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DENSITY FUNCTIONAL THEORY (DFT) AND QUASI HARMONIC APPROXIMATION (QHA) ON ISOTOPE EFFECT OF METHANE ABSORBED ON AG(111) SURFACE

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ABSTRACT

We examined the isotope effect of methane (CH_4) on Ag(111) using the van der Waals density functional and quasi-harmonic approximation. This study combined two methods to investigate the nuclear quantum effect in methane adsorption on an Ag(111) surface. Our findings revealed that the adsorption potential energies of CD_4 on fcc Ag(111) surfaces are shallower than those of CH_4, while the equilibrium distances from the surface are greater. A similar finding was also observed in our previous study, however, the adsorption on Ag(111) surface gives smaller energies. The isotope effect in this is attributed to the softening of the C-H bond pointing towards the surface, which lowers the vibrational frequency and results in a large zero-point energy difference between CH_4 and CD_4.

Keywords: Ag(111); methane; isotope; vibrational frequency

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INTRODUCTION

Researchers have extensively studied methane as it relates to the production of syngas and methanol synthesis. The catalytic oxidation of methane to syngas has been suggested as a promising method, where the activation of C-H bond is one of the rate-limiting steps [1] . Therefore, understanding the C-H surface interaction and its activation is an essential step in hydrogen production.

Methane activation has been investigated theoretically and experimentally on various metal catalysts[2], [3] . Coinage metals, such as copper (Cu), gold (Au), and silver (Ag), are known to be far less active in the oxidative coupling of methane (OCM) due to the weak interaction of CH_x with them[4], [5] . A theoretical study is necessary to investigate and evaluate the CH_x interaction with metal surfaces. Our previous theoretical studies have reported the methane adsorption on the several metal surfaces[6–10], however, Ag surface has not yet been studied comprehensively.

The Hydrogen-Deuterium substitution (isotope effect) is used to study the CHx bond interaction with the metal surface [2], [11–16] . The isotope effect is used to study the chemical and reaction mechanism, as substitution between hydrogen and deuterium alters some molecular properties. Meanwhile, the potential energy surface is not affected as long as the Born-Oppenheimer approximation is valid, which is expected for the ground state of electronic calculations. Furthermore, the vibrational frequencies and moment of inertia are affected by the geometry of the molecules. The magnitude of potential quantum effects is influenced by changes in mass resulting from isotopic substitution. Thus, these substitutions will provide much information about the surface molecule interaction. Theoretically, the combination of density functional theory (DFT) and quasi-harmonic approximation (QHA) have been successfully used in the isotope effect investigation on several metal surfaces. Recently, Putra et al. [3] clarified the quantum nature of CH bonds over several metal surfaces [2], [3]. Meanwhile, the nature of methane adsorption and its isotope effect over CH bond on coinage materials, especially Ag, is less studied.

In this work, we study the adsorption of methane and its isotope effect on the Ag(111) surfaces by using the combination of DFT and QHA. We also considered the van der Waals (vdW) inclusive exchange-correlation functions [17], [18] , which have been enabled to accurately describe the weakly adsorbed system, such as methane. Therefore, we expect similar isotope effect of CH on the Ag(111) surface.

METHOD

In our research, we used the STATE [19], [20] code to carry out electronic calculations with plane-wave and ultrasoft pseudopotentials [21] based on Density Functional Theory (DFT). Wave functions and augmentation charges were expanded using kinetic energy cutoffs of 36 and 400 Ry, respectively. A variant of the van der Waals functional (vdW-DF) [22] was employed namely, rev-vdW-DF2 [23], [24] exchange-correlation functional. Previous research has shown that the rev-vdW-DF2 functional has been demonstrated to accurately describe methane adsorption in metal-organic interaction [25]. We obtained the equilibrium lattice parameters for Ag is 4.0392 Å, and the C-H bond length of 1.0962 Å for the gas-phase CH_4. The Ag(111) surfaces of fcc metals were modeled by six-layer slabs with a vacuum of ≈31 Å thick. The slabs were built using lattice parameters that were optimized theoretically. Surface supercells of size (2 × 2) were employed, and the surface Brillouin zone was probed using a k-point grid of 9 × 9 × 1. The geometries were adjusted until the forces on the atoms were reduced to less than the threshold by $5.14 \times 10{-}4$ eV/ Å (10^{-5} Hartree/Bohr).

In this study, the adsorption energy (E_{ads}) was calculated to represent the energy change when a molecule or atom is adsorbed onto a surface. Therefore, the E_{ads} is defined by

$$E_{ads} = \{E_{tot}[(CH_4)_n/M\,] - E_{tot}\,[M\,] - E_{tot}\,(CH_4)\}\ , \qquad (1)$$

where $E_{tot}[(CH_4)_n/M]$, $E_{tot}[M]$, and E_{tot} (CH_4) are the total calculated energies of the adsorption system, clean metal surface, and the gas phase CH_4 molecule, respectively. Based on this definition, a negative value means that the adsorption process releases heat and is exothermic. This indicates that the adsorbed state is more stable than when the molecules are isolated.

This study examined the nuclear quantum effect (NQE) in methane adsorption on surfaces using the quasi-harmonic approximation (QHA). In this method, vibrational frequencies are computed using the harmonic approximation, and zero-point energy (ZPE) is added to the total energy calculated with the classical treatment of nuclei. The isotope effect is accounted for solely through the mass difference between hydrogen and deuterium. The QHA was effectively used to elucidate the isotope effect of methane and hydrocarbons on metal surfaces [2],[3],[26]. The finite difference method was used to compute the harmonic vibrational frequencies. During the vibrational calculation, the movements of atoms in both the adsorbed methane and the slab's first layer were considered. Only the vibrational frequencies of the adsorbed molecule, including its hindered translational and rotational modes, were factored into the zero-point energy (ZPE) calculations. Therefore, the inclusion of zero-point energy (ZPE) in calculations generally results in less negative adsorption energy compared to calculations without ZPE. It's important to note that our analysis only took into account the vibrational frequencies at the Γ-point.

RESULTS AND DISCUSSION

We constructed two types of adsorption configurations, namely the 1H and 3H configurations as seen in Figure 1. These configurations are similar to those in the previous study by Putra et al. [3].

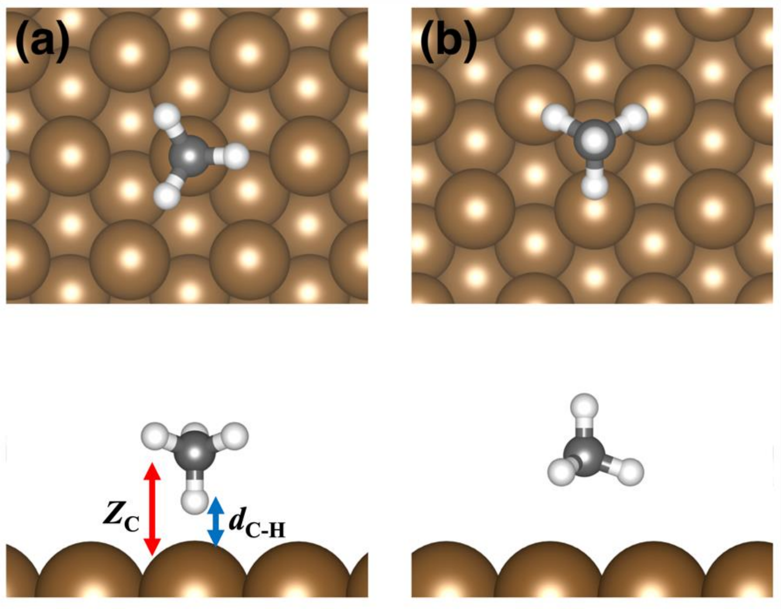

Figure 1. The adsorption geometries of CH4 in the (a) 1H- and (b) 3H-configurations on the Ag(111) surface. The brown, grey, white sphere represent the silver, carbon, and hydrogen atoms, respectively. Red and blue solid line represent distance, respectively.

We investigated the adsorption energy (E_{ads}) of methane as a function of the height of the C atom (Z_C), as seen in Figure 2. The calculations were performed by fixing the z-coordinate of C atom and relaxing all the remaining degrees of freedom. At each Z_C, we performed harmonic vibrational frequency calculations to take into account the ZPE correction. Then, the equilibrium Z_C and E_{ads} were obtained by using the cubic spline interpolation. In this study, we found that the calculated Z_C and E_{ads} by fixing the z-coordinate and full geometry optimization are the same. Table I shows a summary of E_{ads} and Z_C for 1H- and 3H-configurations of CH_4 on the surface. It is found that the calculated

E_{ads} without ZPE correction 3H-configuration is 0.016 eV more stable than the 1H-configuration. By including the ZPE correction, the calculated E_{ads} of 1H and 3H-configuration at equilibrium Z_C are -0.064 eV and -0.074 eV, respectively. Meanwhile, Ohkawa et al. [27] and Au, et al. [28] reported that the calculated E_{ads} of CH_4/Ag(111) is 0.004 eV and -0.10 eV, respectively. Those calculated E_{ads} were performed by using Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, resulting in repulsive E_{ads}. Therefore, by including the vdW functional shows improvement of the calculated E_{ads} to describe the weakly interact system in more details. Furthermore, previous calculation indicated that the CH_4/Ag(111) is slightly more reactive than Cu(111) and Ir(111), which is originate from the different reactivity of the metal surfaces [3].

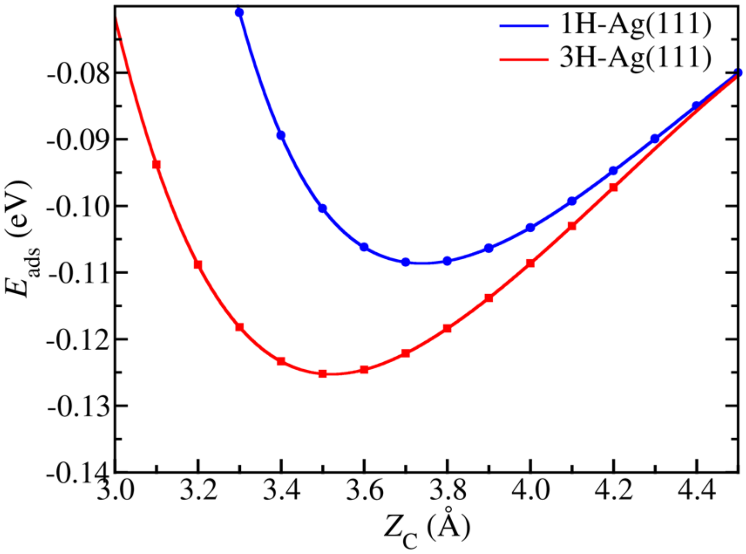

Figure 2. The calculated potential energy surface (PES) of CH4 on the Ag(111) surface.

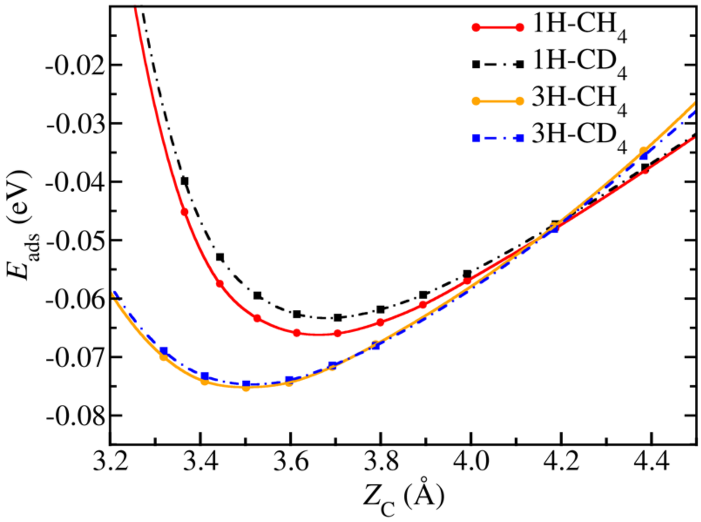

Figure 3. The calculated potential energy surface (PES) of the (a) 1H- and (b) 3H-configurations of CH4 and CD4 on Ag(111) surface.

The calculated E_{ads} of CH_4 and CD_4 are shown in Fig. 3 and Table I. On the surface, the calculated E_{ads} for CH_4 is greater than that for CD_4, while the equilibrium Z_C for CH_4 is smaller than that for CD_4." The differences E_{ads} and Z_C of adsorbed molecules are 5-10 meV and 0.03-0.07 A, respectively. These is the indication of "inverse" kinetic isotope effect as reported by the previous study, where the desorption energy of deuterated is smaller than CH_4 on the surface [2],[3], [14], [26]. Furthermore, we also performed vibrational frequencies of gas phase and adsorbed methane on the Ag(111) surface. The calculated gas phase CH_4 and CD_4 are shown in the supplementary materials. During the adsorption process, the calculated vibrational frequencies of degenerate deformation modes are slightly perturbed, and stretching modes (*vc*H) are splitting into A_1 and E modes. Those changes are due to the symmetry lowering of the molecule from Td to C3v, similar to the previous result [10].

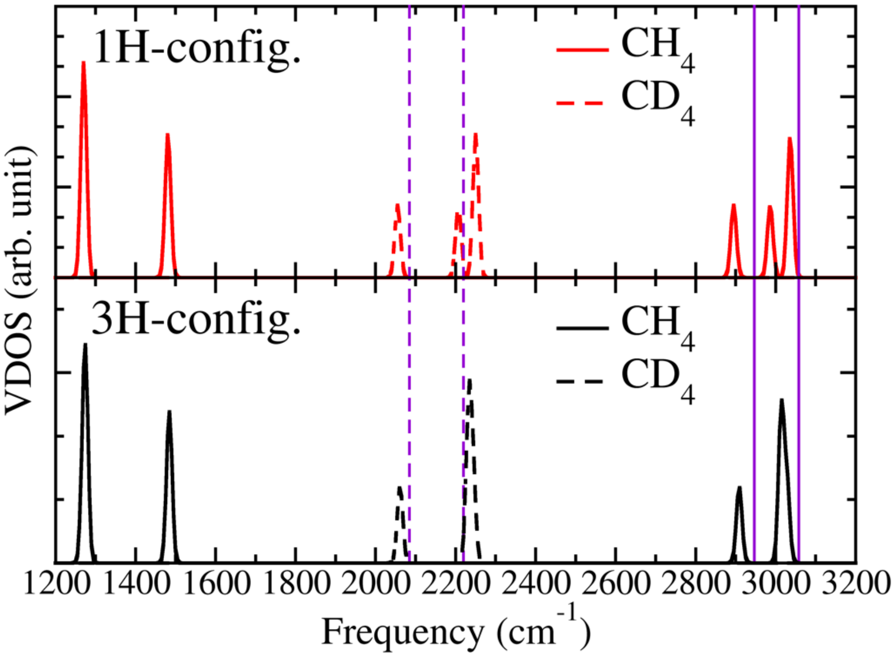

Figure 4. The calculated vibrational density of states (VDOS) of CH_4 (solid line) and CD_4 (dashed line) on the Ag(111) surface in 1H- and 3H-configurations. The solid and dashed lines represent a gas phase of CH_4 and CD_4 gas phase

Figure 4 shows the calculated vibrational density of states (VDOSs) of CH_4 and CD_4 on the surface. It is found that the adsorbed in 1H-configuration gives significantly lower peaks with respect to the gas phase molecule. While the CD4 gives slightly lower vibrational frequencies with respect to the gas phase. Similar lower vibrational frequencies of adsorbed in 3H-configuration which is confirmed by previous calculation[10]. The lowering vibrational frequencies of adsorbed from the gas phase resulting smaller ZPE correction, leading to the lower adsorption energy of CH_4, i.e., the inverse isotope effect. It is also confirmed that the substitution of the atoms alters the geometry of the molecule, yielding the change in the vibrational frequencies. Furthermore, the smaller atomic mass differences gives different bond length yielding smaller vibrational frequencies.

Table 1. Adsorption energies (E_{ads}) and C-surface distances (Z_C) of CH_4 and CD_4 in the 1H configuration on different metal surfaces were calculated, including those without zero-point energy (ZPE) correction, at equilibrium. Note that the calculated energies are in eV.

	CH_4		CD_4		w/o ZPE	
	E_{ads} (eV)	Z_c(Å)	E_{ads} (eV)	Z_c(Å)	E_{ads} (eV)	Z_c(Å)
Ag(111)	−0.0660	3.	−0.0633	3.685	−0.1063	3.
Cu(111)[a]	−0.090	3.625	−0.085	3.685	−0.131	3.717
Rh(111)[a]	−0.133	3.352	−0.125	3.404	−0.163	3.446
Pd(111)[a]	−0.165	3.243	−0.156	3.261	−0.188	3.301
Pt(111)[a]	−0.131	3.441	−0.125	3.466	−0.162	3.524
Ir(111)[a]	−0.110	3.534	−0.104	3.572	−0.145	3.645

Assuming a quantum harmonic oscillator, the findings are unexpected. The vibrational frequencies of the C-H stretching mode are greater than those of the C-D mode, resulting in a larger ZPE correction to the total energy of CH_4 than CD_4. As a result, one might anticipate that the adsorption energy of CH_4 would be lower than that of CD_4.

CONCLUSION

We using the vdW-DF and QHA to study the methane adsorbed CH_4 molecule on the Ag(111) surfaces. It is found that the E_{ads} of CH_4 than CD_4 consistent with our previous calculated isotope effect. We also observed the vibrational frequency shift of the C-H bond of methane due to the C-H bond elongation upon adsorption. In this study we also confirmed the origin of the isotope effect of methane on Ag(111) surface. We expect to see a similar effect of isotopes in a range of hydrocarbons that are adsorbed on metal surfaces.

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