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# Theoretical studies of surface reactions on metals. I. Ethyl to ethylene conversion on Ni(1 0 0). II. Photodissociation of methane on platinum

J.L. Whitten*, H. Yang

*Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8201, USA*

**Abstract**

The goal of this research is the development and application of theoretical techniques that will provide a molecular level understanding of surface processes, especially reaction mechanisms and energetics. Electronic structures are described by an ab initio embedding formalism that permits an accurate determination of energies and adsorbate structure. An overview of the theoretical method is presented and applications to catalytic and photochemical reactions on nickel and platinum surfaces are discussed. Preliminary studies of ethylene production from ethyl adsorbed on nickel are reported. A second study concerns the photodissociation of methane physisorbed on platinum. Results are reported for a methane molecule interacting with a Pt ring model of the surface. Configuration interaction theory is used to sort out states resulting from electron attachment to methane from lower energy states that correspond to metal excitations. A mechanism is proposed for the photodissociation process.


*Keywords:* Photodissociation; Ethylene; Surfaces; Catalysis

## 1. Introduction

The goal of this research is the development and application of theoretical techniques that will provide a molecular level understanding of surface processes, especially energetics, adsorbate structure and reaction mechanisms. The work relates to two broad subject areas: catalytic processes on metals and properties of electronic materials. First-principles theoretical methods are employed to obtain an accurate description of these systems [1,2].

The difficulty in treating surface reactions using first-principles theory is that there are conflicting demands on the theory. At the surface, the treatment must be accurate enough to describe surface–adsorbate bonds and energy changes accompanying chemical reactions (generally, this is most readily achieved if systems are small); while, for a metal, a large number of atoms is required to describe conduction and charge transfer processes (in this case methods for treating large symmetric systems are most appropriate). The objective of the embedding theory employed in this work is to balance the accuracy and size aspects of the problem [2].

The present paper deals with two topics: catalytic reactions leading to ethylene formation on nickel and photochemical dissociation of methane on platinum. The ethylene study which involves consideration of α

*Corresponding author.

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and β elimination pathways in the reaction of ethane with nickel is motivated by the short contact time catalytic studies of Schmidt and coworkers [3–6] who observed a high degree of selectivity in several transition metal systems. The methane work is related to experiments by Watanabe and coworkers [7,8] on photochemical processes involving physisorbed methane on Pt(1 1 1) in which 193 nm photons absorbed by the substrate lead to dissociation of methane to form adsorbed $CH_3$ and H.

## 2. Theory

In order to describe reactions at a metal surface the theoretical treatment must be adequate to deal with the complexities of chemical bond formation or dissociation and accompanying effects of charge transfer, polarization and electronic correlation. Ab initio configuration interaction theory provides an attractive way to proceed only if systems are of manageable size.

The purpose of the embedding approach adopted in the present work is to organize the theoretical treatment in such a manner that an accurate many-electron treatment of the adsorbate/surface portion of a system can be carried out while coupling this region to the bulk lattice [2]. Localized orbitals extracted from a treatment of the clean surface are used to define an electronic subspace encompassing the adsorbate and neighboring surface atoms.

Calculations are carried out for the full electrostatic Hamiltonian of the system (except for core electron potentials), and wavefunctions are constructed by self-consistent-field (SCF) and multi-reference configuration interaction (CI) expansions

$$\Psi = \sum_k \lambda_k \det(\chi_1^k \chi_2^k \cdots \chi_n^k).$$

In work to date, surfaces have been modeled by a large cluster of atoms and the system subsequently reduced to a smaller effective size by the embedding procedure. In the treatment of transition metals, the first stage deals only with the most delocalized part of the electronic system, the s,p band; d functions on surface atoms are added after a surface s,p electronic subspace is defined. SCF calculations are performed on the s band of the initial cluster and the resulting occupied orbitals are localized by a unitary transformation based on the maximization of exchange interactions with bulk atomic orbitals. Final electronic wavefunctions, including the adsorbate, are constructed by configuration interaction, and the coupling of the local electronic subspace and adsorbate to the bulk lattice electrons, $\{\phi_j, j=1, m\}$, is represented by the modified Hamiltonian:

$$H = \sum_i^N (-1/2\nabla_i^2 + \sum_k^Q -Z_k/r_{ik}) + \sum_{i<j}^N 1/r_{ij} + \sum_i^N V_i^{\text{eff}},$$

where

$$\langle a(1)|V_1^{\text{eff}}|b(1)\rangle = \langle a(1)b(1)|1/r_{12}|\rho(2)\rangle - \langle a(1)b(2)|1/r_{12}|\gamma(1,2)\rangle + \sum_m \lambda_m \langle a|Q_m\rangle\langle Q_m|b\rangle$$

and $\rho$, $\gamma$ and $Q_m$ denote densities, exchange functions and atomic orbitals derived from $\{\phi_j, j=1, m\}$, respectively. Numerous applications to adsorption on transition metal surfaces have been reported and details of the procedure are reported in [1,2]. For platinum, relativistic atomic solutions are used to construct core electron potentials.

## 3. Ethane conversion to ethylene on nickel

Effective utilization of alkanes to produce desirable products requires high selectivity pathways that overcome the difficulty of activating CH bonds. A great deal of research has been carried out on the optimization of catalytic processes to achieve the desired selectivity at low cost. Our previous contributions to this subject have involved an accurate theoretical treatment of the reaction of methane with nickel, including the determination of minimum energy reaction pathways and activation barriers for $CH_4$ dissociation on Ni(1 1 1), and a study of the activation of methane over an Fe/Ni(1 1 1) alloy surface [1].

During the past several years, Schmidt and coworkers [3–6] have studied the production of olefins by oxidative dehydrogenation of ethane and other alkanes on gauze-like supports coated with Pt, Rh

or Pd by very short contact time, millisecond, processes. On Pt, the selectivity for $C_2H_4$ is found to be greater than 70% and the conversion of $C_2H_6$ exceeds 80%. The most probable initiation step is thought to be the oxidative dehydrogenation of $C_2H_6$ by reaction with adsorbed oxygen atoms

$$C_2H_6 + O\,(ads) \rightarrow C_2H_5\,(ads) + OH\,(ads)$$

or possibly with adsorbed hydroxyl

$$C_2H_6 + OH\,(ads) \rightarrow C_2H_5\,(ads) + H_2O\,(ads)$$

Following $C_2H_5$ adsorption, gaseous ethylene can be formed by elimination of a β-hydrogen:

$$C_2H_5\,(ads) + OH\,(ads) \rightarrow C_2H_4\,(gas) + H_2O\,(ads)$$

or

$$C_2H_5\,(ads) + O\,(ads) \rightarrow C_2H_4\,(gas) + OH\,(ads)$$

or possibly by direct interaction of H with the surface. Elimination of an α-hydrogen leads to adsorbed ethylidene ($-CHCH_3$) and eventually to undesired products. How these various pathways compete, through their different activation energies and probabilities of reaction, is the subject of the present theoretical study.

The interaction of ethyl groups with transition metals has been examined experimentally under ultrahigh vacuum conditions at low temperature (100–400 K) by temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy, high-resolution electron energy loss spectroscopy, and secondary ion mass spectroscopy [9–13]. The first hydrogen is apparently abstracted from the ethyl by β-elimination to form $C_2H_4$. The $C_2H_4$ may desorb or react on the surface to form ethylidyne ($-CCH_3$). In TPD studies, $C_2H_4$ was shown to desorb at temperatures below 170 K; thus, at high temperature, one would expect $C_2H_4$ to desorb immediately after being formed on the metal surface, thereby averting ethylidyne formation. These and other experimental studies suggest that the more noble metals tend to favor β-elimination rather than α-elimination and cracking to carbon, but these metals are catalytically less active than nickel.

In order to investigate the hierarchy in selectivity, high quality first-principles calculations on the adsorption of ethyl ($-CH_2CH_3$) on nickel and platinum surfaces will be carried out and the energetics of β-hydrogen elimination by direct interaction with the surface

$$CH_2CH_3\,(ads) \rightarrow C_2H_4\,(ads) + H\,(ads)$$

calculated. In this paper, we report the results of preliminary calculations on Ni(1 0 0). Calculations on Pt(1 0 0) are in progress. The goal is to understand the α- and β-hydrogen elimination mechanisms by calculation of the reaction energetics, activation barriers and geometric features of the pathways.

Insight into the reaction mechanism can be obtained by concentrating on two key questions: (a) the energetics of adsorbed ethyl as it tilts toward the surface and (b) the energetics and geometry of ethylene coadsorbed with hydrogen. We begin with a consideration of ethylene on the surface. When ethylene adsorbs on Ni(1 0 0), several adsorption sites are plausible. Fig. 1 gives the energies for planar and non-planar ethylene at fourfold, bridge and other sites on Ni(1 0 0).

The classical di–σ configuration (C–C axis above an Ni–Ni bond) with the HCH plane of nuclei tilted away from the surface by 20° is found to be strongly bound, $E_{ads}$=8.9 kcal/mol. However, the di–σ configuration at the fourfold site is slightly more stable, $E_{ads}$=9.8 kcal/mol. While the latter result is perhaps surprising, the opportunity to form one di–σ bond with a pair of surface Ni atoms can have advantages over forming a bond with a single Ni atom since there is a different pattern of rupture of surface Ni–Ni bonds. At all sites studied, going from a planar to non-planar ethylene geometry lowers the energy by ∼3 kcal/mol. The ethylene C–C bond lengthens from the gas phase value of 1.35 to 1.43 Å. Fig. 2 shows the energy variation with C–C distance for ethylene adsorbed perpendicular to the bridge site. This is not the preferred ethylene orientation and the C–C bond length does not increase appreciably compared to that of gas phase ethylene. The overall shape of the curve, however, is characteristic of that for other sites and orientations, i.e., the energy increases sharply in going from the equilibrium C–C distance for adsorbed ethylene to a longer distance typical of that for a C–C single bond, 1.53 Å. This observation will be an important factor in explaining what geometry changes must accompany H transfer to the surface to produce ethylene from adsorbed ethyl.

Next we consider adsorbed ethyl. Calculations show that the C–C bond length remains close to that

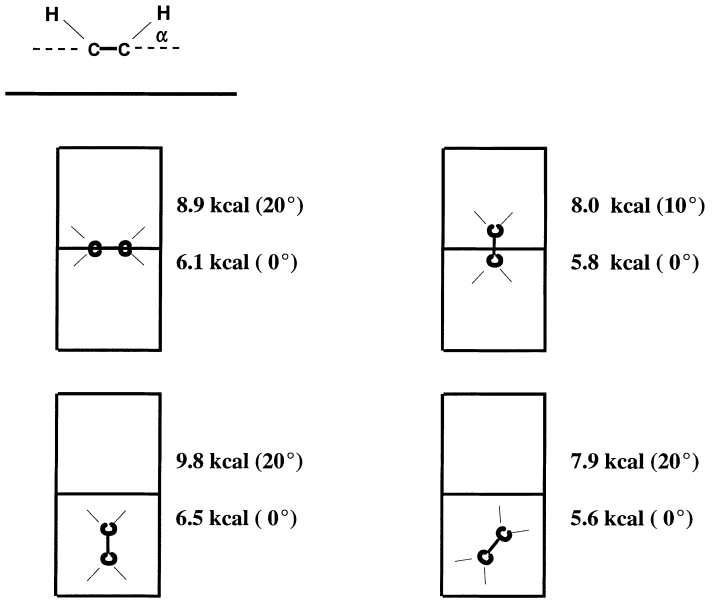


Fig. 1. Ethylene adsorption at several sites on Ni(1 0 0). Energies from embedded cluster calculations are reported for planar and non-planar geometries. For the non-planar geometry, the HCH tilt angle $\alpha$ is 20° from the horizontal, unless otherwise indicated. The C–surface distance is 2.35 Å and the C–C distance is 1.38 Å for the planar cases, and 2.28 and 1.43 Å, respectively, for the non-planar cases. These values correspond to the equilibrium distances for the most favorable adsorption site.

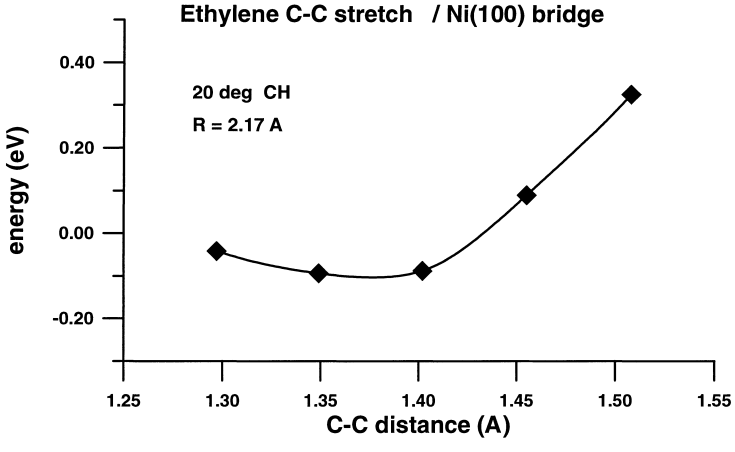


Fig. 2. Ethylene is adsorbed parallel to the Ni(1 0 0) surface at an Ni–Ni bridge site. The C–C bond axis is perpendicular to the Ni–Ni bond. This is not the preferred orientation for adsorption at a bridge site (see Fig. 1) and the graph shows only a slight increase in the C–C bond length compared to ethylene. The HCH plane of nuclei is tilted 20° from the horizontal. The C–surface distance is 2.17 Å.

of a typical single bond. Fig. 3 shows that tilting ethyl toward the surface gives an equilibrium geometry corresponding to a 50° tilt from perpendicular. This tilt angle is primarily a consequence of the nearly tetrahedral orientation of bonds around the α-carbon. On tilting further, the graph shows a sharp increase in energy as a hydrogen on the β-carbon comes too close to the surface. For a tilt angle of 90°, the β-hydrogen

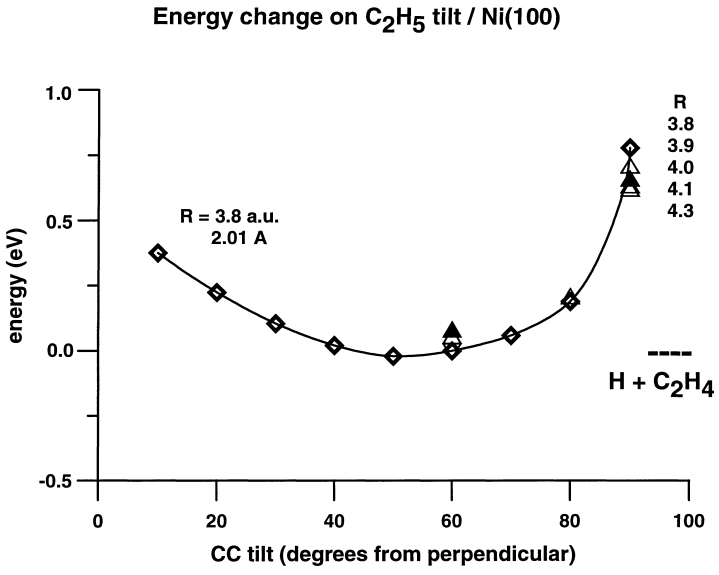


Fig. 3. Ethyl is adsorbed on Ni(1 0 0) at the center of a fourfold site. The equilibrium geometry corresponds to a 50° tilt from the surface normal. The sharp rise in energy at larger tilt angles is due to repulsion between a β-hydrogen and the surface. Symbols at 60° and 90° indicate changes in energy when the distance from the α-carbon to the surface is increased from 3.8 a.u. (2.01 Å). The total energy of H and ethylene coadsorbed at adjacent fourfold sites is indicated.

would be within 0.8 Å of the surface which is much too close for a hydrogen that remains bonded to another atom. For tilt angles of 60° and 90°, other symbols in the figure denote the change in energy when the distance from the α-carbon to the surface is increased. At 60°, the energy increases slightly as the C–surface distance is increased from its equilibrium value. At 90°, the energy decreases as the C–surface distance is increased until the stabilization gained by moving the β-hydrogen away from the surface is matched by the destabilization from the increased C-surface distance.

In Fig. 4, the results for ethyl tilt are shown for a case in which O is coadsorbed at an adjacent fourfold site. The ethyl fragment remains at the center of its fourfold site. The energy variation shown in Fig. 3 of ethyl on Ni(1 0 0) when no O is present is reproduced for comparison. The two curves have the same characteristic shape: ethyl tilts until a β-hydrogen moves too close to the surface or too close to the oxygen. The explanation for the onset of repulsion is the same. Interactions are strongly repulsive when H bonded to another atom is moved into the region of high electron density within the van der Waals radius of either the surface or of an adsorbed atom.

Returning to the surface without coadsorbed oxygen, the total energy of ethylene and H coadsorbed at adjacent fourfold sites on Ni(1 0 0) is indicated on the graph in Fig. 3. The fact that the energy is comparable to that of ethyl on the surface means that the conversion to ethylene would be approximately energetically neutral.

A very favorable case for H transfer from an adsorbed ethyl should be to a coadsorbed O to form OH. If we consider ethyl tilted 50°, a tilt angle before the onset of sharp repulsion (see Fig. 4), the distance from the β- hydrogen to oxygen is 1.69 Å. For OH in its equilibrium geometry on the surface, the O–H distance would be approximately 0.98 Å. If the C–H bond is simply stretched in order to move H toward O the energy increases sharply. For example, the figure shows that for an ethyl tilt of 50°, a C–H stretch that would produce an OH distance of 1.58 Å increases the energy by about 9 kcal/mol. The same is true for the clean surface: starting with the equilibrium geometry of adsorbed ethyl (50° tilt), simply increasing the C–H distance to produce a smaller H–surface distance results in a large increase in energy. Thus, neither the clean surface nor the surface with O coadsorbed provides a strong enough driving force

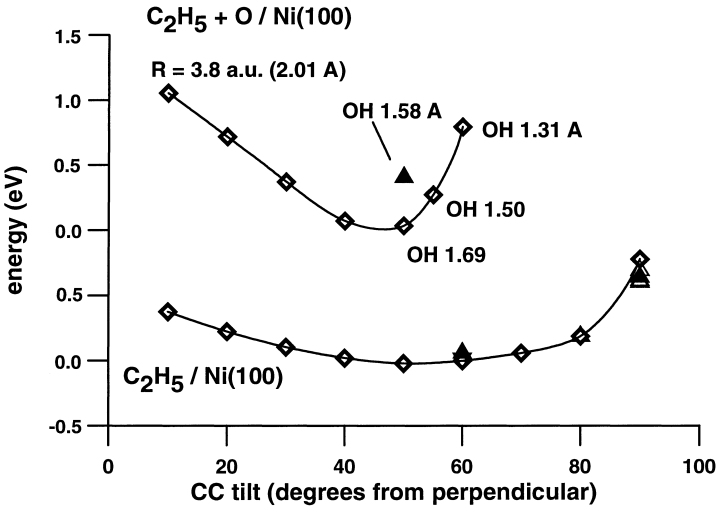


Fig. 4. Ethyl is adsorbed on Ni(1 0 0) at the center of a fourfold site; an O atom is coadsorbed at the adjacent fourfold site. The energy variation with ethyl tilt angle is shown with and without coadsorbed oxygen. For the oxygen case, the sharp rise in energy at larger tilt angles is due to repulsion between a β-hydrogen and oxygen; the OH distances produced by these tilt angles are shown. The case without oxygen is the same as shown in Fig. 3. At 50°, stretching the C–H bond to decrease the OH distance to 1.58 Å results in a large increase in energy (▲). For comparison, the OH distance in adsorbed OH on Ni(1 0 0) is 0.98 Å.

to allow C–H stretch to occur if the remainder of the ethyl group remains rigid.

In order to calculate the energy barrier, it is necessary to allow simultaneously a relaxation of the resulting $–CH_2–CH_2$ geometry as H is transferred to the surface (or to oxygen). As noted earlier, and depicted in Fig. 2, one of the principal coordinates affecting the energy is the C–C distance where a large decrease in energy is expected in going from a single to double bond distance. Studies involving optimization of the geometry of the $–CH_2–CH_2–$ precursor to ethylene, including moving the α-carbon away from the surface and shortening the C–C bond as H is transferred to the surface are underway.

## 4. Photodissociation of methane on platinum

Photochemistry at solid surfaces, induced by direct irradiation of adsorbates, is severely limited by the absorption cross-section and short lifetimes of excited electronic states

$$A_{ads} + h\nu = A^*_{ads}.$$

However, direct excitation of metal electrons followed by transient attachment of emitted electrons to adsorbates can induce desorption or other chemical reactions

$$A_{ads} + h\nu + e = A^-_{ads}.$$

Studies of a variety of photochemical processes at metal surfaces have been reported [14–22].

First-principles studies of excited electronic states or resonances of complex adsorbates on metals are not yet available, and there is a lack of quantitative understanding of transient species resulting from electron excitation of adsorbates.

Recent experimental studies of methane physisorbed on Pt(1 1 1) by Matsumoto and coworkers [7,8] have shown that 193 nm radiation absorbed by the metal can cause dissociation of methane to $CH_3$ and H. Since the polarization dependence does not follow that of the metal, they interpret their results as implying the formation of a local surface complex as opposed to a substrate mediated process.

Ab initio embedded cluster calculations that should prove helpful in understanding the photodissociation mechanism are in progress. In the present work, we consider a simple model system: a ring of 10 Pt atoms interacting with $CH_4$. Configuration interaction theory is used to sort out the states of interest from lower energy states corresponding to metal excitations. The

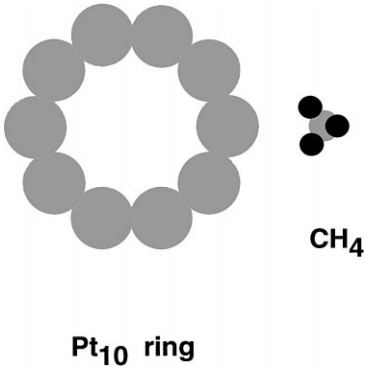


Fig. 5. The $Pt_{10}$ ring model used to study interactions of Pt with $CH_4$. The ring nuclei, carbon and two hydrogens lie in the same plane. The other two hydrogens are located above and below the plane in the tetrahedral geometry of gas phase methane.

model is depicted in Fig. 5. In all calculations, the Pt ring nuclei, the methane C and two H atoms lie in the same plane. The other two methane hydrogens, located above and below this plane, are kept in the tetrahedral geometry of gas phase $CH_4$.

The objectives are as follows: (a) to locate and characterize excited states, and in particular to distinguish between ring excitations and electron attachment to form $CH_4^-$ and (b) to calculate the potential energy curves for ground and excited states as a function of Pt–$CH_4$ distance, and CH stretch and bending distortions.

We begin with a self-consistent-field solution of the electronic structure of the $Pt_{10}$–$CH_4$ positive ion. This solution, after adding an electron back to an unoccupied virtual orbital of the positive ion, shows excited states at −0.01, −0.03, −0.04, −0.13, −0.17 and −0.21 a.u. below the ionization limit. The −0.01 a.u. level corresponds to electron attachment to $CH_4$ in which a C 3s Rydberg-like orbital is occupied. The lower lying electronic states correspond to Pt ring excitations in which only very small C or CH contributions occur.

We denote the electron attachment state as $CH_4^-$. If the Pt–C distance is less than the distance corresponding to physisorption, i.e., a distance within the van der Waals limit, the charge distribution of the Pt ring 6s band changes so as to form an image charge on the Pt atoms near $CH_4^-$. In addition, the Pt atom closest to $CH_4^-$ undergoes a change in 5d–6s hybridization such that the 6s density is depleted and the 5d density is increased. This rehybridization provides a way to increase the attractive interactions between the ring and $CH_4^-$ by decreasing the size of the Pt atomic density and thereby the Pauli repulsion with $CH_4^-$.

Excited electronic states of the $Pt_{10}$–$CH_4$ system are calculated by configuration interaction

$$\Psi = \sum_k \lambda_k \det(\chi_1^k \chi_2^k \cdots \chi_n^k) = \sum_k \lambda_k \Phi_k.$$

The electronic configuration, $\Phi_r$, corresponding to $Pt_{10}^+ CH_4^-$ is formed from the SCF solution mentioned previously. Single and double excitations from this single determinant wavefunction are then generated:

$$\Psi_r = \Phi_r + \sum_{ik} \lambda_{ik} \Gamma_{i\to k} \Phi_r + \sum_{ijkl} \lambda_{ijkl} \Gamma_{ij\to kl} \Phi_r.$$

All configurations, $\Phi_k$ , that interact with $\Phi_r$ such that

$$|\langle \Phi_k | H | \Phi_r \rangle|^2 / |E_k - E_r| > 10^{-4} \text{ a.u.}$$

are retained in the CI expansion. This procedure assures that the representation of the excited state, $\Psi_r$, is orthogonal to and non-interacting with intervening excited states, at least within the CI space considered. When $\langle \Psi_k | H | \Psi_r \rangle = 0$ and $\langle \Psi_k | \Psi_r \rangle = 0$ for all lower energy states, $\Psi_k$, then the energy of $\Psi_r$ is an upper bound to the exact energy.

The variation in energy of the ground and excited states with distance of $CH_4$ from the Pt ring is shown in Fig. 6. In these calculations, the $CH_4$ molecule is kept in its gas phase geometry. The ground state exhibits increased repulsion with decreasing distance typical of that for a rare gas atom or saturated molecule approaching a surface. However, the $Pt_{10}^+ CH_4^-$ curve, corresponding to Rydberg-like attachment of an electron to $CH_4$, shows a slight decrease in energy with decreasing distance. Energies of other states corresponding primarily to ring excitations are shown as dots in the figure.

We now consider stretching one of the CH bonds by a factor of 1.2; the energy variation for a Pt–C distance of 2.5 Å is shown as an inset (▲) in Fig. 6. Moving to the left in the inset corresponds to a 20% increase in CH distance. The energy increase with increasing CH distance is found to be approximately the same for the excited state as for the ground state; thus, the CH bond is not weakened in the excited state even at a Pt–C distance of 2.5 Å.

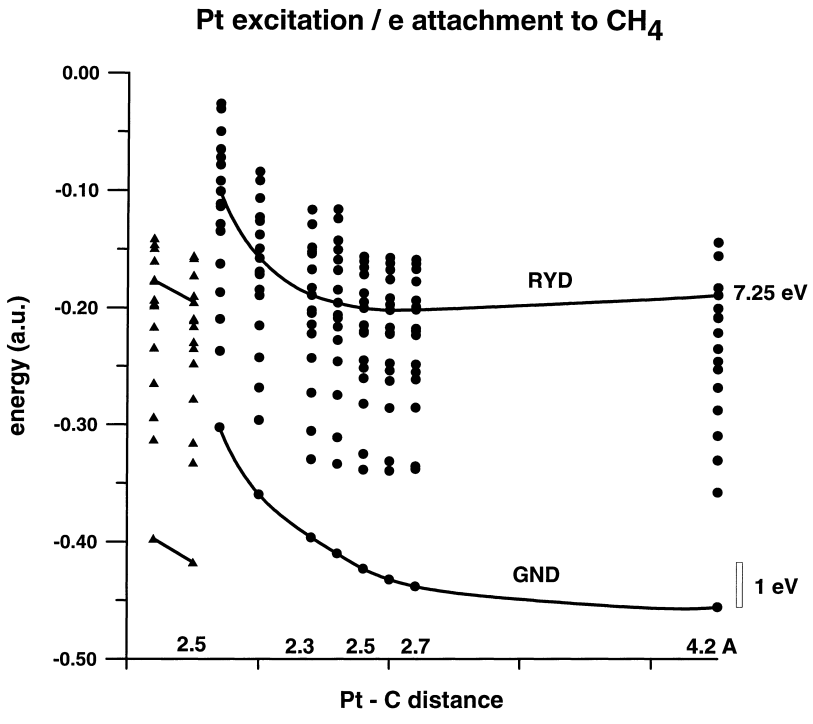


Fig. 6. Ground and excited states of $Pt_{10}$–$CH_4$. The energies as a function of Pt–C distance of the ground state and the excited state formed by electron attachment to a Rydberg-like orbital of $CH_4$ are shown by solid lines. Energies of other states are shown (●). The inset (▲) depicts the increase in energy when a single CH bond of methane (at a Pt–C distance of 2.5 Å) is stretched 20% from a starting value of 1.09 Å.

In Fig. 7, the energy variation with HCH bending (◆) is shown for a Pt–C distance of 2.4 Å. The energy decreases with increasing HCH angle. For the ground state surface the decrease is insufficient to offset the $CH_4$–surface repulsion. However, for the $Pt_{10}^{+}\,CH_4^{-}$ excited state, the increase in HCH angle lowers the Pt–C energy minimum. As $CH_4$ approaches the surface in the $Pt_{10}^{+}\,CH_4^{-}$ excited state, it follows that CH vibrations are activated. If the system now returns to the ground state two possibilities arise: $CH_4$ can be repelled from the surface by moving along the repulsive potential of the ground state, or the vibrationally hot $CH_4$ can dissociate.

In summary, although the Pt ring is a very simple model, if $CH_4$ dissociation were to occur at an atop Pt atom surface site, the model captures some of the essential features of a real surface. Development of an image charge is allowed and local changes in bonding such as 5d–6s rehybridization on Pt can occur during the course of the reaction. For the present model, steps in the photodissociation process are as follows:

1. Absorption of a photon creates a $CH_4$–metal complex with an energy near the ionization limit (work function) of the metal. This state can be described as an electron attachment to $CH_4$ through a Rydberg-like orbital.
2. The $CH_4^{-}$ is attracted by the surface image charge and local changes in the electronic structure of Pt are induced when $CH_4$ comes close to the surface.
3. Dissociation on the excited state surface does not occur since CH stretch is as difficult in the excited state as in the ground state.
4. CH bending vibrations are activated in the excited state.
5. $CH_4$ (vibrationally hot) returns to ground state.
6. Dissociation occurs on the ground state surface.

## 5. Concluding remarks

Since completion of this work, studies of the conversion of ethyl to ethylene on Pt(1 0 0) have been

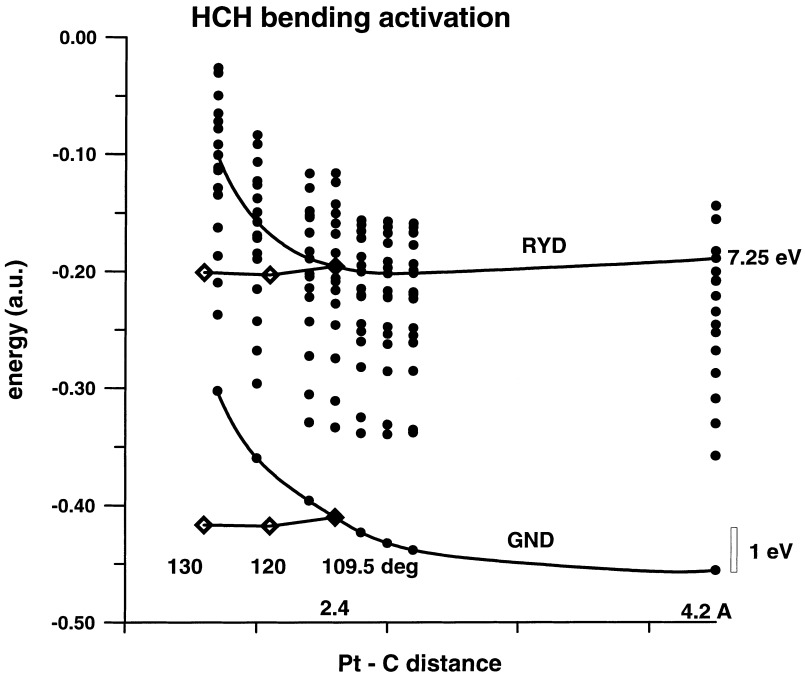


Fig. 7. Ground and excited states of $Pt_{10}$–$CH_4$. The variation in energy with Pt–C distance is the same as in Fig. 6. At a Pt–C distance of 2.4 Å, an increase in HCH angle from 109.5° to 120° and 130° decreases the energy. The energy increases sharply on further increases in angle.

carried out and the barrier to β-hydrogen transfer has been calculated for both nickel and platinum surfaces [23]. The potential curve for tilting ethyl toward the Pt(1 0 0) surface is similar to that found for Ni(1 0 0); however, the barrier is reduced from a value of 17 kcal/mol for Ni(1 0 0) to 14 kcal/mol on Pt(1 0 0). Studies have also been completed on the photodissociation of methane on an embedded cluster model of Pt(1 0 0) [24]. Interestingly, the results are found to be qualitatively similar to those found for the ring model reported in this work.

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