

# Methane Activation on Pt and Pt<sub>4</sub>: A Density Functional Theory Study

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The activation mechanisms of a methane molecule on a Pt atom (CH<sub>4</sub>–Pt) and on a Pt tetramer (CH<sub>4</sub>–Pt<sub>4</sub>) were investigated using density functional theory (B3LYP and PW91) calculations. The results from these two functionals are different mostly in predicting the reaction barrier, in particular for the CH<sub>4</sub>–Pt system. A new lower energy pathway was identified for the CH<sub>4</sub> dehydrogenation on a Pt atom. In the new pathway, the PtCH<sub>2</sub> + H<sub>2</sub> products were formed via a transition state, in which the Pt atom forms a complex with carbene and both dissociated hydrogen atoms. We report here the first theoretical study of methane activation on a Pt<sub>4</sub> cluster. Among the five single steps toward dehydrogenation, our results show that the rate-limiting step is the third step, that is, breaking the second C–H bond, which requires overcoming an energy barrier of 28 kcal/mol. On the other hand, the cleavage of the first C–H bond, that is, the first reaction step, requires overcoming an energy barrier of 4 kcal/mol.

## 1. Introduction

Methane, as one of the most important chemicals, has been widely used in chemical synthesis, hydrogen production, and energy production. As such, methane activation has been studied extensively by both experimentalists and theorists. The first direct observation of methane activation by unsupported or bare Pt clusters of 2–24 atoms was made using time-of-flight mass spectroscopy by Trevor et al. in 1990.<sup>1</sup> The experiment showed that the most reactive neutral clusters are Pt<sub>2</sub>–Pt<sub>5</sub>, while other clusters Pt<sub>6</sub>–Pt<sub>24</sub> are less reactive, and the Pt atom is less reactive by at least 1 order of magnitude. Among the Pt<sub>2</sub>–Pt<sub>5</sub>, the reactivity oscillates with the trimers and pentamers being slightly more active.

Since then, many studies have been carried out on the activation of methane molecules on neutral, cationic, and anionic Pt clusters.<sup>2–59</sup> In the experimental studies using the Fourier-transform ion cyclotron resonance mass spectrometer on methane dehydrogenation on anionic and cationic Pt clusters of 1–5 atoms,<sup>6,7,34,56</sup> the catalytic activity of Pt tetramers was the most controversial with respect to the other cluster sizes. In the experiment by Achatz et al.,<sup>34</sup> the researchers found that anionic Pt<sub>4</sub> clusters have the maximum activity on methane activation. In the most recent work by Adlhart and Uggerud,<sup>6</sup> however, the anionic Pt<sub>4</sub> clusters were found to be less active than the Pt<sub>2</sub> and Pt<sub>3</sub> clusters. Both experiments by Achatz et al.<sup>34</sup> and by Koszinowski et al.<sup>56</sup> showed that the cationic Pt<sub>4</sub> clusters were the least active. Therefore, theoretical studies of methane activation on Pt<sub>4</sub> clusters are necessary to further understand the methane activation process on Pt clusters.

Theoretical investigations have been made for methane dissociation on a Pt atom,<sup>2–4</sup> Pt dimer,<sup>4</sup> and Pt trimer<sup>5</sup> as well. Very recently, Xia and Cao reported their density functional theory (DFT) studies of methane activation on a cationic Pt tetramer.<sup>57</sup> It was found that the cationic Pt<sub>4</sub> is less active than the Pt<sub>2</sub> and Pt<sub>3</sub> clusters toward the dehydrogenation of methane. In this paper, we report the DFT results on the methane

activation on a neutral Pt tetramer. Two functionals, B3LYP and PW91, were used in our study. We obtained the methane dehydrogenation pathway on a tetrahedral Pt<sub>4</sub> cluster.

To make better comparisons with the previous theoretical work on CH<sub>4</sub> activation on neutral Pt clusters,<sup>2–5</sup> we also carried out DFT calculations for CH<sub>4</sub> activation on a Pt atom. In the work by Carroll et al., it has been shown that CH<sub>4</sub> dehydrogenation on a neutral Pt atom cannot take place at room temperature due to a huge energy barrier, that is, >60 kcal/mol, and the four-centered transition state being above the reactant asymptote by 31 kcal/mol.<sup>3</sup> In the present study, we found a lower energy pathway toward dehydrogenation, in which the reaction proceeds via a three-centered transition state where the Pt atom forms three bonds with carbene and both dissociated hydrogen atoms.

## 2. Computational Details

Full geometry optimizations for reactants, intermediates, transition states, and products, as well as frequency calculations, were performed using the B3LYP functional,<sup>60,61</sup> implemented in the Gaussian 03 program.<sup>62</sup> The relativistic effective core potential (ECP) of the Los Alamos National Laboratory 2 (LANL2) was used to describe the 60 core electrons of a Pt atom.<sup>63–65</sup> The 5s, 5p, 5d, and 6s valence electrons of the Pt atom were described with split-valence (double- $\xi$ ) basis sets. A rather large basis set, that is, aug-cc-PVTZ, was used for carbon and hydrogen atoms due to the large variation in hydrogen and carbon distances in several transition states along the reaction pathways.<sup>66,67</sup> To examine the effect of the choice of the exchange-correlation functional and the basis set, we calculated the properties of PtH and PtC species. Our calculation for Pt–C (X<sup>1</sup> $\Sigma^+$  state) gave the bond distance of 1.686 Å, which is in good agreement with the experimental value of 1.679 Å.<sup>68</sup> The calculated dissociation energy of PtC is 138.1 kcal/mol, which agrees fairly well with the experimental value of 145.3  $\pm$  1.5 kcal/mol.<sup>69</sup> Our calculated bond length for the PtH molecule is 1.527 Å, which is in great agreement with the experimental value of 1.5285 Å.<sup>70</sup> The calculated dissociation energy for the PtH molecule is 83.4 kcal/mol and agrees fairly

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with the experimental value of 74.6 kcal/mol.<sup>70</sup> As for the errors that may be introduced by the use of unbalanced basis sets, that is, using triple- $\zeta$  for C and H but double- $\zeta$  for Pt, our tests show that the difference between using the mixed basis set and using the double- $\zeta$  set for all atoms is less than 0.006 Å in bond distance and less than 1.3 kcal/mol in energy for PtH and PtC species.





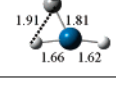

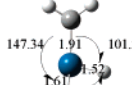

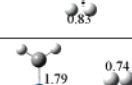

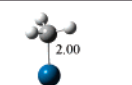
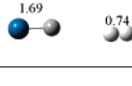
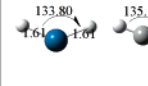
To further examine the effect of the choice of basis sets and the exchange-correlation functionals, single point calculations using the structural data obtained from the B3LYP calculations for all of the reactants, intermediates, transition states, and products were performed using PW91,<sup>71</sup> encoded in the Vienna ab initio simulation package (VASP).<sup>72–74</sup> Furthermore, full geometry optimizations for the reactants, intermediates, transition states, and products were performed using PW91. The electron–ion interactions were described by the ultra-soft pseudopotential.<sup>75</sup> The relativistic effect of Pt atoms was incorporated in the ultra-soft potential. A cutoff energy of 300 eV was employed for the plane wave basis set, which was shown to be sufficient from the convergence test. One  $k$  point, that is, the  $\Gamma$  point, was used in the calculations. To eliminate the interactions between neighboring images, we ensured that the distance between two images is no less than 1.0 nm, and the convergence test showed that this choice is sufficient. We also calculated the bond distances and dissociation energies of the ground-state PtH and PtC molecules using the PW91 functional. The bond distance is 1.531 Å for PtH and 1.700 Å for PtC, which are in good agreement with our B3LYP data of 1.527 and 1.686 Å, respectively. The dissociation energy is 82.3 kcal/mol for PtH, which agrees well with the B3LYP results of 83.4 kcal/mol. The PtC dissociation energy is 151.7 kcal/mol, which agrees fairly with the B3LYP value of 138.1 kcal/mol.

### 3. Results and Discussion

**3.1. Methane Activation on a Pt Atom.** The results obtained from our B3LYP and PW91 calculations for the CH<sub>4</sub>–Pt system are summarized in Table 1. Before discussing the methane activation pathways, we would like to compare the results obtained by B3LYP and PW91 calculations. First, both calculations provided similar structures, but the energies of these structures can be very different. For instance, the PW91 and B3LYP gave very close energies for the triplet adduct configuration. However, there is an energy difference of 4.95 kcal/mol between the two methods for the singlet adduct configuration. An even larger energy difference, that is, 12.32 kcal/mol, exists between the two methods for (H)<sub>2</sub>–Pt–CH<sub>2</sub>. The discrepancy between the two methods exists profoundly in the calculations of transition states. For instance, the PW91 calculations provided lower barrier heights than the B3LYP calculations for the first two transition states, that is, TS1 and TS2, while the B3LYP barrier height for the third transition state, TS3, is smaller than the PW91 result. As for the products, the PW91 energy for the products PtH<sub>2</sub> + CH<sub>2</sub> is 25 kcal/mol higher than the B3LYP value. Because the comparisons will be made between our results and the previous work on the CH<sub>4</sub> activation on the neutral Pt–Pt<sub>3</sub> clusters, which were studied using B3LYP, in what follows, we will discuss the results based on the B3LYP calculations.

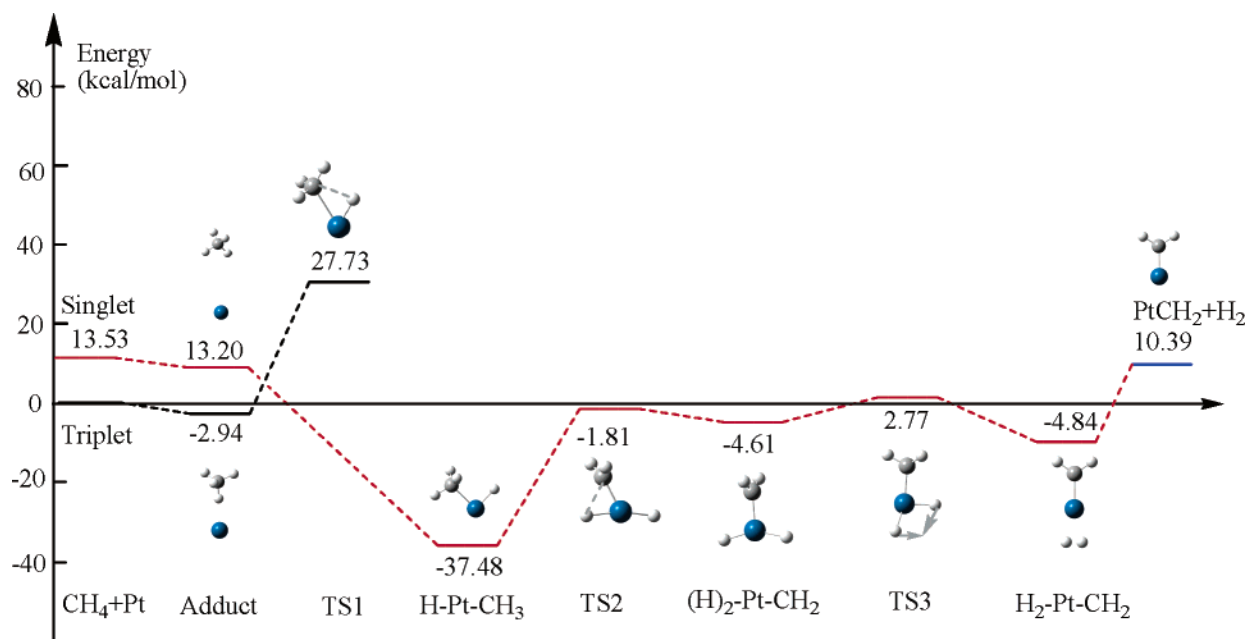
Methane dehydrogenation in the presence of a neutral Pt atom has been investigated experimentally<sup>1</sup> and theoretically.<sup>3,4</sup> The reaction pathway based on our B3LYP calculations was plotted in Figure 1. The ground-state Pt atom, <sup>3</sup>D (d<sup>9</sup>s<sup>1</sup>), is triplet, while the singlet Pt atom, <sup>1</sup>S (d<sup>10</sup>), is above the triplet state by 13.53 kcal/mol. A CH<sub>4</sub>–Pt adduct was formed as the methane

**TABLE 1: Relative Energies (kcal/mol) of Intermediates, Transition States, and Products for CH<sub>4</sub> Activation on a Pt Atom Calculated by B3LYP and PW91 Functionals<sup>a</sup>**

Name	Structure	B3LYP	PW91 (without relaxation)	PW91 (with relaxation)
Singlet Asymptote	CH <sub>4</sub> + Pt(singlet)	13.53	6.42	6.42
Adduct (Triplet)		-2.94	-2.45	-2.57
Adduct		13.20	8.18	8.19
TS1 (Triplet)		27.73	17.87	N/A
H-Pt-CH <sub>3</sub>		-37.48	-45.58	-45.64
TS2		-1.81	-14.42	-14.46
(H) <sub>2</sub> -Pt-CH <sub>2</sub>		-4.61	-17.03	-17.10
TS3		2.77	-5.08	-9.73
H <sub>2</sub> -Pt-CH <sub>2</sub>		-4.84	-14.53	-14.77
PtCH <sub>2</sub> +H <sub>2</sub>		10.39	6.58	6.54
PtH (Doublet) +CH <sub>3</sub> (Doublet)		27.54	28.54	28.56
PtCH <sub>3</sub> (Doublet) +H (Doublet)		44.39	36.17	36.08
PtC+2H <sub>2</sub>		60.77	58.53	58.56
PtH <sub>2</sub> (Triplet) +CH <sub>2</sub> (Triplet)		76.52	102.13	102.13

<sup>a</sup> The structural information (in Å and deg) refers to B3LYP results. The PW91 relative energies were calculated with the B3LYP structures and with structural relaxation. The structures without explicit electronic state shown are in the singlet states. The energy reference is the triplet reactant asymptote, that is, Pt (triplet state) and CH<sub>4</sub>.

molecule approached the triplet Pt atom, and this triplet adduct is 2.94 kcal/mol below the (triplet) reactant asymptote. The C–H bond close to the Pt atom is lengthened slightly in the triplet adduct. On the other hand, the singlet adduct is weakly bound at only 0.33 kcal/mol below the singlet reactant asymptote but



**Figure 1.** The CH<sub>4</sub> activation pathway to form PtCH<sub>2</sub> + H<sub>2</sub>. The energy of the reactants, for example, Pt (triplet state) and CH<sub>4</sub>, is set as the reference energy. The black lines are for triplet electronic states, and the red lines are for singlet states. The data and structures were obtained from the B3LYP calculations.

is 13.20 kcal/mol above the (triplet) reactant asymptote. No significant C–H bond stretch was found in the singlet adduct. To break the first C–H bond, our calculation showed that the triplet adduct has to overcome a transition state (TS1) with the energy barrier of 30.67 kcal/mol. Obviously, this is not energetically favored. Alternatively, the singlet adduct can form an intermediate H–Pt–CH<sub>3</sub>, which is 37.48 kcal/mol below the reactant asymptote. Moreover, the Pt–H bond length is 1.52 Å, which is typical for Pt hydride, and the Pt–C bond length is 1.99 Å. These suggest that the first C–H activation takes place most likely through a crossover between the singlet and triplet potential surfaces. The above conclusion and the reaction pathway leading to the formation of the intermediate H–Pt–CH<sub>3</sub> agree well with those from the previous studies.<sup>3,4</sup> Furthermore, the work by Carroll et al.<sup>3</sup> showed that the energy at the crossing point is only 1.2 kcal/mol above the reactant asymptote.

The study by Carroll et al. also indicated that the H<sub>2</sub> elimination in the presence of one Pt atom cannot take place at room temperature due to the large barrier, that is, 62.9 kcal/mol, between the H–Pt–CH<sub>3</sub> intermediate and the products, PtCH<sub>2</sub> and the H<sub>2</sub> molecule.<sup>3</sup> The transition state was found to be 30.9 kcal/mol above the reactant asymptote. In this work, however, we found a lower energy reaction pathway that can lead to the dehydrogenation, as shown in Figure 1. Along the lower energy reaction pathway, an intermediate (H)<sub>2</sub>–Pt–CH<sub>2</sub> was formed, in which the Pt atom bonds with two dissociated H atoms and carbene, and it is 4.61 kcal/mol below the reactant asymptote. Although there is an energy barrier of 35.67 kcal/mol between the two intermediates, that is, H–Pt–CH<sub>3</sub> and (H)<sub>2</sub>–Pt–CH<sub>2</sub>, the reaction is still feasible because the transition state (TS2) is below the reactant asymptote. The next step in the dehydrogenation is the formation of a complex H<sub>2</sub>–Pt–CH<sub>2</sub>, in which the hydrogen molecule bonds weakly to the Pt–CH<sub>2</sub>. The bond distance between the two hydrogen atoms in the H<sub>2</sub> unit is 0.83 Å, which is slightly longer than the H–H bond of H<sub>2</sub> in the gas phase, that is, 0.74 Å. The distance between the Pt and either H atoms in the H<sub>2</sub> unit is about 1.80 Å, which is much longer than the gas-phase Pt–H value of 1.527

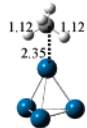
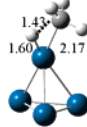
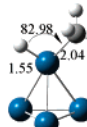
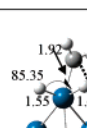
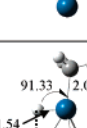
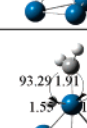
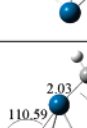
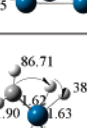
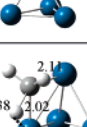
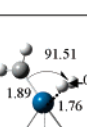
Å that we calculated. It is not surprising that the Pt–C bond of 1.85 Å is also larger than the gas-phase value of 1.686 Å due to the interaction of Pt atom with the H<sub>2</sub> unit. A small energy barrier, for example, 7.38 kcal/mol, has to be overcome to form the H<sub>2</sub>–Pt–CH<sub>2</sub> complex through the transition state (TS3), which is 2.77 eV above the reactant asymptote. As the hydrogenation products, PtCH<sub>2</sub> + H<sub>2</sub>, are 10.39 kcal/mol above the reactant asymptote, methane dehydrogenation in the presence of one Pt atom is endothermic.

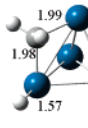
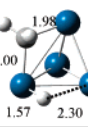
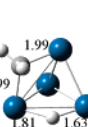
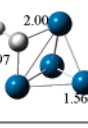
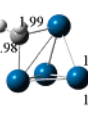
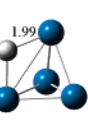
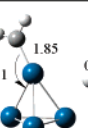
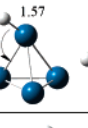
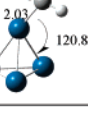
**3.2. Methane Activation on a Pt<sub>4</sub> Cluster.** To the best of our knowledge, we report here the first theoretical investigation on the methane dehydrogenation pathway on Pt tetramers. Our previous PW91 calculations showed that the triplet tetrahedral isomer is the most stable structure among Pt<sub>4</sub> isomers.<sup>76</sup> Earlier studies of Pt<sub>4</sub> clusters indicated, however, that there are two nearly degenerate electronic states, for example, <sup>3</sup>T<sub>1</sub> and <sup>1</sup>A<sub>1</sub>, with tetrahedral geometries,<sup>77</sup> or the singlet state is 9.32 kcal/mol above the triplet state.<sup>78</sup> Therefore, we performed further calculations for the tetrahedral Pt<sub>4</sub> using B3LYP functional. Our B3LYP results showed that the singlet tetrahedral Pt<sub>4</sub> is 17.6 kcal/mol higher than its triplet isomer. As this energy is the highest among the species along the reaction pathway, therefore, our current study focused on the methane activation on the triplet tetrahedral Pt<sub>4</sub>.

The results obtained from both B3LYP and PW91 calculations for the CH<sub>4</sub>–Pt<sub>4</sub> system are summarized in Table 2. The total energy of the reactants is set as the energy reference. It is interesting to point out that, in general, the energies from both DFT calculations agree better than those for the CH<sub>4</sub>–Pt system. The disagreements were found to be the largest between the B3LYP and PW91 results for the transition states, which is the same as for the CH<sub>4</sub>–Pt system. Among four sets of products shown in Table 2, we explored the pathways to the most energetically favorable products, that is, Pt<sub>4</sub>CH<sub>2</sub> + H<sub>2</sub>. In what follows, we will discuss the CH<sub>4</sub> dehydrogenation pathways based on the B3LYP results.

We plotted in Figure 2 the CH<sub>4</sub> dehydrogenation pathways in the presence of the triplet Pt<sub>4</sub>. First, a molecular adduct with two slightly stretched C–H bonds was found to be about 9.0

**TABLE 2: Relative Energies (kcal/mol) of Intermediates, Transition States, and Products for CH<sub>4</sub> Activation on a Pt Atom Calculated by B3LYP and PW91 Functionals<sup>a</sup>**

Name	Structure	B3LYP	PW91	PW91 (relaxed)
Adduct		-9.04	-9.35	-9.27
TS1		-5.08	-7.02	-6.83
H-Pt <sub>4</sub> -CH <sub>3</sub>		-19.94	-19.84	-19.64
TS2		13.78	6.05	6.21
TS3		-11.67	-13.32	-13.08
(H) <sub>2</sub> -Pt <sub>4</sub> -CH <sub>2</sub>		9.95	6.03	6.14
H...Pt <sub>4</sub> -CH <sub>3</sub>		-19.10	-20.53	-20.46
TS4		21.02	10.05	9.70
TS5		9.11	0.98	1.00
H <sub>2</sub> -Pt <sub>4</sub> -CH <sub>2</sub>		18.94	6.03	6.14

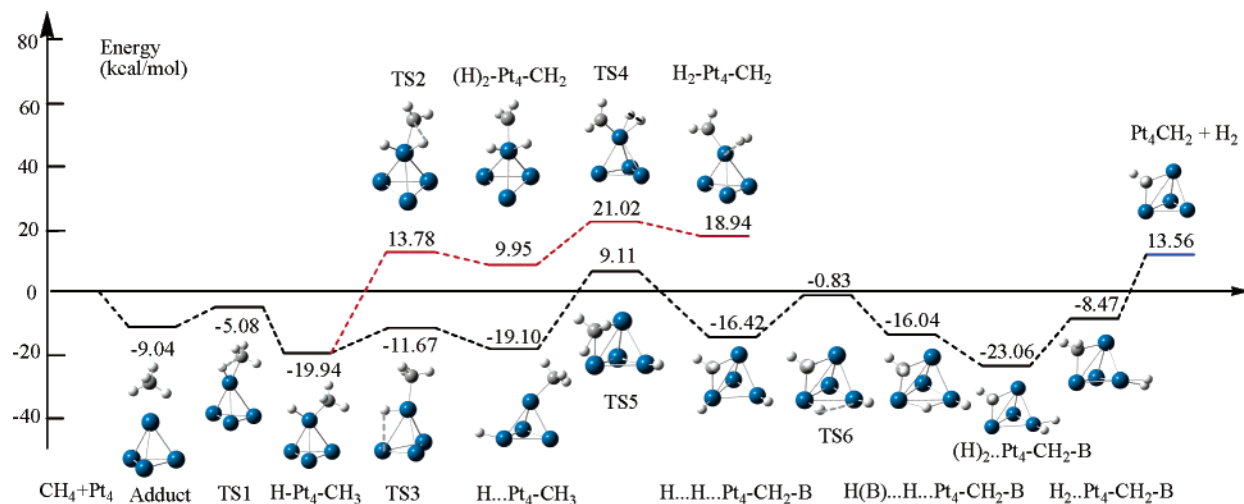
Name	Structure	B3LYP	PW91	PW91 (relaxed)
H...H...Pt <sub>4</sub> -CH <sub>2</sub> -B		-16.42	-19.46	-19.57
TS6		-0.83	-8.19	-7.92
H(B)...H...Pt <sub>4</sub> -CH <sub>2</sub> -B		-16.04	-20.71	-20.53
(H) <sub>2</sub> ...Pt <sub>4</sub> -CH <sub>2</sub> -B		-23.06	-24.66	-25.41
H <sub>2</sub> ...Pt <sub>4</sub> -CH <sub>2</sub> -B		-8.47	-11.37	N/A
Pt <sub>4</sub> CH <sub>2</sub> +H <sub>2</sub>		13.56	12.31	12.64
Pt <sub>4</sub> -CH <sub>2</sub> +H <sub>2</sub>		22.82	22.92	22.94
Pt <sub>4</sub> H (Quartet) +CH <sub>3</sub> (Doublet)		35.85	40.48	40.60
Pt <sub>4</sub> CH <sub>3</sub> (Quartet) +H (Doublet)		50.21	48.19	48.42

<sup>a</sup> The structural information (in Å and deg) refers to B3LYP results. The PW91 relative energies were calculated with the B3LYP structures and with structural relaxation. The structures without explicit electronic state shown are in the triplet states.

kcal/mol below the reactant asymptote. As compared to the adduct in the CH<sub>4</sub>-Pt system, a stronger interaction exists between the CH<sub>4</sub> and Pt<sub>4</sub>. The first C-H bond will be broken if about 4 kcal/mol is provided, and consequently a stable intermediate, H-Pt<sub>4</sub>-CH<sub>3</sub>, will be formed, which is 19.94 kcal/

mol below the reactant asymptote. Furthermore, the transition state, denoted as TS1, is 5.08 kcal/mol below the reactant asymptote. This means that breaking the first C-H bond in the presence of Pt<sub>4</sub> is both a thermodynamically and a kinetically favorable process. As compared to the CH<sub>4</sub>-Pt system, this





**Figure 2.** The CH<sub>4</sub> activation pathway to form Pt<sub>4</sub>CH<sub>2</sub> + H<sub>2</sub>. The energy of the reactants, for example, Pt<sub>4</sub> (triplet state) and CH<sub>4</sub>, is set as reference. The data and structures were obtained from the B3LYP calculations.

illustrated that Pt<sub>4</sub> is more active toward CH<sub>4</sub> dissociation, which was observed in the experiment.<sup>1</sup>

As shown in Figure 2, after the formation of the intermediate H-Pt<sub>4</sub>-CH<sub>3</sub>, there are two pathways that can lead to the breaking of the second C-H bond. One pathway is above the reactant asymptote, which indicates that the reaction is not thermodynamically favorable. In this pathway, two H atoms dissociated from CH<sub>4</sub> are attached to the same Pt atom. A transition state TS2 was found to be 13.78 kcal/mol above the reference, followed by an intermediate (H)<sub>2</sub>-Pt<sub>4</sub>-CH<sub>2</sub> of 9.95 kcal/mol. Furthermore, the reaction barrier is 33.72 kcal/mol, which also indicates a less favorable process kinetically. On the other hand, the second pathway starts from H transfer from one Pt atom to the other before breaking the second C-H bond. This process, as shown in Figure 2, is more favorable energetically. The H transfer involves overcoming an energy barrier of about 8 kcal/mol, but again the transition state (TS3) is below the reactant asymptote. This process is very similar to the H transfer found in CH<sub>4</sub>-Pt<sub>2</sub> and CH<sub>4</sub>-Pt<sub>3</sub> systems.<sup>4,5</sup> The intermediate H...Pt<sub>4</sub>-CH<sub>3</sub> after the H transfer is 19.10 kcal/mol below the reactant asymptote, which is almost as stable as H-Pt<sub>4</sub>-CH<sub>3</sub>.

Once the H transfer is completed, the second C-H bond will be broken if a 30 kcal/mol energy barrier is overcome. Unlike TS1 and TS3, the transition state (TS5) is above the reactant asymptote by 9.11 kcal/mol. This indicates that this process is not thermodynamically favorable. However, this transition state is below the energy level of the dehydrogenation products. Once the second C-H bond is broken, the following steps involve the migration of H atom, combination of H atoms to form H<sub>2</sub>, and finally dissociation of H<sub>2</sub>. As shown in Figure 2 and discussed above, among the five single steps, the step involving breaking the second C-H bond is the rate-limiting step.

**3.3. Discussion of Methane Activation on Pt<sub>n</sub> with *n* = 1–4.** Studies of methane activation processes in the presence of neutral Pt clusters can be classified into two types. One type of research is to study the overall reaction, that is, CH<sub>4</sub> + Pt<sub>n</sub> → products. The experimental work of methane activation on neutral Pt clusters by Trevor et al. belongs primarily to this type, as the amount of unreacted metal was measured.<sup>1</sup> Here, the reaction rate is determined by the rate of breaking the first C-H bonds. Extensive theoretical studies had been made to search for reaction pathways leading to breaking the first C-H bond of CH<sub>4</sub> in the presence of Pt, Pt<sub>2</sub>, and Pt<sub>3</sub>. In the case of the CH<sub>4</sub>-Pt system, a transition between two electronic states

has to take place to break the first C-H bond. An approximate 1.2 kcal/mol energy barrier has to be overcome during this C-H bond activation.<sup>3</sup> As for the CH<sub>4</sub>-Pt<sub>2</sub> and CH<sub>4</sub>-Pt<sub>3</sub> systems, barriers of 2.6 and 0.4 kcal/mol have to be overcome, respectively.<sup>4,5</sup> Although the energy barrier for the CH<sub>4</sub>-Pt is not significant, two other factors are largely responsible for the slow reaction rate observed experimentally for this reaction. First, an electronic transition has to take place to break the C-H bond, as shown in Figure 1. Second, the transition state is above the reactant asymptote. In contrast, none of these factors are present in the CH<sub>4</sub>-Pt<sub>2</sub> and CH<sub>4</sub>-Pt<sub>3</sub> systems. Our current calculations showed that about 4 kcal/mol of energy barrier must be overcome to break the first C-H bond in the CH<sub>4</sub>-Pt<sub>4</sub> system, and the transition state, TS1, is also below the reactant asymptote. This indicates that the CH<sub>4</sub>-Pt<sub>4</sub> system is similar to the CH<sub>4</sub>-Pt<sub>2</sub> system and Pt<sub>3</sub> is slightly more active than Pt<sub>2</sub> and Pt<sub>4</sub>. This conclusion is consistent with the experimental observations.<sup>1</sup>

The second type of CH<sub>4</sub> activation studies is to specifically investigate the dehydrogenation of CH<sub>4</sub>, that is, CH<sub>4</sub> + Pt<sub>n</sub> → Pt<sub>n</sub>CH<sub>2</sub> + H<sub>2</sub>. The rate of dehydrogenation is determined by the slowest single reaction step. So far, no experimental work was done for the CH<sub>4</sub> dehydrogenation on neutral Pt<sub>n</sub> clusters, although there were experimental studies of CH<sub>4</sub> dehydrogenation using cationic and anionic Pt<sub>n</sub> clusters, such as the work by Achatz et al.<sup>34</sup> and by Adlhart et al.<sup>6</sup> The most controversial results from these experiments are for the Pt<sub>4</sub> clusters. For the anionic Pt<sub>4</sub> clusters, Achatz et al. observed the maximum activity in methane dehydrogenation,<sup>34</sup> but Adlhart et al. observed a decreasing activity with respect to Pt-Pt<sub>3</sub> clusters.<sup>6</sup> In the case of cationic Pt<sub>4</sub> clusters, the dehydrogenation is slowest among Pt-Pt<sub>9</sub> clusters as observed by both groups.<sup>6,34</sup> Based on our calculations, if the intermediates reach equilibrium, the rate-limiting step for both Pt and Pt<sub>4</sub> systems is the breaking of the second C-H bond. The barrier height is about 37 kcal/mol for the CH<sub>4</sub>-Pt system and about 28 kcal/mol for the CH<sub>4</sub>-Pt<sub>4</sub> system. The above data indicate that kinetically the dehydrogenation is faster on Pt<sub>4</sub> clusters than on a single Pt atom. As for the thermodynamics of dehydrogenation, neither that on Pt nor that on Pt<sub>4</sub> is favored at room temperature.

## 4. Conclusion

In the present work, we studied the dehydrogenation of methane on a Pt atom and a tetrahedral Pt<sub>4</sub> by performing both

B3LYP and PW91 calculations. The results from these two different functionals differ mostly in the energy barrier, in particular for the CH<sub>4</sub>–Pt systems.

For the CH<sub>4</sub>–Pt system, a new low-energy pathway was located for the dehydrogenation. Instead of a four-centered transition state proposed previously, a three-centered transition state was found to be lower in energy. Therefore, our work showed that the dehydrogenation process could take place by overcoming a 39 kcal/mol barrier rather than a >60 kcal/mol barrier. Furthermore, the transition state is below the reactant asymptote.

We reported here the first theoretical study of methane dehydrogenation on Pt<sub>4</sub>. The reaction pathway consists of five single reaction steps. The first step is the cleavage of the first C–H bond with an energy barrier of 4 kcal/mol. Unlike the CH<sub>4</sub>–Pt system, there is no electronic curve-crossing, and the transition state is below the reactant asymptote. The second step is the H transfer from one Pt atom to the other before breaking the second C–H bond. The transition state in the H transfer process is also below the reactant asymptote, and it resulted in an energetically favorable reaction pathway for dehydrogenation. The third step involves breaking the second C–H bond and is the rate-limiting step in dehydrogenation with an energy barrier of 28 kcal/mol. The fourth and fifth steps are the formation and dissociation of hydrogen molecule, respectively. Based on our work, the CH<sub>4</sub> dehydrogenation takes place faster on Pt<sub>4</sub> kinetically than on the Pt atom, but, thermodynamically, the dehydrogenation in CH<sub>4</sub>–Pt is more favored than that in CH<sub>4</sub>–Pt<sub>4</sub> by about 3 kcal/mol, although both reactions are endothermic.

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