota et al. [6] have reported that the methyl radical stabilized on silica gel shows the hfccs of 20.7 and 21.2 G. Shiotani et al. [7] reported that the methyl radical adsorbed on Linde 4A type Zeolite shows the hfcc of 22.3 G.

In 1995, Ogata et al. [11] observed methyl radicals on metal ion supported silica gel generated by photoactivation of methane. The methyl radicals were detected on Na, Mg, Ca, Sr, Y, and Ti at 77 K. The hfccs of •CH<sub>3</sub> on the several sites were distributed in the range 16.7–23.0 G. In the case of •CH<sub>3</sub> on pure silica gel, hfcc was found to be 22.7 G. All the reported hfccs are thus smaller than 23.04 G (free •CH<sub>3</sub>). The methyl radical can bind several sites of pure and metal supported silica gels. However, it is unclear why CH<sub>3</sub> shows several hfccs on solid surfaces. In particular, there is no direct information on the binding site of •CH<sub>3</sub> on the surface.

In the present paper, structures and electronic states of methyl radicals trapped on the silica gel surface have been studied by means of hybrid density functional theory (DFT) and direct ab-initio molecular dynamics (MD) calculations. In order to elucidate interactions between methyl radicals and trapping sites, we attempted to search the trapping sites of •CH<sub>3</sub> and calculate hfccs. We focus our attention on the relation between trapping sites and hfcc in order to shed light on the interpretation of ESR spectra of •CH<sub>3</sub> on several trapping sites. In addition, temperature dependence of the hfcc has examined on the basis of direct ab-initio (MD) calculations and the hfccs at several temperatures have been predicted theoretically.

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**Fig. 1.** Schematic illustrations of cluster models of silica gel and binding structures of methyl radical to the cluster models. Models I and II indicate a surface Si–OH model, while models III and IV are Si–O–Si siloxane model.

## 2. Method of calculations

### 2.1. Static *ab-initio* and hybrid DFT calculations

As models of silica gel, two clusters were examined in the present calculations. Schematic structures of the clusters used are given in Fig. 1. One is a surface model of silica gel given as models I and II. It is known that the silica gel surface is generally covered with a silanol group ( $\equiv\text{Si-OH}$ ) [13]. Hence, the cluster having a Si–OH group was examined as a model of the silica gel surface. A cluster model of silica gel lattice composed of siloxane (Si–O–Si) is given as models III and IV. The lattice model has no silanol group.

To determine the trapping sites of methyl radicals, several initial geometries of methyl radicals around the clusters were randomly generated and then the geometries were fully optimized at the B3LYP/6-311G(d,p) level. Twenty geometrical configurations around each cluster were generated as an initial one in each cluster. The structures were fully optimized without any structural restrictions. The hybrid density functional theory (DFT) calculations were carried out at the B3LYP/6-311G(d,p) level of theory, where the B3LYP is Becke's three-parameter hybrid functional using the Lee–Yang–Parr correlation functional. Isotropic hyperfine coupling constant of hydrogen of the methyl radical (denoted by hfcc) was calculated using the optimized structure. All calculations were carried out using the Gaussian03 program package [14].

### 2.2. Direct *ab-initio* MD calculations

To elucidate temperature effects on the hfcc of  $\text{CH}_3$  interacting with a Si–OH group, direct *ab-initio* MD calculations [15,16] were

carried out using a simplified  $\text{H}_3\text{SiOH-CH}_3$  complex. The optimized structure was chosen as an initial structure of  $\text{H}_3\text{SiOH-CH}_3$ . The four temperatures, 10, 30, 40 and 50 K were chosen as the simulation temperature. The direct *ab-initio* MD calculations were carried out at the HF/6-311G(d,p) level. Twenty-six snapshots of the geometries generated at the simulation time between 0.50 and 1.00 ps were sampled at each temperature. Time interval of the sampling point was 0.02 ps. The hfcc of each sampled structure was calculated at the B3LYP/6-311G(d,p) level of theory. The hfccs calculated for each structure were then averaged for each temperature to obtain the hfcc at each temperature.

Temperature dependence of hfccs of the metal supported system was investigated by means of the direct molecular orbital–molecular dynamics (MO–MD) method at the PM3 level. Details of direct *ab-initio* MD and direct MO–MD methods are described elsewhere [17,18].

## 3. Results and discussion

### 3.1. Methyl radical interacting with the surface silanol group ( $\equiv\text{Si-OH}$ )

First, the geometry optimizations were carried out for the methyl radical on model I. The initial geometries of the methyl radical around the silica gel were randomly generated and then the geometries were fully optimized. Twenty geometrical configurations around the silica gel were generated as initial geometries. After the geometry optimizations, two structures were obtained at the B3LYP/6-311G(d,p) level as shown schematically in Fig. 1.

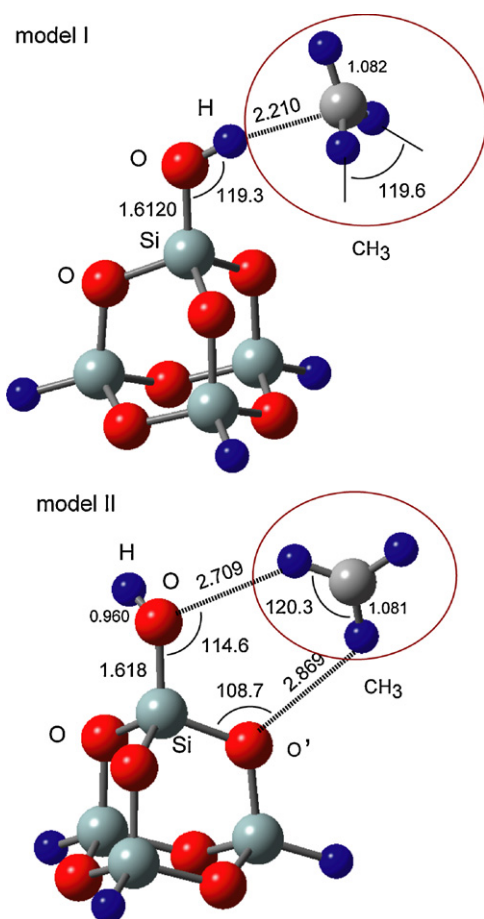


Fig. 2. Optimized structures of models I and II calculated at the B3LYP/6-311G(d,p) level of theory. Bond lengths and angles are in Angstrom and in degrees, respectively.

Models I and II indicate that a methyl radical interacts with a silanol group ( $\equiv\text{Si}-\text{OH}$ ) on the surface of silica gel. In model I, an OH group orients to the carbon atom of  $\bullet\text{CH}_3$ . The optimized structures calculated at the B3LYP/6-311G(d,p) level are illustrated in Fig. 2. The 2p-orbital of  $\bullet\text{CH}_3$  orients to the proton of Si-OH, where 2p-orbital means a spin orbital of  $\bullet\text{CH}_3$  with an unpaired electron. The distance of  $\bullet\text{CH}_3$  from the Si-OH group is estimated at 2.210 Å as a C-HO distance. The methyl radical in model I has a non-planar structure and the averaged H-C-H bond angle of 119.6°, which is slightly smaller than that of the free methyl radical (120.0°).

In model II, two hydrogen atoms of  $\bullet\text{CH}_3$  interact with the oxygen atoms of the Si-OH and Si-O-Si groups. The distances of  $\bullet\text{CH}_3$  from the oxygen atoms are  $r(\text{O}-\text{H}) = 2.709$  and  $r(\text{O}'-\text{H}) = 2.869$  Å. The averaged H-C-H bond angle of the methyl radical is close to 120.0°, indicating that the methyl radical in model II has a planar structure.

The hyperfine coupling constants (hfccs) of the methyl radicals in models I and II were calculated with the optimized geometries. The hfcc of free  $\bullet\text{CH}_3$ , also, was calculated for comparison. The hfcc of the free methyl radical was estimated at  $-23.03$  G at the B3LYP/6-311G(d,p) level. The magnitude of hfcc (denoted by  $a_{\text{H}}$ ) was estimated at  $a_{\text{H}} = 23.03$  G, which is in good agreement with the experimental value ( $a_{\text{H}} = 23.04$  G [4]). This agreement indicates that the level of theory used in the present study, i.e., B3LYP/6-311G(d,p), gives a reasonable hyperfine coupling constant of the methyl radical.

The electronic state of methyl radicals was significantly affected by the interaction with the silica gel. The average of hfccs of  $\bullet\text{CH}_3$  in model I was found to be 20.98 G, which is significantly smaller

than that of free  $\bullet\text{CH}_3$  ( $a_{\text{H}} = 23.04$  G). The shift of  $a_{\text{H}}$  from free  $\bullet\text{CH}_3$  is  $-2.08$  G in model I.

In addition to  $a_{\text{H}}$  of  $\bullet\text{CH}_3$ , the calculation shows that the proton of Si-OH group has a large hfcc of  $-4.01$  G. This result suggests strongly that the methyl radical interacting with the Si-OH group has a satellite splitting in its ESR spectrum. The second shift caused by the proton of Si-OH is estimated at 4.01 G. This result suggests that  $\text{CH}_3$  interacting with the Si-OH shows an ESR spectrum with quartet of doublets.

In model II, the average of hfccs was estimated at  $-22.93$  G, which is slightly shifted from that of free  $\bullet\text{CH}_3$  (shift is 0.13 G). It is also expected that the ESR spectrum of model II shows a ratio of 1:3:3:1 (i.e., normal ratio of free  $\bullet\text{CH}_3$ ), but a slightly smaller hyperfine coupling constant.

The hyperfine coupling constant of  $^{13}\text{C}$  was also calculated for free and surface methyl radicals. The calculated  $^{13}\text{C}$ -hfccs are 26.61 G (free) and 26.33 G (on the Si-OH site), indicating that the  $^{13}\text{C}$ -hfcc is slightly shifted by the interaction with the Si-OH group. The corresponding experimental value of  $^{13}\text{C}$ -hfcc of free  $\text{CH}_3$  is 38.34 G, which is significantly larger than the calculated values (26.61 G).

### 3.2. Methyl radical interacting with the surface Si-O-Si group

Next, the bindings of  $\bullet\text{CH}_3$  to the siloxane Si-O-Si group were considered with the similar technique. The optimized structures are given in Fig. 3. Two binding sites were found for the methyl radical on the cluster. One is that a hydrogen atom of  $\bullet\text{CH}_3$  binds directly to an oxygen atom of siloxane (model III). The bond distance between  $\text{CH}_3$  and Si-O-Si group is 2.600 Å as an O-H distance. On the other hand, in model IV, the hydrogen atom binds to three oxygen atoms of siloxane sites. The binding distances in model IV are 2.886–3.384 Å, which are longer than that of model III.

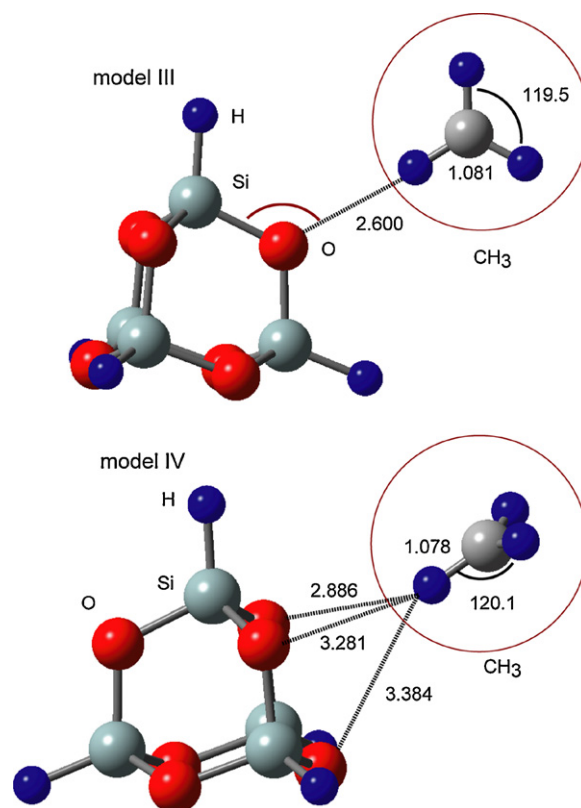
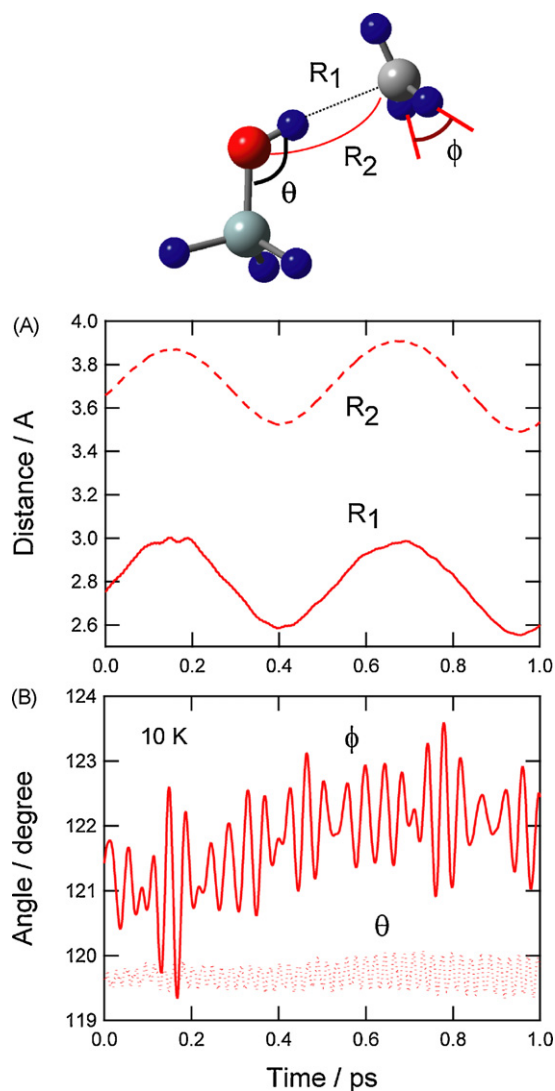


Fig. 3. Optimized structures of models III and IV calculated at the B3LYP/6-311G(d,p) level of theory. Bond lengths and angles are in Angstrom and in degrees, respectively.



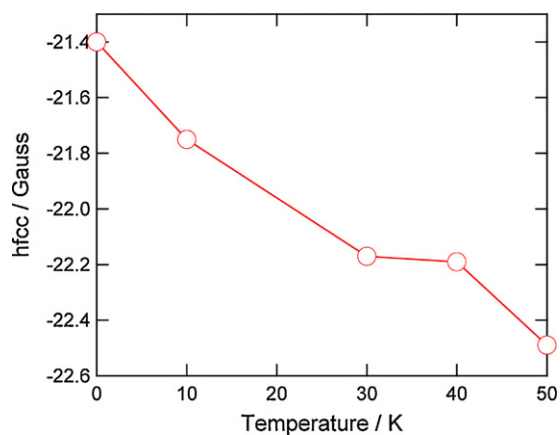
**Fig. 4.** Time profiles of bond distances ( $R_1$  and  $R_2$ ) and angles ( $\theta$  and  $\phi$ ) of model system  $\text{H}_3\text{Si-OH-CH}_3$  obtained by direct ab-initio MD calculation. Mean temperature is 10 K.

The hfccs of methyl radicals in models III and IV are  $-22.97$  and  $-22.94$  G, respectively. The  $a_{\text{HS}}$  in the siloxiane site are larger than that of silanol group, and it is close to that of the free methyl radical.

### 3.3. Temperature dependence of hfcc of $\bullet\text{CH}_3$ interacting with Si-OH

In the actual system, the methyl radical on the surface of silica gel is affected by thermal activation. To elucidate the thermal effect on the hyperfine coupling constants of the methyl radical, direct ab-initio MD calculations were carried out for a model system in the temperature ranges 10–50 K. The direct ab-initio MD calculation needs a large memory and long CPU time. Therefore, a simple model composed of  $\text{H}_3\text{Si-OH}$  and  $\bullet\text{CH}_3$  was used in the dynamics calculation. The dynamics calculations were carried out at the HF/6-311G(d,p) level, and then hfccs were calculated at the B3LYP/6-311G(d,p) level using the geometries sampled from the dynamics calculation.

Fig. 4 shows the model system used in the calculation,  $\text{H}_3\text{Si-OH-}\bullet\text{CH}_3$ , and the results of calculations at 10 K. In this model system, the methyl radical interacts with the silanol group of



**Fig. 5.** Temperature dependence of proton hfccs of methyl radical in the model system  $\text{H}_3\text{Si-OH-CH}_3$  calculated by direct ab-initio MD calculation.

$\text{H}_3\text{SiOH}$ . The binding energy of  $\bullet\text{CH}_3$  to  $\text{H}_3\text{Si-OH}$  is estimated at 2.5 kcal/mol, which is close to that of model I (3.2 kcal/mol).

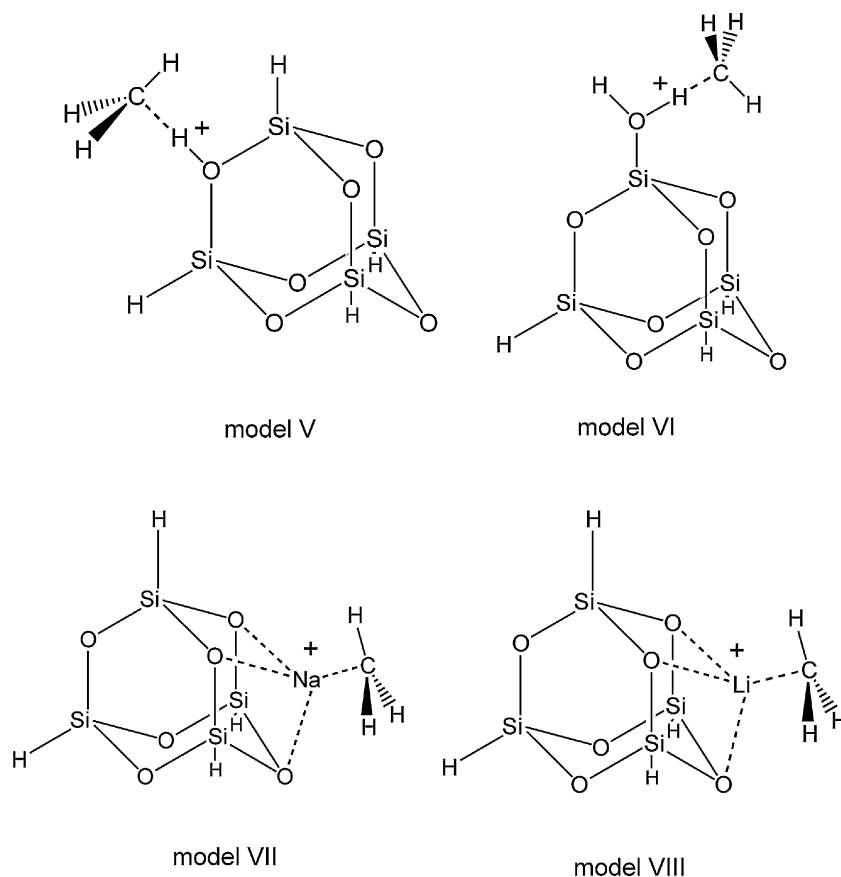
Time profiles of bond distances ( $R_1$  and  $R_2$ ) and angles ( $\phi$  and  $\theta$ ) were plotted as a function of time. The bond distance between  $\bullet\text{CH}_3$  and Si-OH ( $R_1$ ) is varied in the range 2.58–3.0 Å, indicating that the intermolecular stretching mode between  $\bullet\text{CH}_3$  and SiOH ( $R_1$ ) is excited by thermal activation. The bending angle of  $\bullet\text{CH}_3$  ( $\phi$ ) also vibrates strongly at 10 K. On the other hand, the variation of Si-O-H angle ( $\theta$ ) is significantly small.

The temperature dependence of the averaged hfcc is shown in Fig. 5. At zero temperature, hfcc is estimated at  $-21.40$  G, by the static calculation at the B3LYP/6-311G(d,p)//HF/6-311G(d,p) level. The dynamics calculations showed that the hfccs at 10, 30, 40 and 50 K are  $-21.75$ ,  $-22.17$ ,  $-22.19$ , and  $-22.49$  G, respectively. The hfcc of  $\bullet\text{CH}_3$  interacting with a Si-OH group decreases with increasing temperature. This indicates that  $a_{\text{H}}$  is gradually close to that of free  $\text{CH}_3$  as temperature is increased. The result shows that the interaction between the methyl radical and the silanol group will be weaker with increasing temperature due to the enhancement of the large amplitude stretching mode between  $\bullet\text{CH}_3$  and Si-OH by thermal activation. The structure of the methyl radical becomes closer to that of the free methyl radical as temperature rises.

### 3.4. Effects of proton on the binding structure of $\bullet\text{CH}_3$

In order to elucidate the effects of proton on the hfcc of  $\bullet\text{CH}_3$ , the DFT calculation was carried out for two model systems. Structural modes are illustrated in Fig. 6 as models V and VI. In model V, a proton is bound to an oxygen atom of Si-O-Si, and  $\bullet\text{CH}_3$  interacts with the proton. The  $\text{CH}_3$  radical interacts with the protonated Si-OH group of the surface of silica gel in model VI.

In model V, the 2p-orbital of  $\bullet\text{CH}_3$  is oriented to the proton of the surface. The bonding distance of  $\text{CH}_3$  is 1.924 Å as a C-H<sup>+</sup> distance and a O-H distance is 1.003 Å. The hfccs of  $\text{CH}_3$  and proton are 15.37 and 0.04 G, respectively. In model VI, the bond distances of O-H<sup>+</sup> and H<sup>+</sup>- $\text{CH}_3$  were estimated at 1.031 and 1.784 Å, respectively. The binding energies of  $\bullet\text{CH}_3$  models V and VI are 9.2 and 12.6 kcal/mol, respectively. The hfccs of  $\bullet\text{CH}_3$  and proton H<sup>+</sup> were  $-13.51$  and 11.16 G, respectively. The  $a_{\text{H}}$  of the methyl radical calculated was significantly smaller than that of the free methyl radical. However, the experiments showed that  $a_{\text{HS}}$  of methyl radical are in the range of 17.0–23.0 G. Therefore, it can be concluded that a proton does not contribute to the hfcc of  $\bullet\text{CH}_3$  on silica gel.



**Fig. 6.** Schematic illustrations of cluster models of protonated and alkali metal supported silica gels and binding structures of methyl radical to the cluster models. Models V and VI indicate a protonated surface model, while models VII and VIII indicate alkali metal supported model.

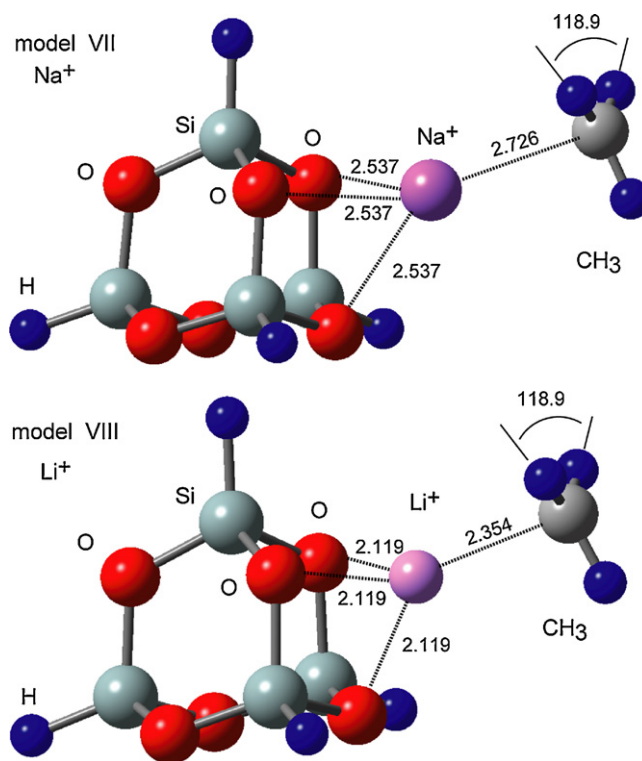
### 3.5. Methyl radical interacting with alkali metal supported silica gels

From ESR experiment, Danilczuk et al. [12] indicated that methyl radicals on alkali metal supported Na-A zeolite interact with alkali metal ions. On the basis of their suggestions, the structural models of alkali metal supported silica gel were constructed as shown in Fig. 6 (models VII and VIII). The methyl radical directly interacts with  $\text{Na}^+$  and  $\text{Li}^+$  in the present models.

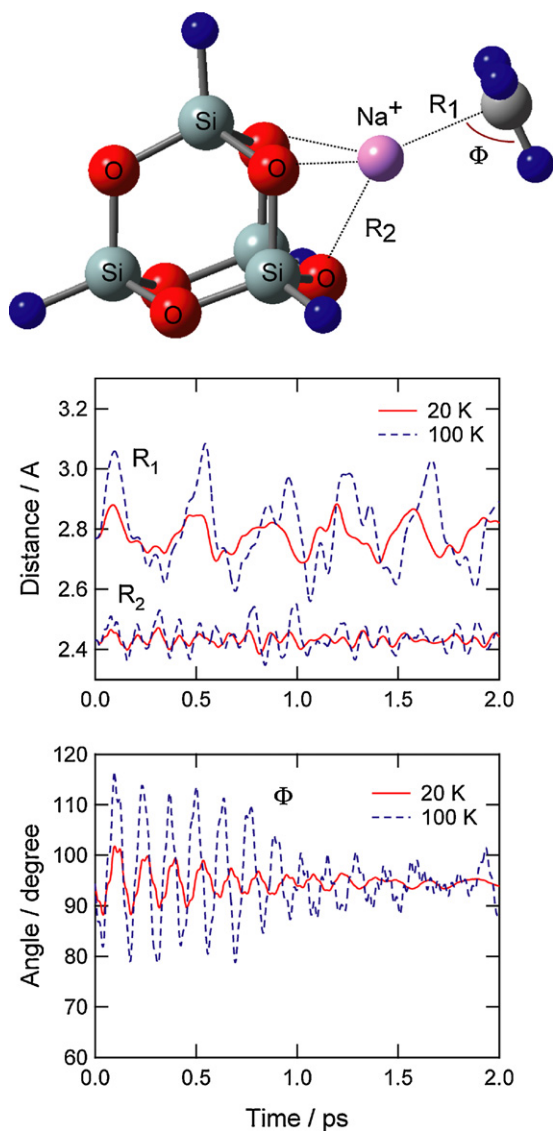
The optimized geometry of model VII is given in Fig. 7. In the optimized structure, the  $\text{Na}^+$  ion binds three oxygen atoms of silica gel lattice (Si–O–Si) with a Na–O bond distance of 2.537 Å. The binding distance of  $\bullet\text{CH}_3$  is estimated at 2.726 Å. The  $a_{\text{H}}$  of  $\bullet\text{CH}_3$  was estimated at 16.08 G which is significantly smaller than that of free  $\text{CH}_3$  (23.04 G). In the case of  $\text{Li}^+$ , the distance of  $\bullet\text{CH}_3$  from  $\text{Li}^+$  is estimated at 2.354 Å, which is shorter than that of  $\text{Na}^+\text{--}\bullet\text{CH}_3$ . The  $a_{\text{H}}$  is  $-15.38$  G, which is also smaller than that of free  $\bullet\text{CH}_3$ .

To elucidate the temperature effect on the hyperfine coupling constant, the dynamics calculations were carried out at the PM3 level, and then hfccs were calculated at the B3LYP/6-311G(d,p) level. The simulation temperatures were 20, 50, 75, and 100 K. The results of 20 and 100 K are given in Fig. 8 (upper). By thermal activation, the bending mode of  $\bullet\text{CH}_3$  is activated. In addition, the intermolecular stretching mode of  $\text{Na}^+\text{--}\bullet\text{CH}_3$  is also excited. Amplitudes of  $\bullet\text{CH}_3$  bending and intermolecular stretching modes are found to be  $15.0^\circ$  and 0.4 Å, respectively.

The average of hfccs obtained by the dynamics calculation is given in Table 1. The hfccs of  $\bullet\text{CH}_3$  at 0, 20 and 100 K are estimated at +17.52,  $-17.58$  and  $-17.55$  G, respectively. This result indicates that thermal activation of  $\bullet\text{CH}_3$  on  $\text{Na}^+$  cluster slightly increases hfcc of  $\bullet\text{CH}_3$ .



**Fig. 7.** Optimized structures of models VII and VIII calculated at the B3LYP/6-311G(d,p) level of theory. Bond lengths and angles are in Angstrom and in degrees, respectively.



**Fig. 8.** Time profiles of bond distances ( $R_1$  and  $R_2$ ) and angles ( $\theta$  and  $\phi$ ) of model VII obtained by direct MO–MD calculation. Mean temperatures are 20 and 100 K.

However, it should be noted that the increase of hfcc of  $\bullet\text{CH}_3$  in  $\text{Na}^+$  is smaller than that in the Si–OH group. This is due to the fact that binding energy of  $\bullet\text{CH}_3$  to  $\text{Na}^+$  is larger than that of Si–OH– $\text{CH}_3$ . Therefore, deformation of  $\bullet\text{CH}_3$  in the  $\text{Na}^+$  cluster caused by thermal activation is smaller than that of the Si–OH group. Hence, the thermal activation of the bending mode is small in the  $\text{Na}^+$  cluster.

**Table 1**

Temperature dependence of hyperfine coupling constants of proton of  $\text{CH}_3$  interacting with  $\text{Na}^+$  supported silica gel. The values are calculated at the B3LYP/6-311G(d,p) level.

$T$ (K)	(hfcc) (G)
0	–17.52
20	–17.58
100	–17.55
300	–17.84

**Table 2**

Isotropic proton hyperfine coupling constants (hfcc in gauss) of methyl radical ( $\text{CH}_3$ ) binding to several sites of silica gel calculated at B3LYP/6-311G(d,p) level. Their binding energies (in kcal/mol) are also listed. Binding energies of methyl radical to several clusters were calculated at the B3LYP/6-311G(d,p) level.

System	hfcc (G)	$^{13}\text{C}$ -hfcc (G)	Binding site	Binding energy
Model I	–20.98	26.33	Si–OH	3.2
Model II	–22.93	25.56	Si–OH	0.6
Model III	–22.97	24.68	Si–O–Si	0.7
Model IV	–22.94	24.94	Si–O–Si	0.9
Model V	–15.37	24.79	O– $\text{H}^+$ proton	9.2
Model VI	–13.51	21.61	O– $\text{H}^+$ proton	12.6
Model VII	–16.08	24.05	$\text{Na}^+$	8.8
Model VIII	–15.38	24.68	$\text{Li}^+$	10.7
$\text{SiH}_3\text{OH}-\text{CH}_3$	–21.40	26.54		2.5
Free $\text{CH}_3$	–23.03	26.61		
Experimental				
$\text{CH}_3/\text{SiO}_2$	22.7		Ogata 1995	
$\text{CH}_3/\text{SiO}_2$	20.7		[6]	
$\text{CH}_3/\text{SiO}_2$	22.2 <sup>a</sup>		[19]	
$\text{CH}_3/\text{Vycor}$	20.2		[5]	
$\text{CH}_3/\text{zeolite (4A)}$	22.3		[7]	
$\text{CH}_3/\text{Na}^+/\text{zeolite (Na-A)}$	22.9		[12]	
$\text{CH}_3/\text{Na}^+/\text{SiO}_2$	19.3		Ogata 1995	

<sup>a</sup> Anisotropic hyperfine coupling constants are  $|A_{\perp}| = -22.6 \pm 0.2$  and  $|A_{\parallel}| = -21.9 \pm 0.2$ .

## 4. Discussion

### 4.1. Summary

In the present study, the hyperfine coupling constants of methyl radicals interacting with the surface silanol ( $\equiv\text{Si}-\text{OH}$ ) group and Si–O–Si site have been investigated by means of the hybrid DFT method using model systems. The calculated hfccs of  $\text{CH}_3$  on several binding sites are summarized in Table 2. The results derived from the present study can be summarized as follows:

- (1) The methyl radical interacting with the surface Si–OH group shows a significantly smaller hyperfine coupling constant than that of free  $\bullet\text{CH}_3$ . In addition, it is predicted that the proton of Si–OH causes a satellite splitting of  $\bullet\text{CH}_3$ . The  $a_{\text{H}}$  of main peak is estimated at 21.0 G, and that of satellite splitting is 4.0 G. This result suggests that the methyl radical interacting with the Si–OH group shows quartet of doublet lines ( $4 \times 2$ ) in the ESR spectrum.
- (2) The methyl radical interacting with the Si–O–Si oxygen sites of silica gel shows a slightly smaller hyperfine coupling constant than that of free  $\bullet\text{CH}_3$ . The ESR spectrum of the  $\bullet\text{CH}_3$  in the Si–O–Si site shows no-satellite bond and shape of the spectrum is close to that of free  $\bullet\text{CH}_3$ , but the hfcc is slightly smaller than that of free  $\bullet\text{CH}_3$  (4 lines with a typical ratio 1:3:3:1).
- (3) Temperature dependence of the hfcc of the methyl radical interacting with the Si–OH group has been newly predicted in the temperature range of 10–50 K. The magnitude of the hfcc,  $a_{\text{H}}$ , increases significantly with increasing temperature and gradually reaches  $a_{\text{H}}$  of the free methyl radical.

### 4.2. Comparison with previous works

Kubota et al. [6] reported that the hfcc of methyl radicals on the silica gel surface was significantly smaller than that of the free methyl radical (23.04 G): i.e., hfccs are 20.7 and 21.2 G (on silica gel). They also reported that the methyl radical shows satellite lines in the ESR spectrum (11.5 G) when the silica gel was preheated at low temperature below 300 K. They speculated that the methyl

radical adsorbed on the silica gel preheated at low temperature would interact with the proton of the surface silanol group. Garbutt and Gesser [5] have also proposed a similar interpretation. The present calculation suggests that the methyl radical interacting with a silanol Si–OH group shows a satellite line in the ESR spectrum. In addition, it is suggested that the methyl radical interacting with Si–O–Si site shows a slightly smaller hfcc than free  $\bullet\text{CH}_3$ . These results are in good agreement with previous experimental results.

Danilczuk et al. [12] observed a methyl radical in alkali metal supported Na–A zeolite using ESR spectroscopy and indicated that methyl radicals interact with alkali metal ions. The present calculations indicated that the binding energies of  $\bullet\text{CH}_3$  to  $\text{Na}^+$  and  $\text{Li}^+$  supported silica gels are 8.8 and 10.7 kcal/mol, respectively. These binding energies are significantly larger than those of the other structures (0.6–3.2 kcal/mol). Therefore, the methyl radical binds preferentially to the alkali metal site. This result is in reasonable agreement with Danilczuk's experimental result.

Shiga and Lund [19] measured hfcc of the methyl radical on silica gel and analyzed the asymmetric ESR spectrum. The spectrum has an apparent hyperfine splitting of 22.2 G, which is smaller than free  $\bullet\text{CH}_3$ . By analyzing the parameters, it was found that the methyl radical has  $A_{\perp} = -22.6$  G and  $A_{\parallel} = -21.9$  G at 77 K. This indicates that the methyl radical on the silica gel surface shows anisotropic hfccs. In the present study, the isotropic hfccs were only discussed. The analysis of anisotropic hfccs may be required to elucidate the detailed electronic states of methyl radical. The present dynamics calculations suggested that the rotation of methyl radical occurs easily along the  $C_3$  axis, but the other rotations are strongly restricted. This effect causes the anisotropy of hfcc of methyl radical on the silica gel surface.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.06.022.

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