Theoretical Calculations of Dissociative Adsorption of CH_4 on an Ir(111) Surface

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The activation energy for chemisorption of CH_4 at an Ir(111) surface is determined using density functional theory combined with an estimate of the long range dispersion interaction. The results are found to be in good agreement with published results of bulb and beam experiments analyzed with a precursor model. A surprisingly large surface relaxation is found where an Ir surface atom is displaced outwards by as much as 0.6 Å. A strongly bound *molecular state* at kinks and adatoms involving η^2-H, H bonding was also found.

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Alkanes are potentially an important source of raw material for the petrochemical industry. However, the severe reaction conditions currently required to activate the strong bonds in hydrocarbons make selective catalysis difficult. The dissociative adsorption of alkanes on transition metal surfaces is a key step in the catalytic process. Improved insight into the fundamental mechanism is important for development of selective conversion of small hydrocarbons to chemicals of greater value. Extensive experimental measurements have been carried out in the last decade on various transition metal surfaces [1–7]. Much of the work has focused on Ir(110) and Ir (111) surfaces [2,4,6]. Theoretical studies have also been done, both on the energetics [8–10] and on the dynamics [11–13], but it is still unclear what the basic mechanism of alkane dissociative adsorption is, especially under temperature and pressure conditions relevant to industrial catalysis. The interpretation of experimental measurements is, in some cases, also controversial.

Seets *et al.* have carried out extensive experimental studies of the initial, zero-coverage dissociative sticking of CH_4 on Ir(111), using both bulb experiments and molecular beam experiments [6]. The surface temperature was kept high, between 900 and 1100 K. Since the dissociative adsorption probability is low, less than one in one thousand collisions of a CH_4 molecule with the surface lead to dissociative adsorption. The gas near the surface is, therefore, expected to heat up to the surface temperature before most of the dissociative sticking events. We will assume the methane gas is thermally equilibrated with the surface in our calculations. Under such conditions, transition state theory (TST) can be applied. For H_2 sticking on Cu(110) it has been shown that TST gives an excellent approximation (within a factor of 2) of the exact, classical dynamical result [14].

In the high energy molecular beam experiments, Seets *et al.* observed the typical increase of the dissociative sticking probability with beam energy, indicating a direct mechanism where the initial kinetic energy of the molecule helps overcome the activation energy barrier to dissociation. The sticking probability increased gradually by 4 orders of magnitude as the energy was increased from 0.1 to 1.2 eV. It is unclear how to interpret such data in terms of the energy surface describing the interaction of the CH_4 with the surface. At high beam energy, the trajectories of the dissociating CH_4 molecules are probably not close to the optimal path characterizing dissociative adsorption in the low energy range relevant for thermal activation. A novel feature of the beam experiments of Seets *et al.* was their ability to lower the beam energy to very small values. At low energy, a drop in the sticking coefficient was observed with beam energy. Such a behavior can be ascribed to a precursor mechanism. Seets *et al.* analyzed their data in terms of a precursor model and extracted the ratio of the rate of desorption to the rate of chemisorption from the precursor state. More recently, an analogous drop in sticking probability with beam energy was observed in CH_4 dissociation on Pt(110), but there it was attributed to steering rather than precursor effects [7].

We calculated the minimum energy path (MEP) [14] for CH_4 dissociation on Ir(111) using density functional theory (DFT). The path connects the CH_4 molecule above the surface to the dissociated H and CH_3 fragments adsorbed on the surface. Within the harmonic approximation to TST, the activation energy for sticking is given by the highest maximum on the MEP, a saddle point on the energy surface. The calculated activation energy can be compared directly with the activation energy deduced from the bulb experiments. We have also estimated the depth of the physisorption well and this can be compared indirectly with the results of the beam experiments. Our calculations do not include tunneling as a possible adsorption mechanism. For H_2 dissociation on Cu(110), it has been estimated that tunneling becomes important below 400 K [14,15], a much lower temperature than used by Seets *et al.*

The DFT calculations were carried out using the PW91 functional [16]. Ultrasoft pseudopotentials were used [17] with a 350 eV energy cutoff in the plane wave representation of the wave function. The calculations were done with the VASP code [18]. The Ir metal was represented by a slab including up to six layers with 12 atoms per layer. It was found to be sufficient to use only the gamma point in the k-point sampling for this large simulation cell. The minimum energy path was calculated using the nudged elastic band (NEB) method [19,20] with eight images of the system forming a discretization of the path between the fixed end points. The exact location of the saddle point and, thereby, the value of the activation energy barrier was found by first interpolating the energy and force between the images and then refining the estimate with the dimer method [20,21].

Several calculations of dissociative adsorption of molecules on surfaces have been carried out in the last few years, using both wave function based methods and DFT. These calculations have provided a great deal of insight and helped answer long standing questions about the interpretation of experimental measurements. The surface has either been represented with a small metal cluster [8,10] or by using slabs [9,22–24]. A particularly great effort has been made to model both energetics and quantum dynamics of H_2 dissociative adsorption on Cu surfaces [25]. In these previous studies, only small surface relaxations have been observed. In several of the calculations the surface has, in fact, been kept rigid to reduce computational effort. Given that the dissociative sticking probability of CH_4 on Ir(111) has been observed to be strongly dependent on surface temperature, we have investigated the importance of substrate relaxations. This requires a large simulation cell and makes the calculations more tedious.

The optimal bonding of the dissociated fragments H and CH_3 on the Ir(111) surface was found to be on top of Ir atoms, 2.88 eV and 2.27 eV, respectively. The H atoms can also bind at bridge sites, but the binding there is 0.05 eV weaker.

We calculated the MEP from an initial state where the CH_4 molecule is 4.3 Å above the surface and a final state where the dissociated fragments are sitting on adjacent on-top sites. The results are shown in Fig. 1. An exponential rise in the DFT energy is observed as the molecule approaches the surface. The barrier for dissociation is found to be 0.3 eV with respect to the molecular state far from the surface. The saddle point configuration is shown in Fig. 2. The long range dispersion energy is not included in the DFT/PW91 calculations because of the semilocal description of correlation. A physisorption well is, therefore, not obtained from the DFT/PW91 results.

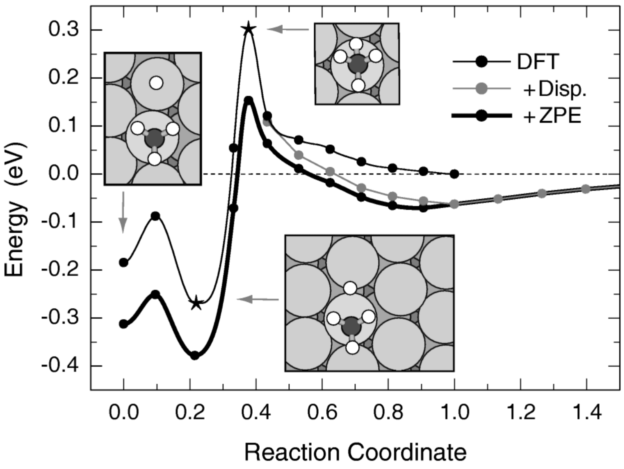

FIG. 1. The minimum energy path for dissociation. Results of DFT/PW91 calculations (thin solid line), with an estimate of long range dispersion interaction added (gray line) and with zero point energy correction also added (thick solid line). The CH_4 molecule 4.3 Å above the surface plane corresponds to a reaction coordinate of 1.0, while the adsorbed H and CH_3 fragments correspond to 0.0. The maximum ($\star$) was found by the dimer method.

The height of the barrier turns out to be highly sensitive to the size of the simulation cell. The dependence on the number of layers in the slab is shown in Fig. 3. When only three layers are included in the slab, the calculated activation energy is 3 times higher. This is due, in part, to a large relaxation of the surface. The underlying Ir atom moves out normal to the surface and has been displaced by 0.41 Å at the saddle point. Further along the MEP, when the molecule is slightly closer to the surface, the Ir atom is displaced outwards by as much as 0.6 Å. Such a large surface relaxation has not been reported in previous calculations of dissociative adsorption. The energy required to distort just the surface to the saddle point configuration is 0.30 eV. This is consistent with the large effect surface temperature has on the measured sticking probability, even in the higher energy regime where the dissociation is direct [6]. The reason for the large outward displacement is likely an upward shift of the d-electron band which strengthens the bonding with the dissociating molecule [23].

After the CH_4 molecule comes apart, a deep minimum is observed in the path. This was already evident from the NEB calculation, but further relaxation of the configuration obtained by interpolation between the images in the NEB gave a converged minimum at nearly -0.3 eV (see Fig. 1). This configuration is more stable than binding of the dissociated fragments on adjacent on-top sites.

Long range, zero overlap dispersion energy needs to be added to the DFT calculations. The leading term in the asymptotic expansion of the dispersion interaction is C_3/z^3 where z is the distance from the surface [26]. The

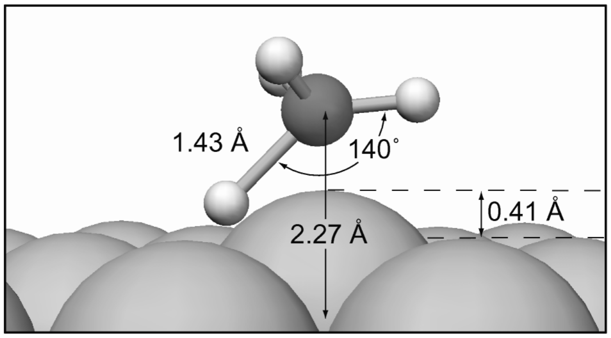

FIG. 2. The configuration of atoms at the saddle point. Note the large displacement of the underlying Ir atom normal to the surface, 0.41 Å.

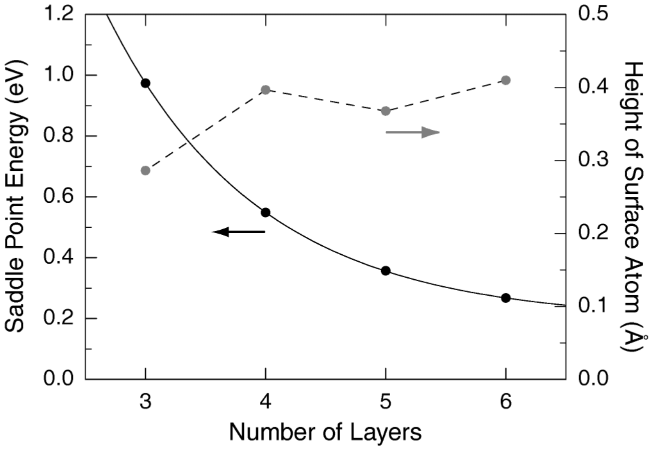

FIG. 3. An exponential drop in the activation energy calculated with DFT occurs when the number of layers in the Ir slab is increased from three to six (solid line). The extent of the displacement of the underlying Ir atom normal to the surface also increases as more layers are added, although not monotonically (dashed line).

C_3 coefficient can be estimated from the polarizability of the CH_4 molecule and the dielectric function of the metal using the Lifshitz formula [27]. In the simplest approximation C_3 is proportional to the static polarizability of the molecule. We have estimated the value of the C_3 coefficient for CH_4/Ir(111) by scaling the value for He/Au(111) [26] (taking Au to be an analog for Ir) with the ratio of the polarizability of CH_4 and He (a factor of 12.6). This gives $C_3 = 3.45\ \mathrm{eV}/\text{Å}^3$.

Close to the surface, where the electron wave function of the CH_4 and Ir start to overlap, the asymptotic expansion gives an overestimate of the dispersion energy. Also, because of the large displacement of one of the Ir surface atoms during the dissociation, the atomic structure of the surface needs to be taken into account when calculating the dispersion interaction. While the dielectric response of the Ir surface should contain contributions from both localized d electrons and delocalized s electrons [28], we have approximated the response entirely in terms of a localized oscillator at each Ir atom and cast the dispersion interaction in terms of a superposition of c_6/r^6 contributions (where r is C-Ir atom distance), as has been done previously for He/metal and semimetal interactions [29]. By matching the long range behavior, the estimate of the C_3 coefficient gives a c_6 coefficient of $7.2\ \mathrm{eV}/\text{Å}^3$ for the induced dipole-induced dipole interaction between the CH_4 and each one of the local oscillators. Higher multipole interactions, such as the induced quadrupole-induced dipole, etc. terms, are effectively taken into account by simply increasing the c_6 coefficient by 20%. The dispersion interaction is turned off as the C atom approaches the outermost Ir atom by using a damping function which has proved to be successful in calculations of atom-atom and atom-molecule interactions [30–32]. Figure 1 shows the estimated dispersion energy.

The vibrational zero point energy (ZPE) of CH_4 is large because of the small mass of the H atoms and the high vibrational frequency. At the saddle point, one of the modes has negative curvature so the corresponding contribution to the ZPE is lost. This effectively lowers the activation energy for chemisorption. We have calculated the Hessian matrix and diagonalized to find the normal modes at each NEB image along the MEP. The change in the total ZPE as compared with the gas phase molecule is then added as a correction to the DFT calculation (see Fig. 1). The ZPE correction is largest at the saddle point (lowered by 1.4 eV) and beyond but is also significant when the molecule is quite far from the surface. The physisorption well has a depth of 0.07 eV with the minimum energy at $z = 4.1$ Å. The depth of the well is within the estimate 0.08 ± 0.04 eV derived from the experimental data of Seets *et al.* using both bulb and beam results: the former giving the activation energy of chemisorption with respect to the physisorbed state ($E_c = 0.28$ eV), and the latter giving the difference between the activation energy of chemisorption and desorption ($E_c - E_d = 0.20$). The good agreement with the results of Seets *et al.* lends support for their interpretation of the molecular beam data in terms of a precursor model. The barrier to go from the physisorbed state to the chemisorbed state is estimated to be 0.23 eV. Typically DFT calculations of barriers are quoted to have an error bar of 0.1 eV. Our results are, therefore, in excellent agreement with the experimental estimate of 0.28 ± 0.04 eV. (A recent theoretical estimate based on cluster calculations gave a much higher barrier, 0.79 eV [10].)

We have also studied the interaction of CH_4 with defects on the Ir(111) surface: a kink and an Ir adatom. The DFT results alone give an energy well corresponding to a strongly bound *molecular* state at the least coordinated Ir atom. The binding energy at the kink on the B-type step edge and at the adatom is 0.22 eV while the binding at the kink on the A-type edge is 0.18 eV. This binding is 3 times stronger than the physisorption well at the flat terrace. This suggests that chemical bonding is taking place between a CH_4 molecule and a highly undercoordinated Ir atom. At the kink, the distance between the C atom and the Ir atom is only 2.5 Å, much closer to the chemisorbed methyl (2.1 Å) than the physisorbed methane (4.1 Å). The Ir-C distance is so short, in fact, that the long range dispersion interaction correction has become negligible. One of the H-C-H bond angles has opened up to 116°. Two of the four H atoms are pointed towards the undercoordinated Ir atom (at the B kink the Ir-H distances are 2.0 Å and 2.3 Å).

Such chemical bonding of methane and other alkanes is well known from studies of transition metal complexes and is referred to as η^2-H, H bonding [33]. A similar strong molecular state has been seen experimentally and by DFT calculations of H_2 on a stepped Cu surface [34]. This strongly bound molecular state could play an important role in precursor mediated mechanisms at low temperature where the lifetime is long enough for the CH_4 molecules to sample the surface and find defects (the high surface temperature in the experiments of Seets *et al.* [6] would prevent this). We find, however, that the activation energy for dissociation at the adatom is not lower than at the terrace site.

The strong molecular binding at kinks is relevant to the possibility of using high index surfaces with periodic arrays of kinks for enantiomeric separation [35]. Our results indicate that larger, chiral alkanes and their derivatives could interact more strongly with kinks and more specificity than if the attractive interaction were purely due to long range dispersion interaction.

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