



Coadsorption of methyl radicals and oxygen on Rh(1 1 1)

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Received 30 May 2003; accepted for publication 13 November 2003

Abstract

The chemisorption of CH₃ on Rh(1 1 1) is studied to understand the origin of the weakened symmetric stretch mode. A few different explanations for this weakened mode have been suggested in previous studies. These include C–H bond depletion and donation into C–H anti-bond orbitals either in an upright or tilted geometry. We investigate these possibilities by performing first-principles density functional calculations. Our results show strong adsorption at all high-symmetry sites with methyl in two possible orientations. A thorough analysis of the adsorption geometry shows that C_{3v} symmetry is preferred over a tilted species, ruling out tilting as a mechanism for C–H mode softening. Evidence of a multi-center bond between methyl and the surface rhodium atoms (similar to the kind shown recently by Michaelides and Hu for methyl on Ni(1 1 1)) is presented, showing that C–H bond depletion is the cause of mode-softening for methyl on Rh(1 1 1). Experimental results have shown that mode-softening diminishes when an electronegative species is coadsorbed, suggesting that donation into C–H anti-bonding orbitals is the mechanism for mode-softening. We therefore examine the coadsorption of oxygen and methyl on Rh(1 1 1). Our results suggest a new model for the effect of O on CH₃. Analysis of charge density differences shows that the dominant initial effects of O coadsorption are the removal of charge from the C-surface bond and the transfer of charge to the C–H bond. Subsequent increase of the H–Rh distance further reduces mode softening.

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Keywords: Chemisorption; Rhodium; Oxygen; Density functional calculations

1. Introduction

The methyl radical is a fundamentally important species which is an intermediate in many chemical reactions. At low temperatures (100–200 K), it is possible to stabilize methyl radicals on

many different transition metal surfaces, making them available for heterogeneous catalysis. Because of widespread industrial applications, there is great interest in harnessing the reactivity of a surface methyl species. Therefore, understanding the chemisorption properties of methyl on transition metals is a crucial line of research. Furthermore, investigating interactions between methyl and rhodium surfaces is important due to the effectiveness of rhodium as a catalytic surface.

One industrially useful application involving methyl radicals is the partial oxidation of methane.

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Since methane is a stable molecule, a lot of energy is needed to break one of its C–H bonds. Also, hydrocarbon fragments are so reactive that reactions most often proceed to complete combustion. Reacting methyl radicals with oxygen directly via heterogeneous catalysis would make the formation of alcohols and aldehydes much more economical. Therefore, it is essential to study the coadsorption of methyl radicals and oxygen on transition metal surfaces.

One particularly interesting feature of methyl adsorption on transition metal surfaces is the presence of a weakened symmetric C–H stretch mode, sometimes shifted by hundreds of cm^{-1} . This has been shown experimentally on Ni [1], Cu [2–4], and Rh [5] surfaces. Softened C–H modes have also been seen for other hydrocarbons on transition metals [6]. Because of the possible relevance to dehydrogenation, there has been much interest in uncovering the mechanism for a weakened C–H stretch. Despite this interest, various investigations of mode-softening have yielded a range of explanations, some contradicting others.

The industrial importance and the unresolved fundamental issues make the methyl–surface interaction an excellent example of where first-principles calculations can provide insight. To this end, we have performed a series of first-principles calculations to investigate the adsorption geometry and energy of methyl at full and $1/3$ coverage. Both upright and tilted geometries have been proposed for adsorbed methyl. Therefore, we focus on this aspect in detail. We also compute the relaxed geometry of an overlayer of methyl radicals coadsorbed with oxygen to learn more about the effect of an electronegative coadsorbate.

2. Method

All calculations in this study were performed using the density functional theory (DFT) code “BH”. The generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [7] was used to describe all exchange and correlation effects. For all systems, optimized pseudopotentials [8] were used. The rhodium pseudopotential used the

designed non-local approach [9] to decrease transferability errors. All pseudopotentials were generated using the PBE-GGA functional. A 50 Ry energy cut-off was required for all pseudopotentials and was used for all calculations.

Using 60 irreducible Monkhorst–Pack [10] fcc k -points, we obtain excellent agreement for the lattice constant (3.805 Å calculated vs. 3.803 Å experiment [11]) and bulk modulus (2.82 Mbar calculated vs. 2.69 Mbar experiment [12]) for the rhodium pseudopotential. Calculation of the free methyl radical in a $10 \text{ Å} \times 9 \text{ Å} \times 9 \text{ Å}$ cell yields a bond length of 1.086 Å compared to the experimental result of 1.08 Å [13].

Two unit cells, a 1×1 cell and a $\sqrt{3} \times \sqrt{3}$ ($R30^\circ$) cell, were used to study the $\theta = 1$ and the $\theta = 1/3$ coverage overlayers. These are shown in Fig. 1. For the 1×1 cell, Brillouin zone integrations used 24 reducible special k -points [14]. This k -point mesh was also used in the $\sqrt{3} \times \sqrt{3}$ ($R30^\circ$) cell by folding into its smaller Brillouin zone. Tests with denser k -point sets show that this sampling yields binding energies that are converged to about 0.1 eV. A 5-layer slab with 7 vacuum layers and methyl adsorbed on one side of the slab was used. To provide a realistic surface, the positions of the bottom three rhodium layers were held fixed for all calculations. Expanding to a 7-layer slab with methyl adsorbed on both sides changes the binding energy by less than 5 meV per molecule, indicating that a 5-layer slab is sufficiently accurate.

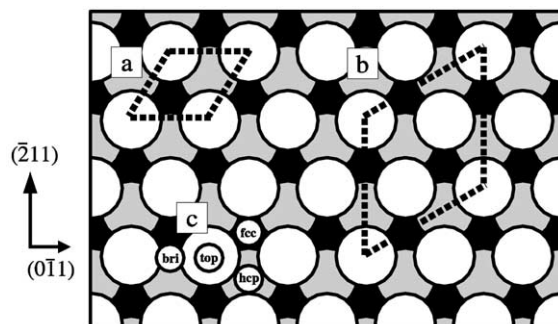


Fig. 1. Illustration of the (a) 1×1 and (b) $\sqrt{3} \times \sqrt{3}$ ($R30^\circ$) unit cells. Also noted in (c) are the binding sites considered in this study.

3. Results and discussion

3.1. $\theta = 1$ Overlayer

In this investigation, we calculated the adsorption of methyl on Rh(111) at full coverage (1 methyl/surface site). We considered all four high-symmetry sites (the fcc and hcp hollow sites, bridge, and top site) available for chemisorption (see Fig. 1). Excluding the bridge site, two high-symmetry orientations of the methyl radical were examined at each site. At the hollow sites these are referred to as eclipsed (C–H bonds aligned with surface Rh atoms) and staggered (C–H bonds between surface Rh atoms). At the top site, the two orientations have C–H bonds aligned with either fcc or hcp hollow sites. For calculations with methyl at the top and hollow sites, C_{3v} symmetry was enforced. No symmetry was enforced for the bridge site calculation. The symmetry of the equilibrium bridge-bonded species was C_s , which makes the C–H bond that lies in the mirror plane distinct from the other two.

Table 1 shows the binding energies and structural parameters for methyl adsorbed at full coverage on Rh(111). For all binding sites and orientations a negative binding energy is obtained (i.e. free methyl + bare Rh(111) is favored over adsorbed methyl at full coverage). This shows that there are significant repulsive interactions between

neighboring methyl radicals and that a full monolayer is much too crowded. Furthermore, all the C–H bond lengths (except for the bridge “A” hydrogen) are compressed shorter than the gas-phase methyl radicals, and the H–C–H angles are all significantly compressed below the tetrahedral angle. All of these results show that lower methyl coverages need to be investigated to make contact with experiment.

3.2. $\theta = 1/3$ Overlayer

Table 2 shows the results of methyl chemisorption at 1/3 coverage on Rh(111). We find that the lowest energy configuration is methyl adsorbed at the fcc hollow site in the eclipsed orientation with the eclipsed hcp hollow site slightly less stable. Compared to the eclipsed configuration, hollow-site bonding in the staggered configuration is nearly 0.5 eV less stable. Since the staggered configuration lies on the methyl rotation pathway, the barrier to rotation is at least 0.5 eV, inhibiting rotation about the C–M axis. There are important structural differences between the equilibrium staggered and eclipsed geometries. In the eclipsed configuration the C–H bond length is expanded by 0.02 Å and the C–M distance is about 0.15 Å smaller.

For the top site, we find that the two orientations (C–H directed at either hollow site) yield

Table 1
Chemisorption energies and structural information for methyl adsorbed at various sites on Rh(111) at full coverage

Site	E_b	C–H	C–M	C–Rh	H–Rh	θ_{M-C-H}	θ_{H-C-H}
hcp/ecl	–2.02	1.06	1.69	2.29	2.41	126	89
fcc/ecl	–1.89	1.06	1.68	2.29	2.40	126	89
top/hcp	–1.68	1.05	1.97	1.97	2.70	123	94
top/fcc	–1.67	1.05	1.96	1.96	2.68	123	93
fcc/stg	–1.59	1.08	1.58	2.22	2.60	127	88
hcp/stg	–1.69	1.08	1.60	2.22	2.61	126	89
bridge A	–1.43	1.11	1.74	2.09	3.35	102	86
bridge B/C		1.05			2.49	149	100

All energies are in eV, all distances are in Å, and all angles are in degrees. “C–M” refers to the distance between the carbon atom and the average position of the surface rhodium atoms along the [111] direction. “C–Rh” is the distance between the carbon atom and the closest Rh atom, and “H–Rh” is the distance between each hydrogen atom and its closest Rh atom. The terms “ecl” and “stg” refer to the eclipsed (C–H bonds aligned with rhodium atoms) and staggered (C–H bonds directed in between surface rhodium atoms) orientations. “Top/fcc” and “top/hcp” refer to top site adsorption with C–H bonds directed toward fcc hollows or hcp hollows respectively. Two entries are required for the bridge site since there are two distinct hydrogen atoms. The first row (A) describes the one hydrogen lying in the mirror plane, the second row (B/C) is for the remaining two hydrogens which are equivalent due to the mirror.

Table 2

Chemisorption energies and structural information for methyl adsorbed at various sites on Rh(1 1 1) at 1/3 coverage

Site	E_b	C–H	C–M	C–Rh	H–Rh	θ_{M-C-H}	θ_{H-C-H}
fcc/ecl	2.20	1.13	1.60	2.23	2.09	113	106
hcp/ecl	2.18	1.13	1.58	2.22	2.08	113	106
top/fcc	1.77	1.10	2.19	2.09	2.66	109	110
top/hcp	1.76	1.10	2.19	2.09	2.66	109	110
fcc/stg	1.67	1.11	1.76	2.35	2.57	112	107
hcp/stg	1.64	1.11	1.76	2.34	2.57	112	107

See Table 1 for column heading descriptions.

binding energies that are within 10 meV of each other. This is understandable since binding at the top site yields the largest H–Rh distance, and therefore the weakest dependence on methyl orientation. Both configurations also have a C–H bond length of 1.10 Å, the shortest C–H bond length of all of the binding sites studied. Also, both configurations have a nearly tetrahedral M–C–H angle.

Bridge site adsorption was investigated, but structural relaxations always proceeded with the methyl radical evolving toward hollow site adsorption. The possibility of a saddle point was not investigated.

The 1/3 monolayer coverage is significantly different from the fully covered surface. Most importantly, this coverage surface has positive binding energies for all sites considered. Furthermore, the H–C–H angles are much closer to tetrahedral for 1/3 coverage, whereas the fully covered surface displays a significant compression of this angle. Because of these results, all further investigations will focus on 1/3 coverage.

The binding energy ordering ($E_{\text{hollow/eclipsed}} > E_{\text{top}} > E_{\text{hollow/staggered}}$) we find for 1/3 monolayer coverage is the same as what is found for methyl on Ni(1 1 1) [15] and Cu(1 1 1) [16]. Furthermore, hollow site adsorption was also found to be preferred for methyl on Ru(0 0 1) [17].

We have computed the symmetric mode frequencies for adsorption at the fcc hollow for both methyl orientations. C–H stretching typically falls in the range of 2900–3000 cm^{-1} . Indeed, for the CH_3 adsorbed in the staggered orientation, we calculate the C–H stretch frequency to be about 2870 cm^{-1} . We find that the eclipsed configuration, however, has a C–H stretch frequency of about

2670 cm^{-1} . This result is in good agreement with the high resolution electron energy loss study of Bol and Friend [5] which finds the softened symmetric stretch to occur at 2620 cm^{-1} . These data also agree with a recent gradient-corrected density functional calculation by Michaelides and Hu [18] which showed that elongation of C–H bonds correlates with a softened C–H symmetric stretch mode for methyl on Ni(1 1 1), Cu(1 1 1), and Pt(1 1 1). According to their results and ours, the C–H bond expands significantly only when the hydrogen atoms are within about 2.2 Å of the surface rhodium atoms which can only occur for eclipsed hollow site adsorption.

In another DFT study by Michaelides and Hu [15], multi-centered bonding (electron density shared by the carbon, hydrogen, and a neighboring metal atom) was shown to occur for methyl adsorbed on Ni(1 1 1). Since delocalization of charge from the C–H bond is associated with C–H stretch mode softening, it is important to determine whether it exists for adsorption onto the Rh(1 1 1) surface. We analyzed the electron density for many of the bands in the fcc/ecl system. Two nearly degenerate electronic bands 7.2 eV below the Fermi level display multi-center bonding, similar to the $\text{CH}_3/\text{Ni}(1\ 1\ 1)$ system. A contour plot of one of these bands is presented in Fig. 2.

3.3. Investigation of tilting

The majority of experimental and theoretical investigations of methyl on transition metal surfaces find that methyl adsorbs upright with C_{3v} symmetry. We have made this assumption for all calculations presented so far where appropriate (the bridge site has C_s symmetry). In another

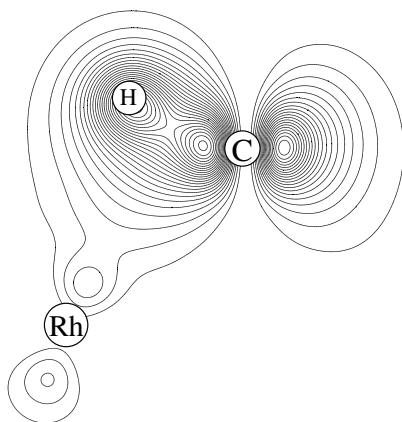


Fig. 2. Band density illustrating multi-center bonding in the adsorbed methyl radical. Contours range from 0.025 to 0.5 $\text{e}/\text{\AA}^3$. The band is 7.2 eV below the Fermi level.

DFT-GGA investigation of methyl on Rh(111), Chen and co-workers [19] find that methyl prefers a tilted fcc geometry with C_s symmetry.

In their paper, tilting was shown to increase the population of a C–H anti-bonding orbital, resulting in a weakened C–H stretch. Tilting was also given as the explanation for mode softening by Yang and Whitten for methyl on Ni(111) [20], although an upright geometry was shown to be energetically favored over the tilted structure.

Because there is disagreement about the symmetry of methyl on Rh(111), we have explicitly investigated the possibility of tilting. We did this in two different ways. First, using the fcc/eclipsed geometry, we removed the symmetry constraints, tilted the methyl geometry toward the top site to form a 90° M–C–H angle and moved the methyl 0.1 Å toward the top site and then repeated the structural relaxation. Even from this distorted geometry, the methyl radical relaxed back to the upright structure, centered at the hollow site. Second, to make contact with the previous theoretical work we computed the energy as a function of M–C–H angle with all H–C–H angles held fixed, as shown in Fig. 3. Contrary to the previous work, we find that any tilt angle is less favorable than the upright geometry. The calculations of Chen and co-workers were performed using 10 and 24 atom clusters to model the Rh(111) surface. The binding energies for methyl in the eclipsed and

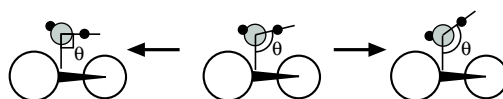
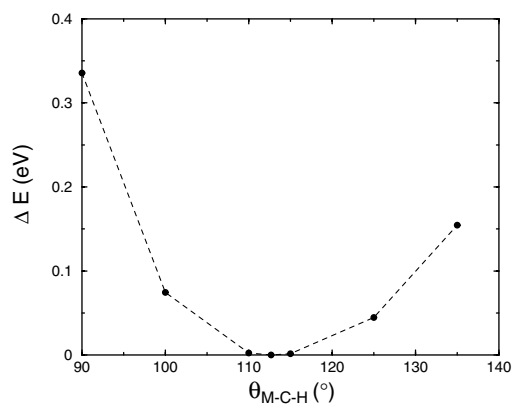


Fig. 3. Plot of energy as a function of M–C–H angle. Energies (in eV) and the angles are in degrees. All energies are relative to the upright geometry ($\theta_{\text{M-C-H}} = 113^\circ$). All H–C–H angles are fixed.

staggered geometries in this cluster study were about 1 eV lower than our results. Vibrational frequencies were deemed to not be reliable and were not reported. Because of these reasons, we feel that this study may have suffered from cluster size effects.

3.4. Coadsorption of oxygen and methyl radicals

We investigate methyl coadsorption with oxygen atoms by studying a prototypical geometry which is locally stable and similar to experimentally-studied coverages. In each $\sqrt{3} \times \sqrt{3}$ ($R30^\circ$) unit cell, methyl is placed in one fcc hollow site and an oxygen atom in another fcc hollow. The resulting overlayer contains 1/3 monolayer coverage of both oxygen and methyl. Total energy calculations of 1/3 monolayers of O on Rh and the free methyl show that binding energy of CH_3 in this mixed 2/3 monolayer coverage is 1.23 eV, demonstrating that this coverage is stable with respect to methyl desorption. Also, similarly dense mixed coverages have been prepared experimentally (up to 0.5 monolayer O coadsorbed with up to 0.3 monolayer CH_3 [5]).

Table 3 compares the relaxed geometry of the fcc/ecl with and without coadsorbed oxygen, and Fig. 4 illustrates these overlayers. The C–H bond shortens by 0.03 Å, and the radical moves away from the surface by over 0.2 Å. Furthermore, the symmetric stretch frequency increases to about 2880 cm^{-1} , which is similar to the staggered hollow site value mentioned before and close to the usual range for C–H stretching. Contrary to methyl adsorption without oxygen, neither the eclipsed nor the staggered geometry is a minimum energy structure. The presence of 1/3 monolayer of oxygen results in an equilibrium methyl overlayer which lies in between these two structures.

These results are consistent with experimental energy loss results for oxygen and methyl coadsorption on Rh(111) [5]. In this experiment, the authors first adsorbed methyl and witnessed a softened C–H symmetric stretch mode. Upon adsorption of oxygen, the softened mode is no longer seen in the vibrational spectrum. Furthermore, in a detailed analysis of C–H mode softening of cyclohexane on Mo(110) [21], it was shown that coadsorbed oxygen (and to a lesser extent sulfur) significantly increases the softened C–H stretch frequencies. This result supported a charge transfer mechanism for methyl mode-softening (from the metal to C–H anti-bonding orbitals) which is hindered upon coadsorption with an electronegative coadsorbate.

To understand the effect that O has on the interaction of methyl with the rhodium surface we have calculated the electronic charge density difference between methyl and rhodium in the relaxed fcc/ecl geometry with 1/3 monolayers of oxygen added (without further relaxation) and the fully relaxed fcc/ecl system. In Fig. 5 we present the regions of electron density loss and gain in separate contour plots. The plots show that the C–M bond loses a significant amount of charge density,

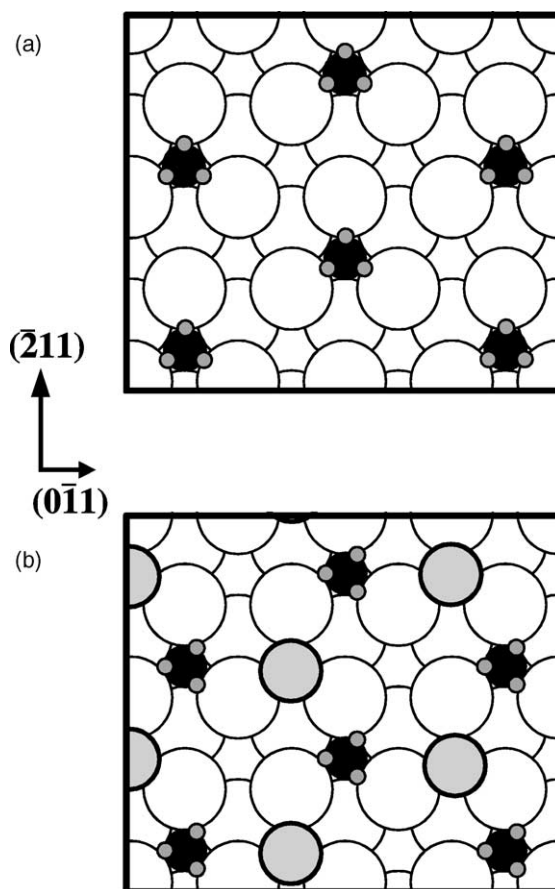


Fig. 4. Comparison of the preferred adsorption geometry of methyl at 1/3 coverage as (a) the sole adsorbant and (b) coadsorbed with 1/3 monolayer of atomic oxygen.

while both the C–H bond and Rh atom gain charge density. Unlike these regions the charge density between the H and Rh (where Rh–C–H multicenter bonding occurs) stays fairly constant. This charge density rearrangement is consistent with the C–M being weakened due to the presence of an electronegative coadsorbate and shows no direct effect on the H–Rh interaction.

Table 3

Comparison of the equilibrium overlayer geometry of fcc/eclipsed methyl with and without coadsorbed oxygen

Overlayer	C–H	C–M	C–Rh	H–Rh	$\theta_{\text{M-C-H}}$	$\theta_{\text{H-C-H}}$
CH ₃	1.13	1.60	2.23	2.09	113	106
O + CH ₃	1.10	1.82	2.40	2.34	111	108

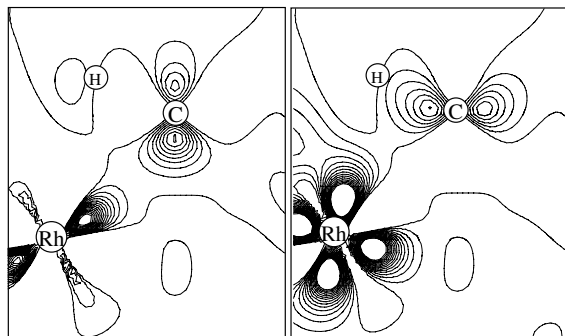


Fig. 5. Charge density difference for O + CH₃(fcc/ecl) adsorbed on Rh(111)—CH₃(fcc/ecl) on Rh(111). The left panel contains contours for where charge density is depleted; the right panel is where charge is gained. Positive (negative) contours range from ± 0.01 to ± 0.15 e/Å³.

When O is adsorbed onto the fcc/ecl system, a large (1.5 eV/Å) force pointing away from the surface occurs on the C atom. This force is much larger than any other force on the H atoms or Rh surface and results in a large relaxation of the methyl more than 0.2 Å away from the metal surface. This motion also causes the H–Rh distance to significantly increase.

The combination of all of our results suggests a new model for how O diminishes the softened C–H stretch in adsorbed CH₃. The O induces significant electronic changes in the initial methyl structure. O adsorption causes charge transfer to the C–H bond, strengthening it. In addition, O adsorption decreases the bonding between C and Rh. The methyl structure then responds to these electronic changes. The weakened C–surface bond causes the methyl to move away from the surface. This move increases the H–Rh distance, weakening multicenter bonding. At the larger equilibrium C–surface separation, the methyl is fairly free to rotate, due to decreased interaction with the metal surface. The equilibrium geometry rotational state suggests that the positions of oxygens may affect the final CH₃ orientation, but this aspect will require further investigation. The fact that the orientation is neither eclipsed nor staggered but intermediate suggests that interactions of CH₃ with its Rh neighbors are much weaker than in the absence of oxygen. The result of these changes is that any multicenter bonding is significantly de-

creased. This is supported by the fact that the C–H stretch frequency of methyl in the 2/3 mixed overlayer is quite similar to the staggered CH₃ C–H stretch frequency without O. The strength of the new model is that it rationalizes the experimental findings and is strongly grounded in chemically reasonable effects.

4. Conclusion

We have computed the relaxed geometries of methyl radicals adsorbed at full and 1/3 monolayer coverage. Our results show that a full monolayer is much too high a coverage to be experimentally relevant. Results for 1/3 monolayer coverage, however, do compare well with other theoretical and experimental work. For this coverage, we find the strongest binding at the fcc hollow sites in an eclipsed geometry, the eclipsed hcp site being only 0.02 eV less stable. A thorough investigation of the symmetry of this overlayer shows that the methyl prefers an upright geometry with full C_{3v} symmetry. Furthermore, we compute the relaxed geometry of 1/3 monolayer of methyl coadsorbed with 1/3 monolayer of oxygen atoms. We show that the oxygen has a dramatic effect on the bonding and structure of the methyl overlayer. The analysis of the charge density difference that occurs when oxygen is adsorbed onto the fcc/ecl system shows depletion of density in the C–M bonding region and C–H bond strengthening but little change in the H–Rh region. The subsequent relaxation of the methyl away from the surface and methyl rotation diminish any remaining multicenter bonding and lead to an increased the symmetric C–H stretch frequency.

Acknowledgements

This work was supported by the Air Force Office of Scientific Research, Air Force Materiel Command, USAF, under Grant No. F49620-00-1-0170, and by NSF MRSEC program, Grant No. DMR00-79909. Computational support was provided by the National Center for Supercomputing Applications and the High-Performance

Computing Modernization Office of the Department of Defense.

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