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Ab Initio Chemisorption Studies of CH_3 on Ni(111)

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Abstract: The adsorption of methyl on the (111) surface of nickel is treated by using a many-electron embedding theory to describe bonding, modeling the lattice as a 28-atom, three-layer cluster. Ab initio valence orbital configuration interaction (multiple parent) calculations carried out on a local surface region permit an accurate description of bonding at the surface. Calculated adsorption energies for CH_3 on the Ni(111) surface are 39 kcal/mol at the 3-fold sites and 36 and 34 kcal/mol at the bridge and the atop atom sites with the equilibrium Ni–C distances of 2.35, 2.34, and 2.03 Å, respectively. Calculated CH_3–(Ni surface) perpendicular stretching frequencies are 369, 296, and 416 cm^{-1} for the 3-fold, bridge, and atop sites. In the equilibrium geometry methyl hydrogens are in a plane parallel to the surface with a nearly tetrahedral structure. A low C–H vibrational frequency is calculated at 2627 cm^{-1} if one of the hydrogens is tilted to give a C–H bond parallel to the surface, and CH_3 is shifted away from the 3-fold center by 0.67 au, which puts one of the hydrogens directly above a Ni atom. This geometry is only 1.6 kcal/mol higher in energy than the calculated equilibrium geometry for which normal C–H vibrational frequencies of around 3000 cm^{-1} are calculated. The reaction of chemisorbed $CH_2(ads) + H(ads) = CH_3(ads)$ on the surface is 13 kcal/mol exothermic. An energy barrier occurs when CH_2 and H are moved from infinite separation to form CH_3. A combination of covalent s and d bonding characterizes the bonding of CH_3 to the nickel surface.

I. Introduction

It has been proposed that the hydrocarbon C_1 fragments are the key intermediates in Fischer–Tropsch synthesis on catalytically active transition-metal surfaces.[1-9] During the past years under vacuum conditions, the C_1 fragments on a variety of metal surfaces, such as Fe, Ru, and Ni, have been observed by electron energy loss spectrometry (EELS), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), etc. In particular, the CH_3 fragments have been identified and characterized by XPS and UPS after adsorption and subsequent decomposition of CH_3Cl on polycrystalline Ni or Co surfaces.[7] CH_3 has been observed in the methanation reaction of CO and H_2 on a Ni(111) single crystal by static secondary ion mass spectrometry (SIMS) and XPS.[8] SIMS data appear to indicate that the CH_3 fragments and CH and CH_2 fragments have similar stabilities on Ni(111). In the dynamical studies of the activated dissociative chemisorption of methane on Ni(111) by molecular beam techniques, CH_3 radicals have also been detected by high-resolution electron energy loss spectrometry (HREELS).[9] An unusually low C–H vibrational frequency of 2680 cm^{-1} has also been obtained from HREELS. The low C–H frequency could be indicative of a formation of a C–H···metal bond.

Theoretical studies of methyl adsorption on metal surfaces have received a great deal of attention in recent years. Among this work, the extended Hückel method was employed in most cases, such as the chemisorption studies of hydrocarbons on Ni(111) by Gavin et al.[10] using cluster model calculations, methyl adsorption on Pt(111) by Minot et al.,[11] the bonding and coupling of CH_3 on metal surfaces of Co, Cr, and Ti by Zheng et al.,[12] and CH_x (x = 0–3) adsorption studies on the (111) fcc metal surface by Baetzold.[13] Using ab initio CI cluster calculations and varying the cluster sizes, Schule et al.[14] have reported CH_3 radical chemisorption on cluster models of the Ni(111) surface. The adsorption energies, Ni–C bond lengths, and vibrational frequencies are given for methyl at the 3-fold and on-top sites. Semiempirical bond-order conservation model calculations for C_1 and C_2 hydrocarbons on Ni(111) have also been reported by Shustorovich and Bell.[15,16] Generalized valence bond ab initio studies have been reported for methyl adsorption on Ni(100) by Upton[17] and for $NiCH_2$ and $NiCH_3$ molecules by Rappe and Goddard.[18]

There remain many unanswered questions concerning the energetics, adsorption sites, geometries, and mechanisms for such hydrocarbon reactions. In the present work, we describe the adsorption of CH_3 on a Ni(111) surface in the context of a many-electron theory that permits the accurate computation of molecule–solid surface interactions at an ab initio configuration interaction level. The adsorbate and local surface region are treated as embedded in the remainder of the lattice electronic distribution which is modeled as a 28-atom, three-layer cluster, extracted from a 62-atom cluster by an orbital localization transformation.

The objectives of the calculations presented in this paper are (a) to determine the adsorption energies, bond distances, geometries, vibrational frequencies and bonding properties of the methyl species on the (111) surface of Ni, (b) to investigate the possibility of a low C–H vibrational frequency of methyl on Ni(111), and (c) to calculate the energetics of the reaction of $CH_2(ads) + H(ads) = CH_3(ads)$ on the surface.

II. Theory and Calculations

The objective of the embedding theory employed in this work is to treat adsorbed species and a surface region of the metal with sufficient accuracy to describe reaction energetics, while at the same time maintaining a proper coupling of the surface region to the bulk. In this approach, one proceeds to define a local region as an N-electron subspace extracted from the remainder of the lattice by a localization transformation.[19-21]

$$\underset{\text{s-band (delocalized)}}{\Psi = A(\varphi_1\varphi_2\varphi_3\ldots\varphi_N)} \xrightarrow{\Psi' = U\Phi} \underset{\text{localized ``s-band'' orbitals}}{\Psi = A(\varphi_1'\varphi_2'\varphi_3'\ldots\varphi_N')}$$

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The adsorbate and local region are then treated at high accuracy as embedded in the Coulomb and exchange field of the remainder of the electronic system. There are various ways to carry out such calculations and the present approach most closely resembles that in refs 22 and 23, where the details of the method are discussed. The use of electron exchange as the basis of a localization transformation has been extensively discussed in refs 19–21.

The current implementation of the theory makes use of an effective potential representation of the bulk electrons interacting with the embedded surface region. Calculations are thereby greatly simplified while maintaining the principal objectives of insulating the surface sites from spurious boundary effects and allowing a response of the bulk electrons to the surface processes. Surface sites are described by an improved basis (radial, polarization, and correlation functions), and in the case of transition metals by variable occupancy.

Final electronic wave functions, including the adsorbate, are constructed by configuration interaction, and the coupling of the local subspace and adsorbate to the bulk lattice electrons, $\{\varphi'\}$, is represented by a pseudopotential.

$$\Psi = \sum_k \lambda_k A(\underset{\text{local region}}{\chi_1^k\chi_2^k\cdots\chi_n^k}\ \underset{\text{pseudo-potential}}{\varphi'_m\cdots\varphi'_N})$$

The cluster geometry and local region of the nickel cluster used to model the (111) crystal face of nickel are shown in Figure 1. The three-layer, 62-atom cluster consists of a surface layer of 28 atoms, a second layer of 17 atoms, and a third layer of 17 atoms. Embedding theory is used to reduce the Ni_{62} cluster to a 28-atom model depicted as shaded atoms: the surface layer of 14 atoms, a second layer of 9 atoms, and a third layer of 5 atoms. For the local surface region of four nickel atoms (see Figure 1) a [1s–3p] core potential is used and valence d orbitals are explicitly included. Other Ni atoms are described by an effective core potential for [1s–3d] electrons. For all boundary atoms, and those in the third layer, the core potential is further modified to account for bonding to the bulk region, as described in refs 22 and 23. The Ni core basis and core density and exchange expansions are the same as those used in a previous study of nickel surface states,[24] and the Ni and H basis sets are the same as those used in previous calculations on H/Ni(111).[22] A double-ζ s and p basis for carbon is taken from Whitten.[25] Polarization functions (4p) perpendicular to the surface were included on the four atoms in the local region; however, in-plane Ni 4p functions were excluded due to their near linear dependency with combinations of Ni 4s functions on surrounding nuclei. The same basis set and core potentials are used in all subsequent calculations on the Ni(111) surface and for CH_3 adsorption calculations.

The sites considered for CH_3 adsorption are as follows: a hollow 3-fold site where there is no second layer nickel atom underneath (fcc extension of the lattice), a filled 3-fold site with a second layer nickel atom underneath (hcp extension of the lattice), a bridge site, and an atop atom site (denoted by A, C, B, and D, respectively, in Figure 1). Distances from the surface were fully optimized.

Calculations are performed by first obtaining self-consistent-field (SCF) solutions for the nickel cluster plus adsorbed species. The occupied and virtual orbitals of the SCF solution are then transformed separately to obtain orbitals spatially localized about the four-atom surface region shown in Figure 1 and the adsorbate(s). This unitary transformation of orbitals is based upon exchange maximization with the valence orbitals of atoms belonging to the surface region and is designed to enhance convergence of the configuration interaction (CI) expansion.[19–21] The CI calculations involve single and double excitations from multiple parent configurations within a 30-electron subspace to 28 possible virtual localized orbitals. All configurations arising from excitations with an interaction energy greater than 1×10^{-5} hartree with the parent SCF configuration are explicitly retained in the expansion; contributions of excluded configurations are estimated with use of second-order perturbation theory. For all sites calculated, the SCF solution is the only dominant configuration, and the next largest coefficient of a configuration in the CI expansion is about 0.1. Details of the procedure are given in ref 26. Basis superposition contributions to the adsorption energy were investigated by calculating the energy of the Ni cluster with the adsorbed species' virtual basis present (but not the adsorbate nuclei) for points near the equilibrium geometries.

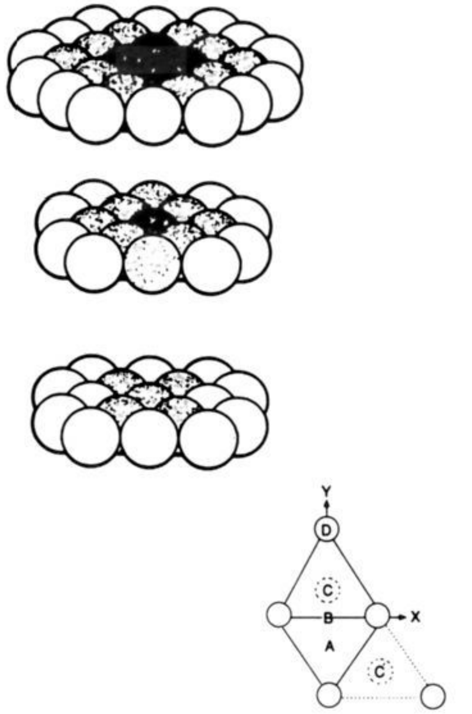

Figure 1. Cluster geometry and local region of the nickel cluster used to model the (111) crystal face of nickel. The three-layer, 62-atom cluster consists of a surface layer of 28 atoms, a second layer of 17 atoms, and a third layer of 17 atoms. Embedding theory is used to reduce the Ni_{62} cluster to a 28-atom model depicted as shaded atoms. Surface sites are A, the hollow 3-fold site where there is no second layer nickel atom underneath (fcc extension of the lattice); C, the filled threefold site with a second layer nickel atom underneath (hcp extension of the lattice); B, the bridge site; and D, the atop atom site. Atoms surrounding the four central atoms in the surface layer and those surrounding the one central atom in the second layer are described by effective potentials for (1s–3p core)$(3d)^9(4s)^{1/2}$ and (1s–3p core)$(3d)^9(4s)^{1/4}$ configurations, respectively. Effective potentials for the shaded atoms in the third layer describe the (1s–3p core)$(3d)^9(4s)^{3/5}$ configuration. Unshaded atoms have neutral atom (1s–3p core)$(3d)^9(4s)^1$ potentials. All atoms have Phillips–Kleinman projectors $\sum|Q_m\rangle\langle Q_m|(-\epsilon_m)$ for the fixed electronic distribution. The nearest neighbor Ni–Ni distance is 2.48 Å.

On the question about the CI size consistency in the present work, the zero-point energy is computed at the distance of 25 au between CH_3 and the substrate, and the same size of 30 electron CI and 28 localized virtual space are used. Our previous chemisorption studies of H, CH, CH_2, CH_4, H_2O, and NH_3 on the same cluster[22,27,31–34] have shown this procedure minimizes size inconsistency errors.

III. CH_3 Adsorption

In the initial carbon–surface distance optimization, the C–H bond lengths are fixed at 1.07 Å and the HCH angle at 109.5°, and the hydrogens are in a plane parallel to the surface, as shown in Figure 2a. Two different hydrogen orientations in CH_3 are considered for CH_3 at 3-fold sites: the H's pointing either toward the nearest Ni atoms or toward the Ni–Ni bond centers. Our recent study of NH_3/Ni(111)[27] and Hoffmann and co-workers' results for CH_3 adsorbed on metal surface[13] indicated that the most stable geometry of CH_3 at a 3-fold adsorption site is for the H's pointing toward the nearest metal atoms. Therefore, the initial

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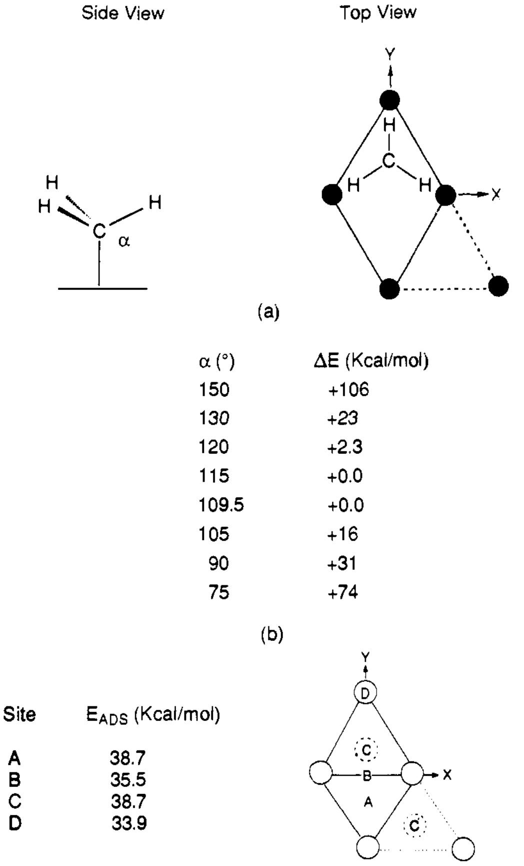

α (°)	ΔE (Kcal/mol)
150	+106
130	+23
120	+2.3
115	+0.0
109.5	+0.0
105	+16
90	+31
75	+74

Site	E_{ADS} (Kcal/mol)
A	38.7
B	35.5
C	38.7
D	33.9

Figure 2. CH_3 adsorption sites on Ni(111) and calculated energies. (a) Geometry of CH_3 adsorbed at the 3-fold site C. α is the angle between C–H bonds and the surface normal. All C–H bonds length are 1.08 Å, unless otherwise indicated. (b) The variation in energy with the angle of α. Adsorption energies for sites A–D are for CH_3 for a near tetrahedral geometry with the hydrogens in a plane parallel to the surface.

optimization reported below is based upon a CH_3 pyramidal geometry with the H's oriented toward the nearest Ni atoms at the 3-fold sites. The CH_3 molecule was translated in the Y direction from the hcp 3-fold site C, as shown in Figure 2a, to obtain the bridge site (B) and the atop atom site (D) geometries. Other orientations and geometries for CH_3 will be discussed in detail in a subsequent section.

The calculated adsorption energies, Ni–C equilibrium distances, and vibrational frequencies for CH_3 on Ni(111) are reported in Table I, along with some other calculated results for CH_3 on nickel surfaces. Adsorption energies are 39 kcal/mol (site A), 36 kcal/mol (site B), 39 kcal/mol (site C), and 34 kcal/mol (site D) with Ni–C bond distances of 2.35, 2.34, 2.33, and 2.03 Å (corresponding to 1.86, 1.98, 1.84, and 2.03 Å perpendicular distances from the surface), respectively. For the CH_3–(Ni surface) perpendicular stretch, the calculated frequencies are 386, 296, 369, and 416 cm^{-1} for adsorption sites A, B, C, and D, respectively. The calculated values for CH_3 at the 3-fold sites are in good agreement with a value of 370 cm^{-1} attributed to the CH_3–Ni stretching mode in EELS measurements by Ceyer and co-workers.[9]

From the present results, it is clear that there is no energetic difference between the hollow and filled 3-fold sites and that these are the most stable adsorption sites for CH_3 on the Ni(111) surface. This finding is somewhat similar to that for hydrogen chemisorbed on nickel, a result not surprising since hydrogen and methyl are chemically somewhat similar. Schule, Siegbahn, and Wahlgren, by using ab initio CI cluster calculations and varying the cluster sizes, have studied methyl chemisorption on Ni(111).[14] Their estimated adsorption energies are 43–48 kcal/mol for CH_3 adsorbed at atop atom sites on Ni_1 and Ni_{10} clusters and 45–50 kcal/mol for CH_3 adsorbed at 3-fold sites on Ni_4, Ni_{20}, and Ni_{22} clusters. The difference between the 3-fold and on-top sites is only 2 kcal/mol with the 3-fold site calculated to be slightly more stable. Their Ni–C bond lengths are 2.38 and 1.90 Å for the 3-fold and atop sites, respectively, consistent with the present results. Their calculated CH_3–(Ni surface) stretching frequencies are 353 cm^{-1} for the 3-fold site in Ni_4CH_3 and 597 cm^{-1} for the atop site in Ni_1CH_3. Calculated C–H stretching frequencies are 2935 and 3141 cm^{-1} for 3-fold and atop adsorption sites in Ni_4CH_3 and Ni_1CH_3, respectively. Their conclusion that the preferred chemisorption site for CH_3 on Ni(111) is the 3-fold site is the same as ours, however, the energy difference between the atop and 3-fold sites is found to be somewhat larger in the present work (4.8 vs 2 kcal/mol). In the calculations by Schule et al.,[14] the Ni 3d orbitals were not explicitly included for CH_3 at 3-fold sites, while for CH_3 at the on-top site, the single nearest Ni atom was described at the all-electron level.

Table I. CH_3 Chemisorption on Ni(111)

site	R,[a] Å	E_{ads}, kcal/mol	H_3C–Ni stretch, cm^{-1}	C–H stretch, cm^{-1}
this work[b]				
3-fold (A)	2.35	38.7 (43.4)	386	
bridge (B)	2.34	35.5 (39.2)	296	
3-fold (C)	2.33	38.7 (43.6)	369	2966
tilted (C)	2.14	37.1 (40.8)	377	2627, 2901[c]
on-top (D)	2.03	33.9 (36.4)	416	
expt			370[d]	2680[d]
Schule et al.[e]				
3-fold	2.38	45–50	353	2935
on-top	1.90	43–48	597	3141
Shustorovich, Bell[f]				
3-fold		30		
on-top		26		
Upton[g]				
4-fold	2.19	66.6		
2-fold	2.08	60.1		

[a] R is the distance from carbon to nearest surface Ni. [b] CI calculations on CH_3 adsorbed at hollow 3-fold (A), filled 3-fold (C), bridge (B), and atop atom (D) sites on a 28-atom cluster model of the Ni(111) surface. Energies in parentheses are uncorrected for basis superposition effects. [c] Two C–H vibrational frequencies are obtained, see text. [d] EELS results from refs 9. [e] Reference 14. The calculated Ni–CH_3 and C–H stretching frequencies are obtained from Ni_1CH_3 for on-top and Ni_4CH_3 for 3-fold site values, respectively. Chemisorption energies are estimated on the basis of CH_3 adsorbed at different clusters, see text. [f] References 15 and 16. CH_3 on Ni(111) based on semiempirical bond-order conservation method. [g] Reference 17. CH_3 chemisorbed on a 20-atom cluster model of Ni(100).

Gavin, Reutt and Muetterties,[10] by performing extended Hückel cluster model calculations, obtained an energy difference between the threefold site and the atop atom site of 19 kcal/mol for methyl chemisorbed on the Ni(111). Although no absolute adsorption energies were given, the relative energies for different sites favored the threefold position on the Ni(111) surface. Minot, van Hove and Somorjai,[11] using the extended Hückel method, reported completely different results for CH_3 chemisorbed on Pt(111) surface. They found methyl to be strongly unbound at the threefold site by 49 kcal/mol, and bound at an atop atom site with a chemisorption energy of 38 kcal/mol. In a recent extended Hückel study, Zheng, Apeloig and Hoffmann[12] found that the most stable adsorption site for CH_3 on Co(111) is the atop atom site with an adsorption energy of 85 kcal/mol. The threefold site was higher by 32 kcal/mol. An adsorption energy of 58 kcal/mol for CH_3 at the three-fold site on the (111) fcc metal surface like Ni is reported by Baetzold[13] using extended Hückel method. These varying results obtained by the extended Hückel methods are difficult to understand unless they are caused by differences in the parametrization schemes used in the different studies.

A recent theoretical study by Shustorovich and Bell, using a semiempirical bond-order conservation method,[15,16] provides another reference point for CH_3 adsorption on nickel. This method has been successful in rationalizing trends in atomic chemisorption.[15c] In their earlier calculations, chemisorption energies of 32 and 26 kcal/mol have been reported for CH_3 at a 3-fold and

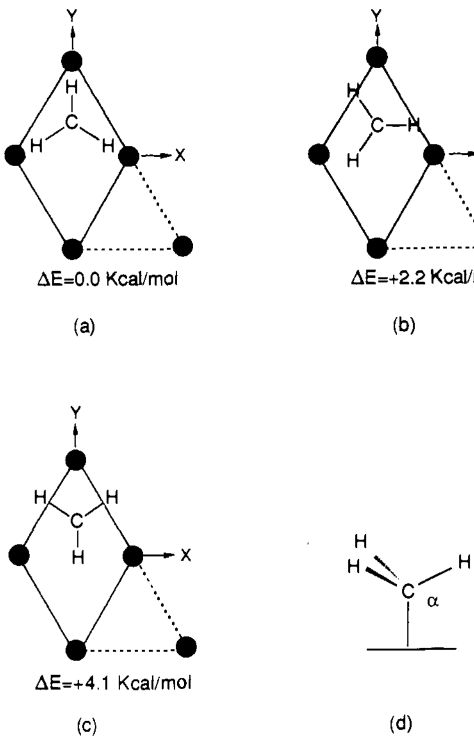

Figure 3. The orientations of hydrogens in CH_3 on Ni(111). (a-c) Top views for CH_3 at the 3-fold site C. (d) A side view. The corresponding adsorption energy for CH_3 with preferred hydrogen orientation in (a) is 38.7 kcal/mol. Hydrogens are in a plane parallel to the surface with a tetrahedral geometry.

an atop adsorption site on the Ni(111) surface. Most recently, their method has been improved to take into account the difference between the "strong" and "weak" chemisorption bond as two distinct cases requiring different formalisms.[16] With this modification the calculated chemisorption energy of CH_3 at the 3-fold site on Ni(111) is 48 kcal/mol. An earlier ab initio study of the interaction between methyl and nickel surfaces is reported by Upton.[17] By applying the generalized valence bond (GVB) method and using a 20-atom cluster model of Ni(100), binding energies of 67 kcal/mol for CH_3 adsorption in the 4-fold hollow site and 60 kcal/mol in the bridge site were obtained. These binding energies are higher than that of Schule et al.[14] and our results for Ni(111) but similar to the bond energy of 60 kcal/mol for the $NiCH_3$ molecule calculated by Rappe and Goddard using the GVB method and CI calculations.[18] The Ni–C bond length obtained in the $NiCH_3$ calculations is 1.87 Å, which is close to the present Ni–C bond distance of 2.03 Å at an atop site. Again, the preferred adsorption site for CH_3 is not an on-top site but is a 4-fold hollow site, i.e., the highest coordination site of the (100) surface.

IV. CH_3 Geometry

For CH_3 adsorbed at the filled 3-fold site C, Figure 2b shows the energy differences as a function of the angle between the surface normal and the C–H bond with the distance of carbon from the surface fixed at the equilibrium distance. These results show that the energy is essentially unchanged from α = 110–115° (corresponding to an angle of HCH of 109.5° and 103.4°). Thus, we conclude that chemisorption of methyl on the Ni(111) surface allows low-energy fluctuations in the C–H bond angles about an equilibrium value of 112 ± 2°. A similar equilibrium value of α = 112° was obtained by Schule et al.[14]

The above results assume an orientation of the CH_3 pyramidal geometry with the H's pointing toward the nearest Ni atoms at the 3-fold sites A and C and bridge and on-top geometries obtained by translation of the 3-fold site C orientation. Figure 3 depicts three different hydrogen orientations for CH_3, at the filled 3-fold site C. Rotating the H's by 30° about the surface normal, as shown in Figure 3b, increases the energy by 2.2 kcal/mol. If the H's are rotated by 60° about the surface normal to orient the C–H bonds between neighboring nickel atoms, as shown in Figure 3c, the barrier goes up to 4.1 kcal/mol. No rotational barrier is found for CH_3 at an atop atom site, and a barrier of about 0.5 kcal/mol is calculated at the bridge site for a 60° rotation. A similar conclusion was drawn by Zheng, Apeloig, and Hoffmann.[12] They reported that an adsorbed methyl radical on the Co(111) surface can freely rotate at on-top and bridge sites. They obtained a rotational barrier of 6.3 kcal/mol (for 60° rotation about the surface normal) at the 3-fold site with the preferred orientation of hydrogens pointed toward the nearby metal atoms, the same as found in the current study. They interpret the hydrogens of the CH_3 group as interacting with both metal-metal (M–M) bonding and antibonding states in the stable geometry, whereas in the less stable geometry they interact only with the M–M bonding state.

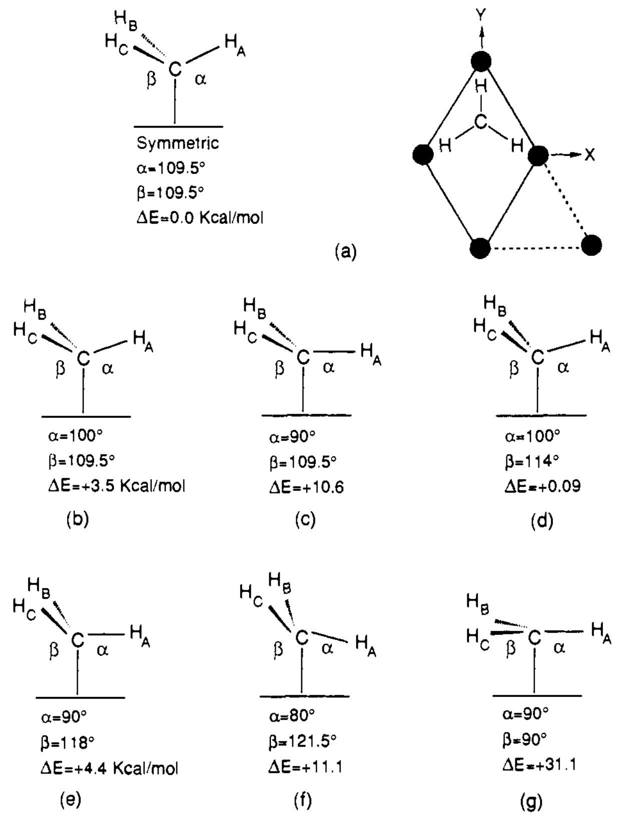

Figure 4. Geometries and energies of CH_3 intermediates on Ni(111). Energies (kcal/mol) are relative to that of the most stable geometry depicted in (a) which corresponds to adsorption at the 3-fold site C with E_{ads} = 38.7 kcal/mol. α is defined as the angle between the C–H_A bond and the surface normal and β as the angle between H_BC or H_CC and the surface normal; the angle H_BCH_C is 109.5° for all the geometries shown.

The results presented thus far in this work are based upon the symmetric distortion of methyl on the nickel surface. For asymmetric distortions of CH_3, Figure 4 depicts the most important intermediate structures calculated. Figure 4 shows several distortions of hydrogen(s) or approaches the hydrogen(s) to the surface to be energetically unfavorable. If the H_B–C and H_C–C bonds are kept unchanged and only the H_A–C bond is distorted (see Figure 4b and c), the energy increases 3.5 kcal/mol relative to the equilibrium geometry when the angle α between the H_A–C bond and the surface normal is decreased by 9.5°. The energy is further increased to 10.6 kcal/mol for a change of α = 19.5°. When the HCH angles are kept at 109.5° and H_A is rotated toward the substrate (Figure 4, d–f), the energy also increases compared to the most stable geometry. For a decrease in angle α between the H_A–C bond and the surface normal of 9.5°, 19.5°, and 29.5°, the energy increases 0.09, 4.4, and 11 kcal/mol, respectively. If the methyl is distorted into a planar configuration above the surface (see Figure 4g), the energy increases by 31 kcal/mol. On optimization of the distance from carbon to the surface for the planar geometry of Figure 4g, the minimum energy is still 23 kcal/mol higher than the equilibrium geometry of Figure 4a, for a perpendicular distance of 2.67 Å. It can thus be concluded that the direct bonding between H atoms and the lattice is too weak to attract one of the hydrogens toward the surface, i.e., there is no evidence of an agostic interaction. This conclusion is similar to that of Hoffmann and Upton,[28] who argued that the CH–metal interaction is repulsive. It does not agree with the inference by Demuth et al.[29] and Ceyer and co-workers[9] from the observation of low or soft C–H frequencies that the CH–metal bond exhibits an attractive H-bonding interaction between the surface.

Other discussions of C–H...metal interactions have been given by Raval and Chesters.[30] By using EELS measurements, they studied cyclohexane adsorbed on Pd(110) and Ni(110) and reviewed spectra in the literature of this adsorbate on Pt(111), Pd(111), Ni(111), Cu(111), and Ru(001) surfaces. The strength of the cyclohexane–metal bond was found to be related to the extent of CH mode softening, with higher desorption temperatures exhibited as the softening increases until sufficient CH bond softening occurs to cause dehydrogenation.[30] Thus, it is concluded that the CH mode softening observed for cyclohexane on a variety of surfaces could be interpreted in terms of C–H···metal interaction, akin to bonding of the molecule, via some of its CH groups, to the surface.

An interesting picture of bonding between CH_x fragments and metal surfaces, which is drawn by Zheng et al.[12] and Minot et al.,[11] using the extended Hückel method, is that the fragments tend to bring back their missing CH bond with CH consequently preferring the 3-fold site, CH_2 the bridge site, and CH_3 the atop atom site. This trend is not reproduced in our ab initio CI calculations, however. The present results and our previous studies of H, CH, and CH_2 on Ni(111)[22,31,32] show that all CH_x and H species are most strongly adsorbed at the 3-fold site, or in some cases with comparable binding at a bridge site, i.e. the higher coordination sites on the Ni(111) surface. According to the present calculations, if an adsorbate has unpaired electron(s), it most likely occupies the site where it will have several nearest neighbors, i.e. the 3-fold site and/or the bridge site on Ni(111). Similar calculations on other systems indicate that if the adsorbate has no unpaired electron, such as CH_4, NH_3, and H_2O, an atop atom site is either preferred or is similar in adsorption energy to bridge and 3-fold sites.[27,33,34]

Since the $3a_1$ symmetry orbital (C_{3v} classification) is not paired in CH_3, the bonding of the adsorbed methyl species to nickel would be expected to involve some electron transfer from the surface accompanied by image charge formation on surface. Our calculations show, at the filled 3-fold site C, that the net charge gained by carbon atom is 0.54 e, 0.40 e transferred from the surface and 0.14 e from the three hydrogens. This transfer of electrons to carbon is consistent with the calculated work function increase of 0.21 eV, calculated by configuration interaction as $E^{+}(\text{Ni–CH}_3) - E(\text{Ni–CH}_3)$. A 0.26-eV increase is estimated by Koopmans' theorem. After CH_3 adsorption, the surface layer has a net positive charge of 0.30 |e| with 0.08 |e| transferred from the d shell; the second layer net charge lost is 0.35 e; and the third layer gains a net charge of 0.25 e. Thus, for CH_3 adsorption on the (111) surface of Ni, lattice polarization effects accompanying adsorption extend beyond the surface layer. Table II lists the Mulliken populations and calculated work function changes for CH_3 at other geometries and adsorption sites.

Table II. CH_3 and Nickel Layer Net Charge Distribution and Calculated Work Function Changes[a]

			layers			
site	C	H	I	II	III	ΔW_f,[b] eV
3-fold	−0.54	+0.14	+0.30	+0.35	−0.25	+0.26 +0.21[c]
3-fold (tilted)	−0.55	+0.18	+0.27	+0.35	−0.25	+0.26
3-fold (rotated)	−0.59	+0.13	+0.33	+0.39	−0.26	+0.25
bridge	−0.50	+0.10	+0.29	+0.38	−0.27	+0.24
on-top	−0.36	+0.12	+0.21	+0.17	−0.14	+0.30

[a] Values refer to the equilibrium geometry of CH_3 at 3-fold, bridge, and atop atom adsorption sites, unless otherwise indicated. Net charge is in units |e| by Mulliken population analysis of SCF solutions compared to the infinite separation between CH_3 and clean surface with basis superposition corrections. The Mulliken partitioning of the overlap distribution between C and surface orbitals overemphasizes the C charges. In the gas-phase CH_3 molecule, the net charge gained by carbon and lost by hydrogens is 0.29 |e|, respectively. [b] Calculated values from Koopman' theorem, unless otherwise indicated. The calculated W_f of the clean surface is 5.38 eV; 5.30 eV is obtained by CI calculations. The experimental W_f for the clean surface of Ni(111) is 5.15–5.35 eV for different coverages. [c] From CI calculations.

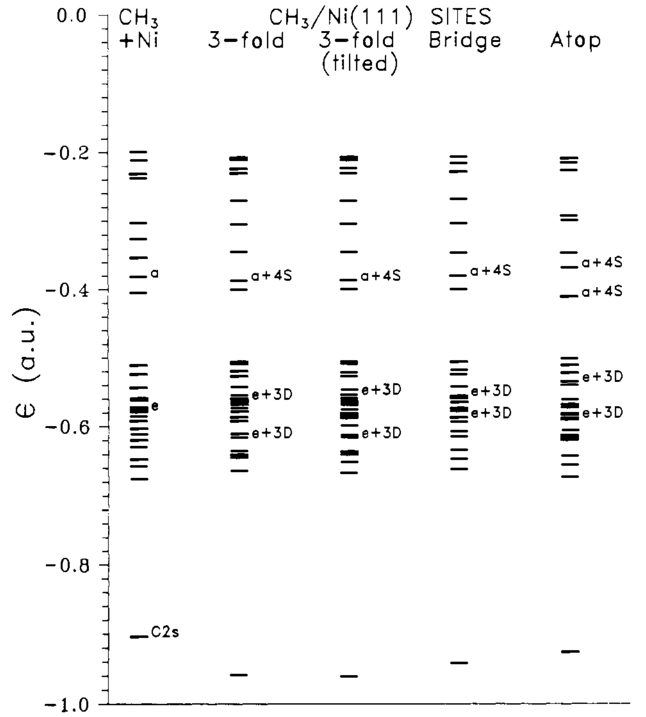

Figure 5. SCF eigenvalues for CH_3 adsorbed on Ni(111). a and e refer to the singly occupied $3a_1$ symmetry orbital and doubly degenerate 1e symmetry orbitals of CH_3 levels (C_{3v} classification), respectively. The left most eigenvalue spectrum is for the clean surface plus CH_3. SCF eigenvalues for 60° rotation of hydrogens about the surface normal are not depicted due to the similarity to hydrogens without rotation. The eigenvalue spectrum for tilted CH_3 corresponds to the geometry in Figure 6b2, in which tilted CH_3 is shifted away from the 3-fold center by 0.67 au and H_A is directly above the Ni atom.

The SCF eigenvalue spectra for the clean surface and with CH_3 adsorbed are shown in Figure 5. These results and the Mulliken population reveal considerable information about orbital interaction on CH_3 adsorption. On bonding to the surface, the degenerate 1e and $3a_1$ in CH_3 are the orbitals principally involved in bonding with the surface. For all the adsorption sites studied, the 1e orbitals interact with the Ni 3d orbitals resulting in a strong mixing of orbitals, and the $3a_1$ orbital forms a strong σ bond with 4s orbitals. The main $3a_1$–4s mixing occurs at 4.9 eV below the Fermi level for CH_3 adsorbed at the most stable 3-fold site with a population (in percent) of [41($3a_1$), 59(4s)]. The nearly degenerate 1e–3d levels are 11.1 eV and 10.9 eV below E_F for $1e_y$ and $1e_x$ with populations (in percent) of [39($1e_y$), 61(3d)] and [53($1e_x$), 47(3d)] for CH_3 adsorbed at the 3-fold sites. Table III tabulates all the principal 1e and a_1 levels of the CH_3 chemsorbed on the nickel at different sites.

It should be pointed out that the availability of the nickel 3d orbitals to interact with the methyl is very important, as was the case for H, CH, and CH_2 adsorption on nickel. Similar conclusions have been reached by Siegbahn et al.,[35] Shustorovich et al.,[36]

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Table III. CH_3 Orbital Levels and Mulliken Populations on the Ni(111) Surface[a]

			Mulliken populations, %		
site	orbital	level,[b] eV	CH_3 orbital	3d (Ni)	4s (Ni)
3-fold	$2a_1$	−20.4	94		
	$1e_y$	−11.1	39	61	
		−9.6	22	78	
	$1e_x$	−10.9	53	47	
		−9.4	21	79	
	$3a_1$	−4.9	41		59
bridge	$2a_1$	−20.0	96		
	$1e_y$	−11.1	28	72	
		−9.5	50	50	
	$1e_x$	−10.3	40	60	
		−9.5	22	78	
	$3a_1$	−4.7	45		55
on-top	$2a_1$	−19.5	91		
	$1e_y$	−10.1	28	72	
		−8.9	26	74	
	$1e_x$	−10.3	24	76	
		−8.9	45	55	
	$3a_1$	−5.5	21		79
		−4.3	34		66

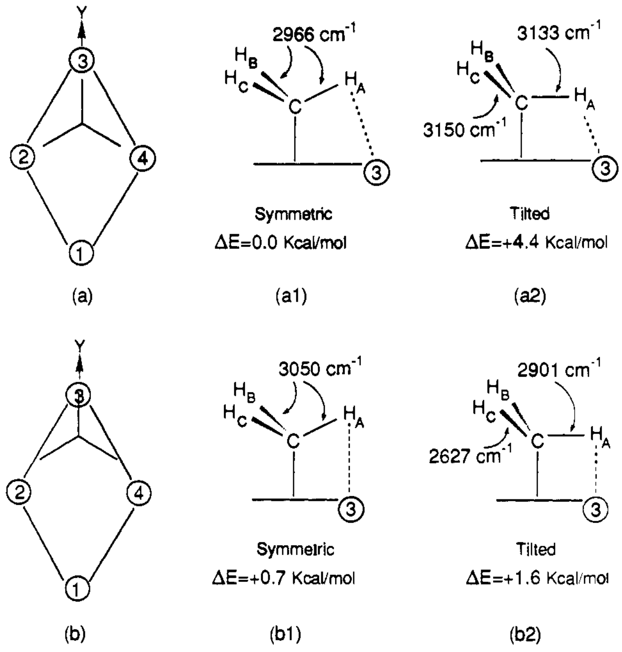
[a] Values are for the minimum energy geometry of CH_3 at 3-fold, bridge, and atop atom adsorption sites, unless otherwise indicated. Orbital levels are relative to the Fermi levels. [b] Energy below the Fermi level.

etc. We conclude that the combination of the covalent s and d bonding characterizes the bonding of CH_3 to the nickel surface.

V. C–H Stretching Frequency of CH_3

In this section, we investigate the possibility of low C–H frequencies of methyl on the Ni(111) surface which have been experimentally observed by Ceyer and co-workers.[9] They report an unusually low C–H stretching frequency of 2680 cm^{-1} for CH_3 obtained from high-resolution electron energy loss spectroscopy (HREELS). The low C–H frequency might be indicative of C–H···metal bonding, and thus it has been suggested that the methyl was tilted toward the surface. Applying EELS and studying ethylene and cyclohexane on Ni(111), Demuth, Ibach, and Lehwald[29] observed for the first time low C–H stretching frequencies for adsorbed hydrocarbons. They interpreted the low C–H frequencies as due to the attractive hydrogen-bonding interactions between the surface and the adsorbate and concluded that this phenomenon could be directly related to the dehydrogenation process.

The present studies show that the CH–metal interaction is not attractive, but repulsive. When CH_3 is in the equilibrium geometry, i.e., the H's in a plane parallel to the surface with a tetrahedral configuration as shown in Figure 6a1, the present results show a C–H stretching frequency for CH_3 adsorption at the 3-fold site of 2966 cm^{-1}. This value is typical of a CH stretching vibration in gas-phase molecules[37] as well as in adsorbed hydrocarbons.[38,39] If CH_3 remains at the center of the 3-fold site, the calculated C–H stretching vibrations are around 3000–3100 cm^{-1} for all the geometries studied, as shown in Figure 4, b–f.



Net Charge Distribution

Geometry	H_A	H_B	H_C	C	Ni(#3) (3d)
a1	+0.04	+0.05	+0.05	-0.54	+0.30 (+0.01)
a2	+0.05	+0.06	+0.06	-0.56	+0.27 (+0.02)
b1	+0.02	+0.06	+0.06	-0.54	+0.29 (+0.03)
b2	+0.08	+0.05	+0.05	-0.55	+0.25 (+0.03)

Figure 6. Calculated C–H vibrational frequencies, energies, and net charge distributions for CH_3 with symmetric and tilted geometries adsorbed at the 3-fold site center in (a) and away from the 3-fold site center by 0.67 au in (b) which places one of the hydrogens directly above the number three Ni atom, Ni(#3). Energies (kcal/mol) are relative to that of the equilibrium geometry depicted in (a1) which corresponds to an adsorption energy of E_{ads} = 38.7 kcal/mol. Net charge is in unit |e| by Mulliken population analysis of SCF solutions compared to the infinite separation between CH_3 and clean surface with basis superposition corrections.

If CH_3, in Figure 6a2, is shifted 0.67 au in the +*Y* direction, which puts the H_A atom directly above a Ni atom, as shown in Figure 6b2, the calculated C–H_B and C–H_C vibration frequencies decrease to 2627 cm^{-1}, and the C–H_A vibration becomes 2901 cm^{-1}. This geometry is 2.8 kcal/mol lower in energy than that for tilted CH_3 at the center of the 3-fold site in Figure 6a2, and it is only 1.6 kcal/mol higher in energy than the equilibrium geometry of Figure 6a1. In contrast, if CH_3 with the symmetric geometry of Figure 6a1 is shifted to the same position as shown in Figure 6b1, the calculated C–H vibrations are 3050 cm^{-1} and the corresponding energy is 0.7 kcal/mol higher than in the center. A Mulliken population analysis shows that the charge distributions are slightly different for the two geometries. Compared with the infinite separation between the CH_3 molecule and the nickel surface, for the shifted CH_3 with C–H_A parallel to the surface, the net charge lost by H_A is 0.08 e, 0.05 e by both H_B and H_C, and 0.55 e net charge is gained by the C atom (including basis superposition corrections). For the shifted CH_3 with symmetric geometry, the net charges lost by H_A, H_B, and H_C are 0.02, 0.06, and 0.06 e, respectively, and the net charge gained by the C atom is 0.54 e. The population analysis also shows that the particular Ni atom directly under H_A transferred 0.04 e more charge for the symmetric CH_3 in Figure 6b1 than for the tilted CH_3 in Figure 6b2. The total charge transferred from the surface to CH_3 is essentially the same in both geometries.

The present calculations indicate that the soft or low C–H frequency of methyl on the Ni(111) surface occurs for a tilted geometry and a shift away from the 3-fold center. The resulting geometry which places one of the hydrogen atoms almost directly above a Ni atom is not the lowest energy (equilibrium) geometry but is only 1.6 kcal/mol higher than the calculated equilibrium geometry. A low C–H vibrational frequency of methyl was not found in the calculations for any other geometry or shifted position. By comparing Ni_4CH_3 and $LiCH_3$, Schule et al.[14] have concluded that the origin of the low C–H frequency of CH_3 on Ni(111) is a simple charge-transfer effect.

It is worth noting that the first-order contribution of the anharmonic vibration is small in the calculations of the C–H vibrational frequency. By using a third degree polynomial for a 5-point fit (CI total energy versus C–H distance), without con-

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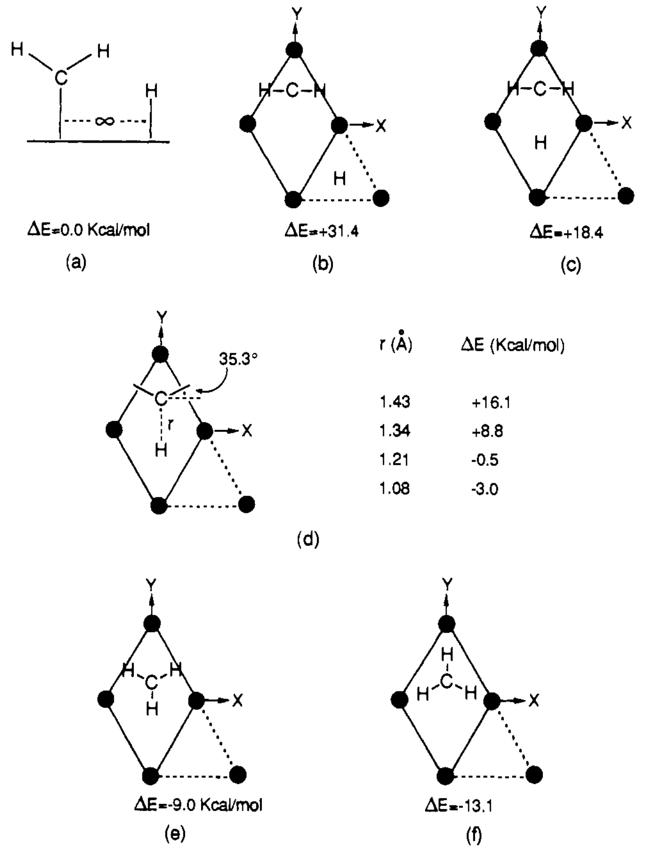

r (Å)	ΔE (Kcal/mol)
1.43	+16.1
1.34	+8.8
1.21	-0.5
1.08	-3.0

Figure 7. Energetics of coadsorbed CH_2 and H on Ni(111). Energies (kcal/mol) are relative to an infinite separation of CH_2 and H on the surface, determined from separate calculations of H/Ni(111) and CH_2/Ni(111). The carbon atom is always above the 3-fold site C at the most stable adsorption site for CH_2. The energy increases as H is moved to 3-fold sites adjacent to CH_2 but then decreases as the CH bond is formed as shown in (d) and CH_3 is rotated to a symmetric geometry above the surface. The overall reaction of CH_2(ads) + H(ads) = CH_3(ads) on Ni(111) is 13.1 kcal/mol exothermic driven by the energy of formation of an additional CH bond. Distances from the surface are not optimized in (b).

sidering the first anharmonic vibration contribution, the calculated C–H_B and C–H_C vibrational frequencies are 2646 cm^{-1}, and the C–H_A vibrational frequency is 2913 cm^{-1} for tilted CH_3 displaced from the 3-fold center (compared to 2627 and 2901 cm^{-1}, respectively, with the contribution of the first-order anharmonic term included). For symmetric CH_3 adsorbed at the 3-fold site, the calculated C–H vibrational frequency is 3003 cm^{-1}; the first-order anharmonic contribution is only 37 cm^{-1}. By performing the same calculations of the C–H stretching frequency for gas-phase CH_3 by using the same basis set, the calculated C–H vibrational frequency for the same 5-point fit is 3003 cm^{-1} for the harmonic vibration and 2961 cm^{-1} including the first anharmonic correction.

VI. Reaction of CH_2 + H = CH_3

In this section, we consider the energetics for the reaction of

$$CH_2(ads) + H(ads) = CH_3(ads)$$

on the Ni(111) surface. The equilibrium geometries of the individual species H, CH_2, and CH_3 are the same as discussed earlier. The choice of the product site was determined by the calculated strong bonding of CH_2 and CH_3 to 3-fold sites.

For the reaction of CH_2(ads) + H(ads) = CH_3(ads), Figure 7 depicts the most important intermediate structures calculated. At infinite lateral separation of CH_2 and H on the surface, the total CI energy is calculated as $E_\infty = E_{Ni} + E_{CH_2} + E_H + D_{0(CH_2)} + D_{0(H)}$. Compared to this reference energy the reaction of CH_2 + H to form CH_3 at the 3-fold site is exothermic by 13 kcal/mol. Moving H and CH_2 into separated 3-fold sites C and C′ shown in Figure 7b, with R = 2.48 Å and without optimization of the geometries, gives an energy 31 kcal/mol higher than for $R = \infty$ for a perpendicular distance of H from the surface of 1.18 Å. An H level is found the SCF eigenvalue spectrum at 6.0 eV below the Fermi level, slightly deeper than the H feature seen in photoemission at 5.8 eV below E_F.[40,41] If H and CH_2 are moved to adjacent 3-fold sites C and A, corresponding to R = 1.43 Å, and an optimized perpendicular distance of H from the surface of 1.85 Å, as shown in Figure 7c, the total energy of the system is only 18 kcal/mol higher than E_∞. Partial formation of the C–H bond is seen by analyzing the SCF solution at this distance, and the corresponding structure is a distorted and stretched CH_3 molecule. Tilting the plane of CH_2 to the $+Y$ direction about 35.3° from the surface normal (this tilting angle makes the HCH angle of 109.5°) and keeping R = 1.43 Å, the energy is lowered by 2.3 kcal/mol, and the corresponding geometry is 16 kcal/mol higher in energy than E_∞ (in Figure 7d). Further decreasing the C–H_A distance from R = 1.43 Å to 1.34, 1.21, and to a normal bond length of 1.08 Å gives a total energy of the corresponding structures of +8.8, −0.5, and −3.0 kcal/mol relative to E_∞, respectively. Tilting CH_3 to give a symmetric CH_3 with hydrogens in a plane parallel to the surface as shown in Figure 7e gives an energy 9.0 kcal/mol lower than E_∞. Finally, rotating the CH_3 molecule 60° into its equilibrium position to produce the H's pointing toward the nearest Ni atoms (in Figure 7f) decreases the energy to a value 13.1 kcal/mol lower than the infinite separation energy of E_∞.

As was the case for CH, adsorption of CH_2 at a 3-fold site on Ni(111) tends to block the nearby 3-fold sites as shown in Figure 7. Coadsorption of CH_2 and H at adjacent 3-fold sites (i.e. sites A and C in Figure 7) and at separated 3-fold sites (i.e. sites C and C′) is unfavorable relative to infinite separation of CH_2 + H on the surface. Our calculations thus show that there is an energy barrier to form CH_3(ads) from CH_2(ads) + H(ads) on the Ni(111) surface. The calculated activation energy for the particular pathway, shown in Figure 7 is a factor of 2 higher than our previous calculated energy barrier for the reaction of CH(ads) + H(ads) = CH_2(ads) for a similar pathway.[31] It is possible that there would exist a pathway with a lower activation energy for the formation of CH_3(ads) from CH_2(ads) + H(ads), for example, if H atom were to bind with the C atom across a nearby Ni atom. This pathway would allow the incoming H (or CH_2) to avoid the higher energy barrier zone, i.e. the adjacent and separated 3-fold sites discussed above. The overall reaction of CH_2(ads) + H(ads) = CH_3(ads) on the surface is exothermic, driven by the energy of formation of an additional CH bond.

The present calculated exothermicity of 13 kcal/mol for the formation of CH_3 from CH_2 and H on the Ni(111) surface is in good agreement with the calculated value of 12 kcal/mol by Bell and Shustorovich.[16] Using extended Hückel theory, Baetzold has calculated an exothermicity of 6 kcal/mol and zero activation energy for the reaction of CH_2 + H = CH_3 on Ni(111).[13]

After submission of this paper, a theoretical ab initio study of CH_x (x = 0–3) chemisorption on small cluster models of the Ni(100) and Ni(111) surfaces was reported by Siegbahn and Panas.[42] The calculated chemisorption energy of CH_3 at the 3-fold site on a three Ni atom cluster is 49 kcal/mol; the C–H vibrational frequency is 2709 cm^{-1}, in good agreement with the experimental value of 2680 cm^{-1}. The formation of CH_3 from CH_2 and H on Ni(111) is estimated to be exothermic by 8 kcal/mol. The Ni–C bond lengths are not given for CH_3 on the three Ni atom cluster. By comparison, the present calculations predict a chemisorption energy of 39 kcal/mol for CH_3 at the 3-fold site and an exothermicity of 13 kcal/mol for the reaction of chemisorbed CH_2(ads) + H(ads) = CH_3(ads) on the surface. Basis superposition corrections of 5 kcal/mol are included in the present work. The basis superposition corrections might be considerable if applied to the calculations in ref 42, since a large

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basis set (6s,5p,2d,1f) is used for the C atom in the Ni_3CH_3 calculations. As in their previous work,[14] Ni 3d orbitals are not explicitly included in ref 42.

VII. Conclusions

The conclusions of the present study of chemisorption of CH_3 on the (111) surface of nickel can be summarized as follows:

(1) Dissociated CH_3 binds strongly to the Ni(111) surface with adsorption energies of 39, 36, and 34 kcal/mol at the 3-fold, bridge, and atop atom sites, respectively. The two 3-fold adsorption sites have comparable stability. Compared to other CH_x fragments, the potential surface of the Ni(111) appears fairly flat for methyl radical adsorption.

(2) In the calculated equilibrium geometry of CH_3 on Ni(111), the hydrogens are in a plane parallel to the surface in a pyramidal configuration pointing in the direction above the nearest nickel atoms. The angle between the surface normal and the C–H bond is 112 ± 2°. Ni–C bond distances are 2.35, 2.34, and 2.03 Å for methyl at the 3-fold, bridge, and atop atom sites, respectively.

(3) Calculated CH_3–(Ni surface) stretching vibrational frequencies are 369, 296, and 416 cm^{-1} for the 3-fold, bridge, and atop sites. The C–H stretching frequency for CH_3 at the center of a 3-fold site is 2966 cm^{-1} for the equilibrium geometry.

(4) A low C–H frequency of methyl on Ni(111) is calculated at 2627 cm^{-1} if CH_3 is shifted away from the 3-fold center by 0.67 au and if one of the hydrogens is tilted to give a C–H bond parallel to the surface. This shift puts one of the hydrogens directly above a Ni atom. This geometry is only 1.6 kcal/mol higher in energy than the calculated equilibrium geometry.

(5) The reaction of $CH_2(ads) + H(ads) = CH_3(ads)$ on the surface is 13 kcal/mol exothermic. An energy barrier occurs when H and CH_2 are moved from infinite separation to adjacent 3-fold sites on the surface for the pathway investigated.

(6) Electron transfer occurs to carbon from the surface, primarily from the 4s band of Ni, accompanied by a work function increase of the lattice by about 0.2 eV. Ni 3d orbitals strongly interact with the 1e symmetry orbitals of CH_3. Covalent s and d bonding characterizes the bonding of methyl to the nickel surface.

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Registry No. Me•, 2229-07-4; Ni, 7440-02-0; CH_2, 2465-56-7; H, 12385-13-6.

Revival of an Old Structure Problem: Trithiapentalene—Real or Time-Averaged C_{2v} Symmetry?

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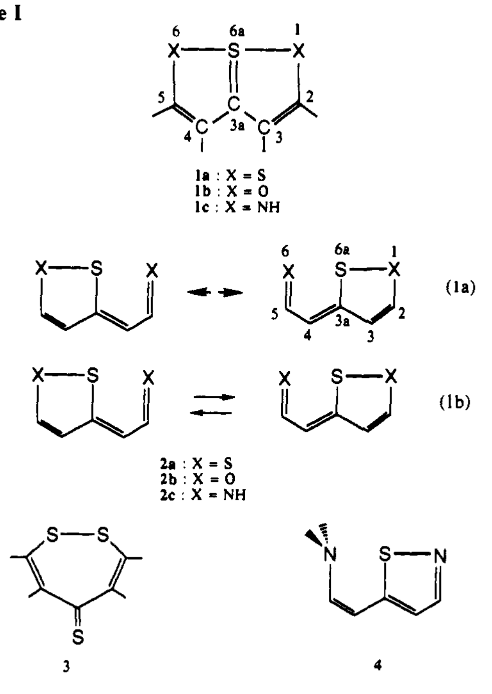
Abstract: The structures of 1,6,6aλ^4-trithiapentalene **1a** and the related compounds 1,6-dioxa-6aλ^4-thiapentalene **1b** and 1,6-diaza-6aλ^4-thiapentalene **1c** were examined on the basis of ab initio MO theory employing the 3-21G(*) and 6-31G* basis sets. In case of the trithia and dioxathia molecules, the bridged C_{2v} structures appear as most stable arrangements when the correlation energy is considered, whereas the corresponding open C_s forms are preferred at the SCF level. The same conclusions can be drawn for the 1,6-disubstituted diazathiapentalenes. Contrary to this, structure **4** with an aromatic isothiazole ring is the most stable form for the unsubstituted compounds.

The systematic study and discussion of the structure of 1,6,6aλ^4-trithiapentalene **1a** and of related compounds, e.g., of types **1b** and **c**, began in 1958[1] and has attracted much attention because of the unusual binding behavior in these systems.[2-5] Compounds belonging to this class had been obtained much earlier. Thus, the 2,5-dimethyl derivative of **1a** was already prepared in 1925, but the completely different structural formula **3** was proposed.[6] Nowadays, most experimental data for 1,6,6aλ^4-trithiapentalene are in agreement with the assumption of C_{2v} molecular symmetry corresponding to **1a**. Nevertheless, a final confirmation of this structure has not been given until now.[2-5] Alternatively to this structure proposition, which is based on the no-bond–single-bond resonance concept, valence tautomerization between the two alternate forms of **2** may be postulated for which the C_{2v} form represents a transition state. Provided that the energy barrier is too low to be observed by the experimental methods used, distinctions between real or time-averaged C_{2v} symmetry may be impossible. In Scheme I, both interpretation possibilities are illustrated by eq 1a and 1b.

Former attempts to contribute to a decision of this question by means of quantum chemical methods were significantly influenced by the type of approximation chosen.[2-5,7] Mostly, semiempirical MO methods and minimum basis set ab initio MO

Scheme I



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