First-principles investigation of the dissociation and coupling of methane on small copper clusters : interplay of collision dynamics and geometric and electronic effects

Varghese, Jithin John; Mushrif, Samir Hemant

2015

Varghese, J. J., & Mushrif, S. H. (2015). First-principles investigation of the dissociation and coupling of methane on small copper clusters : interplay of collision dynamics and geometric and electronic effects. *The journal of chemical physics*, 142(18), 184308-.

<https://hdl.handle.net/10356/102996>

<https://doi.org/10.1063/1.4919948>

© 2015 AIP Publishing LLC. This paper was published in *The Journal of Chemical Physics* and is made available as an electronic reprint (preprint) with permission of AIP Publishing LLC. The paper can be found at the following official DOI: [<http://dx.doi.org/10.1063/1.4919948>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

First-principles investigation of the dissociation and coupling of methane on small copper clusters: Interplay of collision dynamics and geometric and electronic effects

Jithin J. Varghese and Samir H. Mushrif

Citation: *The Journal of Chemical Physics* **142**, 184308 (2015); doi: 10.1063/1.4919948

View online: <http://dx.doi.org/10.1063/1.4919948>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/142/18?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

Dissociation and recombination of D₂ on Cu(111): Ab initio molecular dynamics calculations and improved analysis of desorption experiments

J. Chem. Phys. **141**, 124705 (2014); 10.1063/1.4896058

First-principles insights into interaction of CO, NO, and HCN with Ag₈

J. Chem. Phys. **140**, 084314 (2014); 10.1063/1.4865947

The dissociative chemisorption of methane on Ni(111): The effects of molecular vibration and lattice motion

J. Chem. Phys. **138**, 174705 (2013); 10.1063/1.4802008

Theoretical investigation of the interaction of CH₄ with Al₂ and Al₃ neutral and charged clusters

J. Chem. Phys. **132**, 154701 (2010); 10.1063/1.3376174

Ab initio studies on the reaction of O₂ with Ba_n (n = 2, 5) clusters

J. Chem. Phys. **124**, 224711 (2006); 10.1063/1.2205851

How can you **REACH 100%**
of researchers at the Top 100
Physical Sciences Universities? (TIMES HIGHER EDUCATION RANKINGS, 2014)

With *The Journal of Chemical Physics*.

AIP | The Journal of
Chemical Physics

THERE'S POWER IN NUMBERS. Reach the world with AIP Publishing.

First-principles investigation of the dissociation and coupling of methane on small copper clusters: Interplay of collision dynamics and geometric and electronic effects

Jithin J. Varghese and Samir H. Mushrif^{a)}

School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, 637459, Singapore

(Received 26 February 2015; accepted 28 April 2015; published online 14 May 2015)

Small metal clusters exhibit unique size and morphology dependent catalytic activity. The search for alternate minimum energy pathways and catalysts to transform methane to more useful chemicals and carbon nanomaterials led us to investigate collision induced dissociation of methane on small Cu clusters. We report here for the first time, the free energy barriers for the collision induced activation, dissociation, and coupling of methane on small Cu clusters (Cu_n where $n = 2\text{--}12$) using *ab initio* molecular dynamics and metadynamics simulations. The collision induced activation of the stretching and bending vibrations of methane significantly reduces the free energy barrier for its dissociation. Increase in the cluster size reduces the barrier for dissociation of methane due to the corresponding increase in delocalisation of electron density within the cluster, as demonstrated using the electron localisation function topology analysis. This enables higher probability of favourable alignment of the C–H stretching vibration of methane towards regions of high electron density within the cluster and makes higher number of sites available for the chemisorption of CH_3 and H upon dissociation. These characteristics contribute in lowering the barrier for dissociation of methane. Distortion and reorganisation of cluster geometry due to high temperature collision dynamics disturb electron delocalisation within them and increase the barrier for dissociation. Coupling reactions of CH_x ($x = 1\text{--}3$) species and recombination of H with CH_x have free energy barriers significantly lower than complete dehydrogenation of methane to carbon. Thus, competition favours the former reactions at high hydrogen saturation on the clusters. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919948>]

I. INTRODUCTION

Catalytic chemical vapour deposition (CVD) based growth of graphene on copper and nickel thin films has now become an established process, with the combination of methane as the hydrocarbon source, and copper thin film as the catalyst, being the most popular.^{1–3} One of the most significant steps in the early stages of graphene growth on metal thin films is the decomposition of the hydrocarbon source leading to the formation of carbon precursors on the surface.^{1,2,4} To this end, the activation and dissociation of methane are a challenge due to the extremely stable C–H bonds which have a bond dissociation energy of around 440 kJ/mol.⁵ Theoretical investigations of the dissociation of methane on monocrystalline copper surfaces have revealed the elementary steps of dehydrogenation to be energetically uphill and thus, thermodynamically unfavorable, with activation energy barriers of 95–190 kJ/mol for each step.^{6–9} Thus, typical CVD processes for graphene growth involving methane on copper thin films are carried out at temperatures between 900 °C and 1000 °C.² It is believed that the copper thin film not only serves as the substrate for carbon precursors to nucleate and subsequently grow to graphene but also provides catalytically active sites for the dissociation of

methane. This makes the entire graphene growth on copper a self-limiting surface phenomenon.^{3,4,9,10}

Some groups recently developed a remote catalytic or copper vapour assisted CVD process for the direct growth of graphene on inert substrates like SiO_2 .^{11–15} In this process, Cu atoms in the vapour phase are believed to catalyse the decomposition of hydrocarbons which subsequently deposit and grow on the inert substrate. However, there is no concrete evidence to prove this claim and the decomposition mechanism which may result from the direct collision of methane on the atoms is yet to be elucidated. Theoretical investigations have shown that transition metal atoms like nickel (Ni)¹⁶ and tungsten (W)¹⁷ in the gas phase can activate methane towards dissociation.

Collisions with inert gas atoms like argon (Ar) can activate methane by inducing vibrational excitation by means of transfer of the translational kinetic energy of the atom to the internal modes of methane.¹⁸ Dissociative chemisorption of methane on a Ni surface facilitated by colliding argon atoms (“Chemistry with a Hammer”)^{19,20} or via direct collision on the surface^{21–23} is enhanced dramatically by the translational kinetic energy of the colliding atom/molecule. Thus, Collision Induced Dissociation (CID) of methane opens a lower energy pathway for the reactions involving methane. In this context, formation of a monolayer of graphite on Pt(111) surface was reported in 2004 using a supersonic molecular beam of methane.²⁴ This collision induced growth of graphene

^{a)} Author to whom correspondence should be addressed. Electronic mail: shmushrif@ntu.edu.sg

(referred to as monolayer graphite at the time of publication) was observed to be insensitive to the metal surface features and thus offers a pathway for carrying out reactions on non-homogeneous surfaces.

Small metal clusters, especially those of transition metals like copper with closed d-shells, have captured the attention of both experimentalists and theoreticians due to their peculiar electronic structure and structure/size sensitive catalytic properties.^{25–30} Moreover, small clusters are representative structures of the nano-environment surrounding active sites on bulk surfaces, as only a few surface atoms are involved in the energy exchange in collisional processes.³¹ Thus, an investigation of collision induced dissociative chemisorption and reactions of methane on Cu clusters is imperative to identify the role of collisions and size/structure properties of the cluster on the free energy barriers associated with the processes. Hence, in the light of the great potential of both the technique and the catalytic nano-material, we investigated in this paper, the collision induced dissociation of methane on Cu atom and small Cu clusters using *ab initio* molecular dynamics (MD) simulations, in conjunction with the metadynamics algorithm.³² The free energy barriers for the collision induced dissociation of methane on Cu atom and various Cu clusters at 1273 K were calculated and factors determining the barrier were identified. The subsequent dehydrogenation steps were observed to have barriers which are higher than those of the former. We also investigated the dehydrogenation of chemisorbed methane and possible coupling reactions of the chemisorbed species. Carbon formation has a very high barrier on all the clusters and CH_x ($x = 1-3$) intermediates on these clusters can couple to form C_2 hydrocarbons with negligible free energy barriers. The computational techniques employed in carrying out these simulations are detailed in Sec. II. Collision induced dissociation of methane on various clusters, subsequent dehydrogenation of chemisorbed methane on various clusters, and coupling reactions of CH_x on the cluster are discussed in detail in Secs. III A, III B, and III C, respectively. We summarise our findings in Sec. IV.

II. COMPUTATIONAL METHODS

First principles molecular dynamics simulations implementing the Car-Parrinello scheme³³ in conjunction with the metadynamics algorithm³² were performed using the CPMD

package³⁴ version 3.15.3. In Car Parrinello Molecular Dynamics (CPMD), the finite and constant temperature dynamics of nuclei are coupled to the electronic system, which is treated quantum chemically using the Kohn-Sham formulation of density-functional theory (DFT) via adiabatic fictitious dynamics.³³ The metadynamics algorithm implemented with CPMD enables the efficient exploration of the free energy landscape of a system as a function of suitable collective coordinates.³² It is made possible by the deposition of history dependent potentials at periodic intervals, allowing the acceleration of the crossover of the system to adjacent free energy minima via the minimum energy pathway. This makes the combination of CPMD-metadynamics an ideal simulation strategy to investigate collision induced reactions of methane. A brief review of the CPMD method and its applications to investigate chemical reactions is available in the article by Speybroeck and Meier.³⁵ The implementation of the metadynamics technique and applications/suitability of the technique to investigate chemical reactions have been presented in excellent reviews by Laio and Gervasio³⁶ and Zheng and Pfandtner.³⁷

Thus, CPMD-metadynamics simulations were performed to investigate the collision induced dissociation of methane on various Cu clusters (Cu, Cu_2 , Cu_6 , Cu_8 , and Cu_{12}) and subsequent dehydrogenation of the chemisorbed CH_3 on these clusters. Even numbered Cu clusters (Cu_2 -linear dimer, Cu_6 -planar, Cu_8 -3 dimensional, and Cu_{12} -incomplete icosahedron), as shown in Fig. 1, were considered for the simulations as these clusters have been reported to have paired electrons or closed shell electronic structure.^{38–40} These clusters enable an investigation on size/structure relation to their catalytic efficiency. The chosen structures were based on the available literature^{30,38,40} and no separate calculations were performed to further confirm their ground state structures.

The plane-wave implementation of DFT^{41,42} with the Perdew–Burke–Ernzerhof⁴³ (PBE) exchange-correlation functional and the Vanderbilt ultra-soft pseudopotential⁴⁴ was used for the CPMD section. Nonlinear Core Corrections (NLCC)⁴⁵ were incorporated into the pseudopotential of copper. Prior to investigating the reactive trajectories with CPMD-metadynamics simulations, each of these systems (Cu_n clusters with a methane molecule) was optimized in a cubic simulation box (10 Å–15 Å side) as an isolated system (no periodic boundary conditions). Finite temperature dynamics and thermal equilibration of the systems were performed with the Nosé–Hoover

FIG. 1. Representation of the simulation systems for collision induced dissociation of methane on (a) Cu dimer, (b) planar Cu_6 cluster, (c) capped pentagonal bi-pyramidal Cu_8 cluster, and (d) incomplete icosahedron compact Cu_{12} cluster. In each case, the methane molecule is at a distance greater than 3.5 Å from the nearest Cu atom. The two collective variables (CV1 and CV2) employed in the simulations investigating collision induced dissociation of methane are also shown.

chain thermostat^{46,47} maintaining the temperature of the system at 1273 K. A few simulations were also performed at 300 K for the collision induced dissociation of methane on Cu₈ cluster. The frequency of the ionic thermostat was set at 2900 cm⁻¹ and that of the electronic thermostat at 12 000 cm⁻¹. The time step for the integration of the equations of motion was set at 3 a.u. (0.073 fs), and the fictitious mass for the electron dynamics was set at 400 a.u. The molecular dynamics trajectories were visualized using the Visual Molecular Dynamics (VMD) package.⁴⁸ CPMD simulations were performed with spin restricted closed shell implementation of DFT for all even numbered Cu clusters and with spin polarisation on (local spin density approximation) with a ground state spin multiplicity of two for the system containing just one Cu atom.

It has been shown that for methane dissociation on surfaces, the distance of methane from the surface and the distance of the dissociating hydrogen atom from carbon atom of methane are relevant coordinates and reactive collisions typically occur on metal top sites.^{49,50} Due to the observed mode-selectivity in the dissociative chemisorption of methane on metal surfaces, the inclusion of all degrees of freedom of methane as well as lattice relaxation of the cluster/surface is necessary in all computational investigations.^{49–52} The CPMD technique treats methane with all degrees of freedom (translational, rotational, and vibrational) and allows lattice motion/relaxation of all copper atoms of the Cu clusters at finite temperatures. Due to the limitation in the CPMD technique to access time scales of reactions with high barriers, like the one considered in this manuscript (typically accessible time scales are a few hundred picoseconds), we resort to biasing/accelerating the dynamics with the metadynamics algorithm. Thus, the collision induced dissociation of methane was investigated using CPMD-metadynamics, employing two relevant collective variables. The distance of the carbon atom of methane to one of the Cu atoms of the cluster was the first collective variable (CV1), while the average coordination number of carbon atom to all the hydrogen atoms was the second collective variable (CV2). The C–H coordination number collective variable represents the C–H bond distance, which is a relevant reaction coordinate. Both the collective variables are indicated in Fig. 1. In metadynamics, the dynamics of these collective variables are coupled to the actual finite temperature dynamics of the system and are biased using Gaussian potential hills which are deposited at periodic intervals.^{32,36} These history dependent potentials enable the collective variables to explore the phase space and also accelerate in the process, along the chosen coordinate. The accumulation of Gaussian potentials along the metadynamics simulation enables the system to overcome reaction barriers and it also enables the computation of the free energy landscape of the system. A free energy minimum (well) when filled with sufficiently large number of Gaussian potentials allows the system to spill over to adjacent minima via minimum energy pathways, completing chemical reactions. In our simulations, constraints were imposed on dynamics with the distance between the carbon atom and selected Cu atom as the collective variable to ensure that the methane molecule moves closer to the cluster by restricting the exploration of phase space within 5 Å of the two moieties. These two collective variables

together accounted for the two significant events which form a part of the reaction coordinate: (1) collision of methane with the cluster and (2) dissociation of methane followed by adsorption of the fragments on the cluster. The free energy surface (3 dimensional in our case), analogous to the potential energy surface (PES) for methane dissociation on Ni(111) represented as a function of two variables,⁴⁹ enables the estimation of the free energy barrier as a function of the two collective variables. The free energy landscape explicitly accounts for all dynamic features of the reaction at finite temperature (vibrational activation, lattice motion/relaxation, collision site, and so on) unlike the potential energy surface. When the collective variables are chosen wisely to represent the reaction coordinate completely, the CPMD-metadynamics calculated free energy barriers are actual estimates of free energy barriers for the reaction at the specific temperatures, averaging effects of thermal/collision induced vibrational activation, collision site, and lattice motion/reconstruction.

The investigation of further dehydrogenation of chemisorbed methane employed the collective variables, CV1—the average coordination number of the hydrogen atoms of methane with the Cu atoms of the cluster and CV2—the average coordination number of the carbon atom with all the hydrogen atoms. These two collective variables account for the reactive events of further dehydrogenation of CH₃ and possible surface hopping of the dissociated H atoms. The coupling of CH_x fragments ($x = 1–3$ and of the same kind in one system) on the clusters was investigated using the collective variables, CV1—the distance between the carbon atoms of the CH_x fragments and CV2—the average coordination of the carbon atoms to all the hydrogen atoms. Constraints were imposed on the distance between the carbon atoms to ensure the two fragments moved closer to each other by restricting the exploration of phase space within 4 Å of each other. In all the simulations, metadynamics was propagated by the sequential deposition of Gaussian tube hills of height 5.25 kJ/mol and width 0.12 a.u. at intervals of time sufficiently large for the collective variables to explore the phase space. The collective variables were further used to reconstruct the free energy landscape from which the free energy barriers for the dissociation of methane on the clusters and for the coupling of CH_x fragments to form C₂ hydrocarbons were estimated. Additional details pertaining to the CPMD simulations are provided in the supplementary material—Sec. I, Computational Methods.⁵³

The electronic structure and bonding in pure Cu clusters of different sizes (without methane) were analysed using the electron localisation function (ELF).⁵⁴ Similar analysis was performed for structures from CPMD-metadynamics simulations corresponding to collision and dissociation of methane, as well as those from coupling of CH_x ($x = 1–3$) fragments on these clusters. The ELF topology analysis was performed in the CPMD package and gave insights into the electron delocalization within the clusters and the bonding of the CH_x fragments and H on the cluster. Prior to ELF calculations, the wavefunction of the structures obtained from the CPMD-metadynamics simulations was optimized with strict convergence criteria (10⁻⁸) using the PBE⁴³ exchange-correlation functional and the norm conserving Troullier-Martins⁵⁵ pseudopotential with a plane wave energy cut-off of 120 Ry. Norm

conserving pseudopotentials are employed here, since ELF calculations are not supported with ultra-soft pseudopotentials and a higher cut-off was used to obtain smooth ELF isosurfaces. The ELF data files were converted to cube files for visualisation in VMD.

CPMD-metadynamics simulations cannot ascertain the exact transition states (TSs) corresponding to the dissociation of methane on clusters. However, since a minimum energy reaction pathway is followed, these simulations provide very good guess structures to identify the TS. Thus, quantum chemical calculations implementing DFT with the PBE exchange correlation functional were performed in the Gaussian 09 suite⁵⁶ using these structures to identify the TS for the dissociation of methane on a Cu atom and Cu₂ and Cu₆ clusters. LANL2DZ effective core potential basis set⁵⁷ for copper and 6-311++g(d) for carbon and hydrogen were employed in these calculations. Vibrational frequency analysis showed the presence of a single imaginary frequency, confirming the TS. Each TS was reconfirmed by following the intrinsic reaction coordinate (IRC) on either direction of the TS to reach minima corresponding to reactant and product. The obtained reactant from the IRC was further optimized to obtain the activation energy barrier for the dissociation. Vibrational frequency calculations corresponding to the normal modes were also performed. The structures and vibrations were visualised using Gauss View 05.⁵⁸

III. RESULTS AND DISCUSSION

This section is organised as follows. The collision induced dissociation of methane on the Cu clusters is discussed in Sec. III A. Collision induced vibrational activation of the stretching and bending modes of methane leading to considerably lower free energy barriers for dissociation is discussed in Sec. III A 1. The dependence of the free energy barriers for the dissociation of methane on the cluster size, collision site morphology, and angle of incidence is detailed in Secs. III A 2 and III A 3. Further dissociation of chemisorbed CH₃ on the clusters and free energy barriers associated with each elementary dissociation step are reported in Sec. III B 1. The dependence of the free energy barriers for the dissociation on the cluster size/morphology and the presence of chemisorbed hydrogen on the cluster are discussed in Secs. III B 2 and III B 3, respectively. The coupling of CH_x groups ($x = 1-3$) on Cu₈ cluster and formation/evolution of C₂ hydrocarbons/intermediates are discussed in Secs. III C 1 and III C 2. Section III C 3, gives a perspective on the implications of the different reaction pathways (dissociation and coupling of methane) on graphene growth by chemical vapour deposition.

A. Collision induced C–H dissociation in methane on Cu clusters

1. Reactive trajectories and free energy barriers

All CPMD-metadynamics simulations investigating the collision of methane on the Cu clusters at 1273 K typically show the dissociation of methane with both the CH₃ group and H atom adsorbed at different bridge and 3 fold sites on

the clusters (movie S1 of the supplementary material).⁵³ For the three dimensional clusters, the Cu atom on which methane collides is typically observed to be slightly raised above the plane containing the nearest neighbour Cu atoms, enhancing reactivity (further discussion in Secs. III A 2 and III A 3), as observed with methane dissociative chemisorption on Ni(111) and Pt(111).⁵¹ The hydrogen is observed to be quite mobile and keeps hopping between different sites. The activation energy barrier for the diffusion of hydrogen on Cu(111) surface has been reported to be 12.5 kJ/mol⁹ and thus is expected to be small for Cu clusters as well. However, a preference for the bridge site of two copper atoms was observed from our CPMD trajectories, in agreement with an investigation of hydrogen chemisorption on Cu clusters and quite unlike copper surfaces, where the hollow sites are preferred.²⁶ This trend will be elucidated further in Sec. III A 2.

The free energy landscape for the dissociation of the C–H bond in methane on Cu₈ cluster as a function of the two collective variables has a typical L-shape and is shown in Fig. 2. Structures corresponding to minima in the free energy surface (FES) are also shown. This L-shape is characteristic of the collision induced dissociation of methane on all Cu clusters, irrespective of the size of the cluster and the temperature of the simulation. The basic features of the free energy landscapes reconstructed from simulations of dissociation of methane on different Cu clusters are similar and thus are not shown. It can be seen that C–H coordination number is nearly invariant at around 3.6 until the C–Cu distance is 1.9 Å or less. A complex of the distorted methane molecule and cluster upon collision serves as a “precursor” for the dissociation reaction and is represented by the free energy minimum before dissociation, as seen in Fig. 2. The collisionally activated and distorted methane molecule with its unhindered rotational and lateral degrees of freedom explores multiple configurations at close proximity (less than 2.1 Å) to the relaxed Cu atoms of the clusters. These distorted configurations facilitate higher Cu–methane interactions compared to a physisorbed methane on a Cu(111) surface, which is at a distance of ~3.6 Å from the surface.⁹ These minimum energy configurations resulting from better copper-carbon interaction and lattice relaxation of the cluster, averaged over a trajectory period, result in a deep minimum in the entry channel of the reaction. The free energy barrier for dissociation of methane is calculated with

FIG. 2. The free energy landscape reconstructed from CPMD-metadynamics simulation of collision of methane with Cu₈ cluster with the C–Cu distance and C–H coordination number as collective variables at 1273 K. Representative structures from the trajectory corresponding to significant minima are also shown. Colour scheme for atoms is similar to that in Fig. 1.

respect to this precursor state along the dissociation path, as shown in Fig. 2. This reference reactant state is a contrasting feature of the calculation of the activation free energy barriers from CPMD-metadynamics simulations, compared to an equilibrium calculation where the reference reactant would be physisorbed methane or a methane molecule in the gas phase. However, it should be noted that all gas-surface collisions (methane on copper) in real experiments may not undergo such processes, and this would be one of the pathways for the dissociation of methane molecules colliding on Cu clusters/surfaces with a certain range of translational kinetic energy. Similar to that of our observation, in the collision of methane on Ir(111) in molecular beam experiments, a “precursor” or “trapping mediated” mechanism for dissociation has been observed.⁵⁹

The free energy landscape also suggests that there are significant barriers for the movement of methane towards the cluster. This implies that a significant number of collisions of methane on Cu clusters and surfaces would result in scattering without dissociative chemisorption. This would be one of the factors contributing to the very low dissociative chemisorption probability (8.6×10^{-9} at 1000 K⁶⁰) and sticking coefficient (4.7×10^{-15} at 500 K⁶¹) of methane on copper surfaces. The free energy barriers for collision induced dissociation of methane on Cu clusters of different sizes, obtained from simulations with differences in the collision angle and numbers of nearest neighbour atoms, are reported in Table I. The concerted effects of collision and entropic contributions resulting from the high temperature dynamics induce vibrational activation of methane. The formation of the precursor state further allows the molecule to access lower energy pathways for dissociation, as suggested in the report on precursor mediated reactivity of methane dissociation on Ir(111).⁵⁹ Further detailed discussion on this will be done in Sec. III A 3. Thus, the activation free energy barriers calculated from CPMD-metadynamics simulations are significantly lower than those would be ex-

TABLE I. Free energy barriers for dissociation of methane on Cu clusters of different sizes obtained from the CPMD-metadynamics simulations. Most simulations are performed at 1273 K although we performed two simulations at 300 K and are reported. $\theta = 140^\circ$, $\theta = 165^\circ$, and $\theta = 170^\circ$ refer to the values of the C–Cu–Cu angle at the time of collision (just before C–H dissociation) in the three simulations performed on Cu₂ at same temperature. $n = 1$, $n = 2$, $n = 3$, $n = 4$, and $n = 6$ refer to the number of nearest neighbouring Cu atoms within a distance of 3 Å from the Cu atom on which methane collides, at the time of collision.

Cu cluster size	Sl. No.	Free energy barriers for dissociative chemisorption (kJ/mol)	Temperature (K)
Cu ₂	1	75 ^{$\theta=140$}	1273
	2	120 ^{$\theta=165$}	
	3	125 ^{$\theta=170$}	
Cu ₆	1	60 ^{$n=2$}	1273
	2	90 ^{$n=1$}	
Cu ₈	1	35 ^{$n=4$}	1273
	2	60 ^{$n=3$}	
	3	80 ^{$n=3$}	
Cu ₈	1	110 ^{$n=6$}	300
	2	170 ^{$n=3$}	
Cu ₁₂	1	50 ^{$n=4$}	1273
	2	65 ^{$n=4$}

FIG. 3. (a) Vibrations of the 4 C–H bonds of methane as a function of the C–Cu distance from CPMD-metadynamics simulations on Cu₈ at 300 K. (b) Distortion of the 6 H–C–H angles of methane as a function of the C–Cu distance from CPMD-metadynamics simulations on Cu₈ at 300 K. Thermal vibrations of the C–H bonds and H–C–H angles as well as collision induced enhanced vibrations, particularly at smaller Cu–C distances, can be seen in each of the cases.

pected based on the values of activation energy (enthalpic) barriers reported for dissociation of methane on Cu(111) and Cu(100) surfaces, using conventional density functional theory methods.^{6–9}

Figure 3(a) shows the deviations of the 4 C–H bonds and Fig. 3(b) shows the distortion of the 6 H–C–H angles of methane as a function of the Cu–C distance from the simulation on Cu₈ at 300 K. The enhanced stretching of the C–H bonds and enhanced distortion of the H–C–H angles upon collision, seen in Figs. 3(a) and 3(b), respectively, can be attributed to collision induced vibrational activation. Thus, a combination of stretching and bending vibrations plays a significant role in reducing the free energy barrier for C–H dissociation, as suggested by Bisson *et al.*⁶² and will be discussed further in a Sec. III A 3. Both translational kinetic energy of the colliding molecules^{21–23,63} and vibrational excitation^{62–68} have been shown to dramatically enhance the dissociation of methane on metals surfaces. Collision induced vibrational excitation is observed in all our simulations on all the Cu clusters at temperatures of 1273 K as well. However, since the average thermal vibrations (C–H stretching and H–C–H distortions) at 1273 K are much more prominent than what is shown in Fig. 3, the effect of collision is not as distinctively visible as shown here.

2. Effects of cluster size on free energy barriers

It can be seen from Table I that the barriers for the dissociation of methane decrease with an increase in the size of the cluster and the average value remains around the same for clusters larger than 8 atoms. A similar trend in the dissociative

chemisorption energy values of H_2 on Cu clusters was reported earlier.²⁶ The relative stability of small Cu clusters has been reported to be in the order $\text{Cu}_2 < \text{Cu}_6 < \text{Cu}_{12} < \text{Cu}_8$,³⁹ and the barriers we calculated for dissociation of methane on these clusters are also seen to follow the same order. The activation energy for the dissociation of methane on copper is reported to be strongly dependent on the adsorption energy of CH_3 and H, after the dissociation.⁶¹ Thus, the barriers for dissociation may depend on the number and nature of available bridge and 3-fold copper sites for chemisorption of these species, in the immediate vicinity of the Cu atom on which the collision happens. This explains the trend of the barrier becoming lower with increasing cluster size from Cu_2 to Cu_{12} , as the number of available sites increases with the increase in the cluster size. The number of available sites is important because the dissociation of C–H bonds of methane on copper is facilitated by charge transfer from copper to methane, polarising the C–H bonds, and subsequently to the chemisorbed fragments.⁹

In addition to these geometric effects, the possible contribution of electronic effects in lowering the free energy barrier for the dissociation of methane on these clusters was evaluated using the electron localisation function (ELF) topology analysis. The electron localisation function, a conditional pair probability density function proposed by Becke and Edgecombe, was originally used to characterize the shell structure of atoms.⁵⁴ ELF was designed to have values between 0 and 1, where 1 represented the limit of perfect localisation and 0.5 represented homogeneous electron gas like probability. Silvi and Savin resorted to the mathematical technique of differential topology analysis of the electron localisation function in terms of attractors and basins, characterising them using isosurfaces (3-dimensional surfaces).⁶⁹ This enabled the visualisation of ELF as isosurfaces, whose topology could change at threshold values which can be referred to as bifurcation values. The key feature that enables the ELF topology analysis, as described by Silvi and Savin, to be used in chemical bonding analysis is the spatial arrangement of the localisation domains which are bound by basins and attractors.⁶⁹ The attractors refer to local maxima of the localisation function, and the basins refer to the set of points whose gradients connect with the attractor.^{70,71} Thus, chemical bonding can be analysed based on the types of attractors, namely, the core and the bonding and the non-bonding attractors.⁶⁹ Covalent, metallic, and dative bonds will have at least one bonding attractor between the core attractors of the atoms involved. A basin containing a nucleus is referred to as a core basin and the remaining are valence basins. The synaptic order of valence basins refers to the number of core basins within the valence basin.⁷² A covalent bond connecting two core basins is thus referred to as disynaptic. The C–H bond has a disynaptic basin between the two atoms, the C–C single bond is represented by a spherical ELF attractor in the centre of the two atoms and a C–C double bond is characterised by a dumbbell shaped ELF attractor perpendicular to the axis of the carbon atoms.⁷⁰

The ELF topology analysis provides insights into the bonding within the clusters and into methane-Cu cluster interactions. The ELF isosurfaces of isolated Cu clusters Cu_2 , Cu_6 , Cu_8 , and Cu_{12} at three different isovalues are shown in Fig. 4. The attractors are obtained for isovalues of less than 0.4 for

these clusters and suggest a fair degree of delocalisation of electrons. The topology of the ELF isosurface for Cu_2 shows a disynaptic (as it connects two core basins which are depicted in Fig. 4) torus shaped attractor around the bond axis. In the case of planar Cu_6 , each pair of copper atoms, of which one atom is the vertex of the cluster triangle, has a torus shaped attractor, similar to that of the dimer. However, each set of three non-vertex copper atoms is seen to have their disynaptic attractors merged to form a trisynaptic attractor. A similar ELF topology of trisynaptic attractors was also reported for planar Li_6 cluster.⁷³ ELF topologies of Cu_8 and Cu_{12} are more complicated as there are multiple disynaptic attractors which are interconnected to form a network of polysynaptic (4 core basins considering tetrahedrons) attractor basins. The ELF attractors seem to be concentrated around the outer tetrahedrons of the clusters, with low electron density in the centre of the cluster. Such 4 centre bonding was also reported for Li_8 clusters of similar morphology although the actual topology was slightly different from that shown here.⁷³

The ELF topology, with attractors between every pair of Cu atoms, explains the preferential adsorption of H and CH_3 on bridge sites over the 3-fold sites, as observed in our CPMD-metadynamics simulations. However in Cu_8 and Cu_{12} , we can also see two distinct trisynaptic attractors at comparatively higher isovalues (0.36), unlike Cu_6 . Thus, from the electron localisation in the middle of the Cu–Cu axis in the dimer to intermittent network in planar Cu_6 to contiguous network in 3-dimensional Cu_8 and Cu_{12} clusters, the electronic structure can be observed to be more delocalised in larger clusters, as the transformation from planar to 3-dimensional morphology occurs. This further explains the trend of larger clusters (Cu_8 and Cu_{12} in this case) being more efficient in dehydrogenating methane upon collision, as observed in our CPMD-metadynamics simulations and the analysis of corresponding free energy barriers.

We also investigated the dissociation of methane on a single Cu atom and CPMD metadynamics simulations show that it can dissociate methane upon collision, with a free energy barrier for the dissociation as low as 50 kJ/mol. This validates the recent reports on copper vapour assisted dissociation of methane and remote growth of graphene on non-catalytic substrates.^{11–15} Both the CH_3 group and the hydrogen atom are found to be chemically bound to the Cu atom upon dissociation (Fig. S1).⁵³ The reactivity of a Cu atom being greater than that of the dimer does not fit the size-reactivity/activity trend explained above. To reconfirm and validate our CPMD-metadynamics results, we also computed the activation energy barrier for the dissociation of methane on Cu atom and Cu dimer, using conventional DFT method in Gaussian 09. We found that Cu atom is more active (activation energy barrier for dissociation—157.5 kJ/mol) than the Cu dimer (activation energy barrier for dissociation—170.2 kJ/mol) (refer Table SI).⁵³ The transition states for the dissociation of methane on Cu atom and Cu dimer are shown in Fig. 5. The activation energy barrier was calculated as the difference in the energy of the TS with respect to the optimised reactant, obtained by following the IRC pathway.

A possible explanation for the difference in activities of Cu and Cu dimer lies in the difference between their electronic

FIG. 4. Electronic structure of Cu clusters analysed using the ELF isosurfaces at three different isovalues. The blue balls represent Cu atoms and the grey transparent surfaces represent the ELF. The core basin is identified as a sphere around the atoms while the valence basins are evident in the first two images of each set.

structures. ELF isosurfaces (at two isovalues) of methane colliding with a Cu atom and with the Cu dimer are shown in Figs. 5(a1) and 5(a2) and Figs. 5(b1) and 5(b2), respectively. The structures in Figs. 5(a1), 5(a2), 5(b1), and 5(b2) are taken from the CPMD-metadynamics simulations and are snapshots of the trajectory just before the dissociation. A distinct monosynaptic attractor, characteristic of lone pairs, is observed in Cu-CH₄ system (Fig. 5(a1)), suggesting that the electron cloud is localised away from the colliding methane molecule. The unperturbed electron cloud (without the colliding methane) is found as a sphere around the Cu atom and is a contribution from the unpaired electron, with beta spin in our simulations (Fig. S1).⁵³ However, in the case of Cu dimer, we observe a disynaptic bonding attractor (Fig. 5(b1)) between two Cu

atoms similar to that in Figs. 4(a) and 4(b). Thus, the unpaired electron cloud is distributed over a larger space compared to paired electron region confined to the centre of the dimer axis. We believe that this makes a Cu atom more reactive compared to a dimer. The alignment of C-H vibrations towards the specific direction of the electron cloud in the case of Cu dimer is not required for the Cu atom and will be explained in detail in Sec. III A 3. The ELF isosurfaces of structures resulting from dissociation of methane on Cu atom and Cu dimer at two different isovalues are depicted in Fig. S1⁵³ and confirm attachment of H and CH₃ to the Cu atom and to the Cu dimer.

Thus, we observe a trend of the reactivity of copper clusters increasing with size and order of dimension from 1D to

FIG. 5. (a) TS for the dissociation of methane on Cu atom. (b) Transition state for the dissociation of methane on Cu dimer. Both TSs were identified using DFT with PBE exchange correlation functional and LANL2DZ basis set for copper and 6-311++g(d) basis sets for carbon and hydrogen. ((a1) and (a2)) ELF isosurfaces for two isovalues of methane colliding on a Cu atom, as obtained from a CPMD-metadynamics simulation just before dissociation. ((b1) and (b2)) ELF isosurfaces for two isovalues of methane colliding on a Cu dimer, as obtained from a CPMD-metadynamics simulation just before dissociation. The blue, red, and grey balls represent the copper, carbon, and hydrogen atoms, respectively, and the grey transparent surfaces represent the electron density.

3D from Cu_2 to Cu_8 . An increase in the size and the order of dimension increases the electron delocalisation within the cluster and also enables higher probability of collisions with favourable dynamic parameters. Some of these were discussed in the previous paragraphs and will be further discussed in Sec. III A 3. As the free energy barriers for the dissociation of methane on Cu_8 and Cu_{12} clusters (Table I) are similar, we do not anticipate the barriers to come down further with subsequent increase in the cluster size. In contrast, when the dynamics parameters are not accounted for explicitly in the simulations, the activation energy barriers calculated for the dissociation of methane on small clusters (Cu_2 , Cu_6) do not differ significantly from that on Cu(111) surface (Sec. II A 2 and Table SI of the supplementary material).⁵³

3. Effects of collision site morphology and collision angle on free energy barriers

Analysis of simulation trajectories on different Cu clusters suggests that the collision site on the cluster and features of collision affect the barriers for the dissociative chemisorption of methane on the cluster. The values of free energy barriers obtained from three simulations of dissociation of methane on the Cu dimer with three different collision angles are reported in Table I. Collisions of methane with a smaller value of the C-Cu-Cu angle (angle between the carbon atom of methane and the Cu dimer) were observed to have lower barriers for dissociation compared to the head on coaxial collision (along the axis of the Cu dimer). This can be attributed to the structure of the transition state which has a C-Cu-Cu angle of $\sim 120^\circ$, as shown in Fig. 5(b). This particular configuration of the methane molecule upon collision allows for the C-H stretch vibration to be aligned along the axis of the Cu dimer. The preference for this alignment can be explained based on the ELF topology of the Cu dimer (Figs. 4(a), 4(b), and 5(b1)), where the electron localization is in a torus between the dimer axes. In the case of the Cu dimer, the alignment of one of the C-H bonds towards this high localization space is not just a favourable factor but also a necessary condition for dissocia-

tion. Similar alignment of the C-H bond of methane towards the centre of the edge pair of Cu atoms of Cu_6 cluster has been observed, based on the transition state for the dissociation of methane on that cluster. This implies that larger Cu clusters with higher number of available sites (electron localization regions) enable greater probability of favourable alignment of the C-H bonds of methane during the collision. Alignment of the C-H stretch vibrations along the surface of the metal has been reported to increase the reactivity considerably in experiments on collision of vibrationally excited methane on Ni surfaces.^{74,75} Thus, pre-alignment of the methane molecule along the collision path allows easier access to the transition state and thus lowers the barrier for dissociation. This suggests that stereodynamical steering along the collision path can significantly alter the barrier for the reaction.

During high energy collisions between molecules which can be considered instantaneous events with no change in the internal states of the molecules, the reactivity with respect to specific vibrational degrees of freedom would depend on the coupling of these degrees with the reaction coordinate. On this principle, Guo and co-workers proposed the Sudden Vector Projection (SVP) model to quantify the efficacy of the reactant vibrational states in promoting a reaction based on the overlap of the reactant normal mode vectors with the vector corresponding to the imaginary frequency in the transition state.⁷⁶ This model applied to the dissociative chemisorption of methane on various Ni and Pt surfaces suggests that the stretching (both symmetric and asymmetric) vibrational modes of methane are more effective than the bending modes in promoting the dissociation.^{49,50} We applied a similar technique to estimate the coupling of the normal mode vibrations of the optimized reactants (structure obtained by following the IRC path) of the collision of methane on Cu atom and Cu_2 and Cu_6 clusters with the corresponding reaction coordinate (vibration corresponding to the imaginary frequency). We observed a similar trend, as described above, in the case of reaction of methane on Cu atom and Cu_6 cluster (Sec. II A 3 of the supplementary material),⁵³ and both stretching and bending vibrations can be seen to couple to the reaction coordinate

(Table SII).⁵³ However, in our CPMD-metadynamics simulations, we have not pre-activated any specific vibrational states of methane and all the vibrational degrees of freedom are unconstrained and are thus sampled during collision dynamics. The formation of the precursor as a result of the collision activates both the stretching and bending modes of methane, as shown in Fig. 3. Due to unhindered rotation and lateral movements in the precursor, the stretch-bend vibrations of methane sample various collision sites around the selected Cu atom of the cluster, unlike the typically expected scenario in a very high energy collision.⁵⁰ These rotations and movements align the C–H bond of methane favourably to regions of high electron density within the cluster, thereby facilitating the dissociation via a minimum energy pathway with lowest free energy barriers. Analysis of the normal modes of the various configurations along the collision trajectory and their coupling with the reaction coordinate is beyond the scope of this report and is not attempted. Additionally, with the CPMD-metadynamics technique we employ, it may not be feasible to quantify the relative efficacies of specific modes in promoting the dissociation reaction. The “sudden approximation” necessary for this estimation may not be valid in our CPMD-metadynamics simulations.

The activation free energy values computed for the dissociation of methane on Cu₈ and Cu₁₂ clusters have been observed to vary by 40–50 kJ/mol depending on the number of nearest neighbour Cu atoms in the immediate vicinity of the atom on which methane collides (Table I). Here, we define the nearest neighbours as Cu atoms within a distance of 3 Å from the atom on which methane collides. To reconfirm the effect of number of nearest numbers, simulations were performed at 300 K on Cu₈ and the results are reported in Table I. Room temperature was chosen for these simulations so that the cluster geometry does not change significantly due to lattice reconstruction along the dynamics. We observe significant difference in the barriers for the dissociation of methane colliding on the centre atom (6 nearest neighbours, free energy barrier—110 kJ/mol) and on the capping atom (3 nearest neighbours, free energy barrier—170 kJ/mol) at the same temperature. The greater the number of nearest neighbours, the greater is the number of available sites for the adsorption of CH₃ and H and higher

is the probability of favourable alignment of the C–H bond for dissociation. This explains the trend of the barrier for dissociation reducing significantly with increasing number of nearest neighbours during simulations on the same Cu cluster at the same temperature. It is to be noted that the values of free energy barriers reported for these simulations are much higher than those reported earlier and are a consequence of the 4-fold decrease in the temperature of the simulation (refer Sec. II A 4 of the supplementary material for a brief discussion on the temperature effect on free energy barrier).⁵³

Analysis of the ELF topology of structures representing snapshots of the trajectories from these simulations shows that changes in the cluster geometry resulting from high temperature dynamics alter the electron localisation/delocalisation patterns within the cluster. This is more pronounced in the Cu₆ planar cluster and manifests as high electronic localization, only in the space between the three Cu atoms, as shown in Fig. 6(a). The localisation is evident from the high isovalue (0.59) at which this valence ELF basin can be seen to disappear and is much higher than the isovalues seen for Cu₆ cluster (Fig. 4). The free energy barrier for the dissociation of methane in this case was found to be much higher (90 kJ/mol) than in the case with lesser distortion (60 kJ/mol), as shown in Fig. 6(b). Thus, geometric distortions leading to localisation of electrons in a specific region within the cluster significantly increases the free energy barrier for the dissociation of methane on small and planar clusters. The ELF topology changes with geometric distortions in the 3-dimensional clusters as well (Fig. S2);⁵³ however, the implications of such changes are not as prominent as in planar small clusters.

B. Dehydrogenation of chemisorbed methyl group on the clusters

1. Reactive trajectories and free energy barriers

CPMD-metadynamics simulations were also performed to investigate the dehydrogenation of the chemisorbed CH₃ and the formation of carbon on these clusters. The simulations were stopped after the CH₂ + 2H was formed on Cu₂ cluster and complete dehydrogenation was simulated only for the larger clusters (Cu₆, Cu₈, and Cu₁₂). The free energy landscape

FIG. 6. ELF isosurfaces of the structures representing collision of methane on the vertex atom of Cu₆ cluster showing (a) high degree of electron localisation in a specific region resulting from the distortion of the cluster and higher free energy barrier for the dissociation of methane (90 kJ/mol); (b) little region specific electron localisation and lower free energy barrier (60 kJ/mol) for dissociation. The structures are obtained from CPMD-metadynamics simulations at 1273 K. Colour scheme for atoms is similar to that in Fig. 5.

FIG. 7. The free energy landscape reconstructed from CPMD-metadynamics simulation of the chemisorbed methane on Cu_8 cluster undergoing further dehydrogenation with the average H–Cu coordination number and C–H coordination number as collective variables at 1273 K. The structures from the trajectory corresponding to significant minima and barrier corresponding to each dehydrogenation step are also shown. Colour scheme for atoms is similar to that in Fig. 1.

reconstructed from the metadynamics simulation of the dehydrogenation of chemisorbed CH_3 on a Cu_8 cluster, as a function of the two collective variables as defined in Sec. II, is shown in Fig. 7. The general features of the free energy landscape for the dehydrogenation of chemisorbed CH_3 on other Cu clusters are similar and thus are not shown here. The formation of carbon on the clusters was observed to proceed through the elementary steps, as shown in Figs. 7 and 8. Representative structures from the trajectory, corresponding to the minima ($\text{CH}_3 + \text{H}$, $\text{CH}_2 + 2\text{H}$, $\text{CH} + 3\text{H}$, and $\text{C} + 4\text{H}$), and the free energy barriers associated with each transformation are shown in Fig. 7. Each dehydrogenation step is observed to bring about a decrease in the C–H coordination number (ultimately going to zero) and a corresponding increase in the average Cu–H coordination number (Fig. 7). In the simulation trajectories, CH_3 and CH_2 groups have been observed at the bridge sites and at the 3-fold sites (cf. Fig. 1), frequently hopping between the two kinds, while the CH groups are typically observed to be found at 3-fold sites (movie S2 of the supplementary material).⁵³ The carbon monomer is found to migrate to the subsurface in the case of Cu_8 and Cu_{12} as reported by Zhang *et al.*⁷⁷ and is coordinated to four Cu atoms. However, in the case of Cu_6 , the originally planar Cu_6 cluster evolved into a 3-dimensional cluster and the carbon monomer was observed to be coordinated to at least 4 and occasionally 5 Cu atoms.

Free energy barriers for the dehydrogenation of chemisorbed CH_3 on different Cu clusters at 1273 K are shown

FIG. 8. Free energy barriers for the elementary steps in the dehydrogenation of the chemisorbed CH_3 on Cu clusters of different sizes, as obtained from the CPMD-metadynamics simulations at 1273 K.

in Fig. 8 and are reported in Table SIII.⁵³ These free energy barriers, unlike those we calculated for the collision induced dissociation of methane on the clusters, fall within the range of activation energy (enthalpy) barriers reported for complete dehydrogenation of methane on $\text{Cu}(111)$ surface.^{6–9} This further qualifies the CPMD-metadynamics technique we employ here to be suitable to investigate the reactions under consideration and the free energy barriers reported to be sufficiently accurate, although a direct comparison with DFT based activation energy barriers is to be avoided. It can be seen that the free energy barrier for the dissociation of chemisorbed $\text{CH}_3 + \text{H}$ to give $\text{CH}_2 + 2\text{H}$ on all clusters is significantly higher (double or more) than the corresponding free energy barriers for the collision induced dissociation of methane. This is in contradiction to the trend reported for successive dissociations of CH_4 on copper surfaces where the second dissociation (formation of CH_2) was shown to have a lower activation energy barrier than the first.^{6–9} However, it is to be noted that the reported values and trends in the literature are from 0 K DFT calculations, which do not account for the collision dynamics and the effects thereof. Collision induced vibrational activation of methane is responsible for lowering the free energy barrier for the dissociation of the first C–H bond and is absent in subsequent dehydrogenation steps. However, computational investigation of methane activation on Fe_4 cluster⁷⁸ showed the cleavage of the second C–H bond is more difficult than the first and is in agreement with our observation.

2. Effects of cluster size, geometry, and distortion on free energy barriers for successive dehydrogenation of CH_3

It can also be seen from Fig. 7 that the free energy barrier for the first dehydrogenation of the chemisorbed CH_3 decreases with increase in the cluster size from Cu_2 to $\text{Cu}_8/\text{Cu}_{12}$. This trend is in agreement with that observed during collision induced dissociation on the clusters and can be explained based on the number of available sites description given earlier. Simulations on Cu_8 and Cu_{12} clusters suggest that successive dehydrogenation steps have increasingly higher barriers with the last step of dehydrogenation to carbon having the highest barrier among all elementary steps. This is in agreement with the previous reports which show the formation of carbon to have the highest barrier among the elementary dehydrogenation steps on $\text{Cu}(111)$ surface.^{6,8,9} This trend can be explained based on the reorganisation of the cluster geometry resulting from and necessitated by the successive dehydrogenation steps.

Figure 9 shows the variation of the coordination number of carbon atom of methane with the atoms of the Cu_8 cluster during a CPMD-metadynamics simulation at 1273 K, investigating complete dehydrogenation of chemisorbed CH_3 alongside the dehydrogenation profile. The increase in the C–Cu coordination number, evident from the decrease in C–Cu distances (Fig. 9(b)), coincides with the dehydrogenation of chemisorbed CH_3 (Fig. 9(a)). A significant increase in coordination number (>3) also implies the reorganisation of the cluster and is observed in simulations on Cu_6 and Cu_{12}

FIG. 9. (a) 4 C–H bond distances during the reaction on the Cu_8 cluster, along the simulation trajectory. The average C–H bond length in CH_3 is 1.1 Å. (b) Distance of the carbon atom from the Cu atoms of the cluster. An increase in C–Cu coordination number can be seen along the trajectory. The data are obtained from CPMD metadynamics simulation investigating dissociation of CH_3 on Cu_8 cluster at 1273 K and shows the reorganisation of the cluster as dehydrogenation proceeds. Similar trends are observed in simulations on Cu_6 and Cu_{12} clusters as well.

clusters as well. The planar triangular Cu_6 cluster can be seen to evolve into distorted 3-dimensional structures, as dehydrogenation proceeds (Fig. 10(a)) and the carbon atom can be seen to move to subsurface of the 3-dimensional clusters (Fig. 10(b)).

The increase in C–Cu coordination number with dehydrogenation and the reorganisation of the cluster geometry enables the carbon atom to retain its sp^3 character, with the Cu atoms replacing hydrogen, at each stage of the dehydrogenation. The nature of C–Cu bonding, with carbon retaining its sp^3 character

was confirmed by the ELF topology analysis (Fig. S3)⁵³ and is in agreement with the previous report based on ELF analysis for methane dissociation on a copper slab.⁹ Even without high temperature dynamics, small Cu clusters have been shown to undergo significant geometric changes upon chemisorption of hydrogen molecule, with the magnitude of change being larger for small clusters up to Cu_6 .^{26,27} The reorganisation of the Cu_8 and Cu_{12} clusters is more difficult than that of Cu_6 . This is because the binding energy per Cu atom in small Cu clusters increases with increase in cluster size.²⁶ This explains the trend of the free energy barrier for formation of carbon via successive dissociation of CH_3 increasing with cluster size from 185 kJ/mol on Cu_6 to 220 kJ/mol on Cu_{12} as shown in Fig. 8.

3. Effects of chemisorbed hydrogen

We did not observe hydrogen of the CH_x ($x = 1-3$) being abstracted ($\text{CH}_x + \text{H} \rightarrow \text{CH}_{x-1} + \text{H}_2$)⁶ by another chemisorbed hydrogen on the cluster in these simulations, suggesting that the chemisorbed hydrogen does not aid in further dehydrogenation of CH_x . This is in contradiction to the proposition of Vlassiuk *et al.*⁷⁹ where a catalytic role of surface hydrogen was suggested. We also did not observe the evolution of a hydrogen molecule by the recombination of surface hydrogen atoms within the time span of these simulations. Formation and evolution of hydrogen molecule have been reported to be a high barrier process by Li *et al.*⁶ This report did not explicitly incorporate a collective variable like H–H coordination number in our metadynamics simulations. We also investigated the role of chemisorbed hydrogen in collision induced dissociation of methane on Cu_8 cluster and found that chemisorbed hydrogen neither promotes nor inhibits dissociation of methane on the cluster at these elevated temperatures. The details and results of the simulations are presented in Sec. II B 3 a and Table SIV of the supplementary material, and the trajectory of the collision induced dissociation of methane on Cu_8 cluster with pre-adsorbed $\text{CH}_3 + \text{H}$ is available as movie S3 of the supplementary material.⁵³

FIG. 10. Snapshots from CPMD metadynamics simulations at 1273 K showing the sequence of dehydrogenation of chemisorbed CH_3 on Cu clusters and the corresponding reorganisation of the cluster geometry. (a) From a simulation on Cu_6 cluster showing the transformation of the planar triangular cluster to a 3-dimensional cluster. (b) From a simulation on Cu_8 cluster showing the migration of carbon to the sub-surface of the cluster. The dissociating C–H bond is indicated with a red arrow in each structure. Trends on Cu_{12} cluster are similar to those on Cu_8 cluster and are thus not shown here. Colour scheme for atoms is similar to that in Fig. 1.

The recombination of hydrogen atom on the cluster with the carbon monomer was observed on the Cu_6 cluster (movie S2 of the supplementary material).⁵³ However, this process was not observed on Cu_8 and Cu_{12} clusters. The recombination reaction on Cu_6 could possibly be attributed to the saturation of Cu sites on the cluster. The free energy barrier for the recombination of hydrogen with carbon on the Cu_6 cluster was calculated to be around 105 kJ/mol (Fig. S4)⁵³ and is much lower than that of the elementary dehydrogenation steps on the same cluster. A microkinetic model based analysis by Li *et al.* also showed that the recombination reactions of CH_x ($x = 0-3$) with chemisorbed hydrogen have rate constants higher than those of the corresponding dehydrogenation reactions on Cu(111) surface.⁶ These results suggest that competition of the dehydrogenation reaction and recombination reaction would favour the latter in cases of surface saturation not only in small clusters but also on copper surfaces.

Structures similar to those in right extreme of Fig. 10(a) which are nearly saturated with hydrogen have virtually no free electron cloud. This would affect further dissociative chemisorption of methane on the cluster. Thus, saturation driven inhibition of dissociative chemisorption/dehydrogenation of CH_x ($x = 1-4$) serves to slow down the free supply of CH_{x-1} which is necessary for the formation of larger hydrocarbon precursors on the clusters. This phenomenon in the context of graphene growth on copper thin films is one of the reasons for the “self-limiting” mechanism and combined with the low solubility of carbon in copper bulk, leads to uniform layer control in graphene synthesis by CVD.^{3,10} Since dissociative chemisorption of hydrogen on copper is highly favourable, competitive adsorption of hydrogen from the carrier gas which is a mixture of methane and hydrogen (sometimes argon also) in the CVD synthesis of graphene on copper has been reported to be an inhibitor to graphene growth.⁸⁰ This proposition was based on the dissociation probability of methane being a function of the available copper sites. Thus, high hydrogen partial pressures employed in the CVD growth of graphene would result in a controlled supply of CH_x species on the surface via competitive recombination, an extreme case of which has been reported as etching of graphene.^{79,81} The high surface coverage by hydrogen by dissociative chemisorption on copper surfaces will also inhibit further dissociative chemisorption of methane on the surface. Both these factors can suppress the nanocarbon growth on the surface.

C. Coupling reactions of CH_x on the clusters

The chemisorbed CH_x species may undergo further surface reactions to form larger C_mH_n species. Thus, we investigated the interactions of 2 CH_3 groups, 2 CH_2 groups, and 2 CH groups on a Cu_8 cluster at 1273 K and observed C–C coupling to form C-2 hydrocarbons and hydrocarbon intermediates.

1. $\text{CH}_3 + \text{CH}_3$

Two reactive pathways were observed for the two CH_3 species on the cluster. In the first pathway, one of the CH_3 groups underwent further dissociation before C–C coupling and formed a CH_2 – CH_3 species attached to the cluster, through

the CH_2 moiety (movie S4 of the supplementary material).⁵³ The dehydrogenation and coupling were observed to have a free energy barrier of 165 kJ/mol (Fig. S5(a)).⁵³ The other pathway involved the formation and evolution of ethane to the gas phase (movie S5 of the supplementary material).⁵³ The free energy barrier for the coupling of methyl groups without further dehydrogenation was found to be around 70 kJ/mol (Fig. S5(b)).⁵³ The barrier for diffusion of the methyl groups towards each other on the cluster was calculated to be between 60 and 80 kJ/mol.

The ELF isosurfaces of structures from the simulations investigating the coupling of two methyl groups on Cu_8 clusters, corresponding to the two pathways discussed above, are shown in Fig. 11. Figures 11(a)–11(c) are from the trajectory which showed the formation of a C_2H_5 group attached to the cluster and Figures 11(d)–11(f) are from the trajectory which showed the evolution of ethane. Figure 11(b) shows the onset of the dissociation of the C–H bond of one of the methyl groups and the formation of the C–C bond, which is evident from the disynaptic attractor along the C–C axis. The C–C coupling is completed in the structure shown in Fig. 11(c) and is indicated by the characteristic ELF attractor in the C–C axis. The resulting structure can also be seen to be strongly bound to the Cu cluster. Corresponding structures from the other pathway, as shown in Figures 11(e) and 11(f), can be seen to have the characteristic attractors along the C–C axis, indicating the formation of a C–C bond. However, the two methyl groups in Fig. 11(e) and ethane formed in Fig. 11(f) do not show any signs of attachment to the Cu cluster, suggesting that the coupling is not completely mediated by the surface. The multicentre C–Cu bonding (Figs. 11(a) and 11(b)) and the favourable alignment of the C–H bond towards the electron cloud in the cluster (Fig. 11(b)) enabled the dissociation of the C–H bond in the former trajectory which did not happen along the dynamics in the latter.

2. $\text{CH}_2 + \text{CH}_2$ and $\text{CH} + \text{CH}$

The reaction of two CH_2 species resulted in the formation and evolution of ethylene to the gas phase with a free energy barrier of ~ 70 kJ/mol, while the reaction of two CH groups resulted in the formation of C_2H_2 attached to the surface (movie S6 of the supplementary material)⁵³ with a free energy barrier of less than 50 kJ/mol. The structures and bonding in these cases are depicted in Fig. 12 and are analysed in the context of ELF isosurfaces in the next paragraph. The formation of C_2H_2 on copper surfaces was investigated by Zhang *et al.* using first principles molecular dynamics at 1300 K and was found to be an exothermic reaction with an activation energy barrier of ~ 30 kJ.⁸ However, they observed the C_2H_2 to desorb from the Cu(100) surface within 4 ps of simulation time, contrary to our observation on the cluster. Similar to our observations, Shibuta *et al.*⁸² reported the evolution of ethane and ethylene and formation of C_2H_2 attached to the copper surface resulting from reactions of CH_3 , CH_2 , and CH groups on the surface based on their MD simulations.

Figures 12(a)–12(c) are ELF isosurfaces of structures from a simulation which showed the evolution of ethylene as a result of the coupling of two CH_2 groups on the Cu_8

FIG. 11. ELF isosurfaces of structures from CPMD-metadynamics simulations investigating the coupling of two CH_3 groups and the formation of C_2 hydrocarbons/hydrocarbon intermediates on Cu_8 cluster at 1273 K. (a)–(c) are snapshots from a simulation showing the formation of C_2H_5 bound to the cluster, and (d)–(f) are snapshots from a simulation showing the evolution of ethane to the gas phase. The dissociating C–H bond is indicated with a dotted red line and the significant attractors indicating C–Cu and C–C bonds are highlighted in each structure. Colour scheme for atoms is similar to that in Fig. 5.

cluster. The multicentre bonding of CH_2 groups to the cluster is evident in Fig. 12(a). Unlike the case of CH_3 groups, the formation of C–C bond between the two CH_2 groups seems to be partially mediated by the Cu cluster, as can be seen by the C–Cu bond attractor in Fig. 12(b). Once C–C coupling is

completed, ethylene can be seen to evolve into the gas phase. The dumbbell shaped ELF attractor at the centre of the C–C axis, as seen in Fig. 12(c), is the characteristic of a C–C double bond and confirms the formation and evolution of ethylene. Figures 12(d)–12(f) are ELF isosurfaces of structures from

FIG. 12. ELF isosurfaces of structures from CPMD-metadynamics simulations at 1273 K investigating the coupling of CH_2 and CH groups and the formation of C_2 hydrocarbons on Cu_8 cluster. (a)–(c) are snapshots from a simulation showing the formation and evolution of C_2H_4 into the gas phase, while (d)–(f) are snapshots from a simulation showing the formation of C_2H_2 bound to the cluster. The significant attractors indicating C–Cu and C–C bonding are highlighted in each structure. Colour scheme for atoms is similar to that in Fig. 5.

a trajectory showing the coupling of two CH groups on the cluster. The CH groups are typically observed to be in 3-fold sites, as confirmed by the 3 centre bonding in Fig. 12(d). The onset of coupling is depicted in Fig. 12(e) and it is to be noticed that the two carbon centres are strongly bound to the Cu cluster. The coupling in this case is seen to result in C_2H_2 which is bound to the cluster through both the carbon atoms, as can be seen from Fig. 12(f), while the C–C bond in it retains a partial double bond character, as can be seen by the dumbbell like ELF attractor along the C–C axis. C_2H_2 does not form ethyne and evolve into the gas phase.

From the ELF analysis of structures from four reaction pathways, as depicted in Figs. 11 and 12, it can be seen that the CH group is more strongly bound with the cluster through multicentre bonding throughout the trajectory, as compared to CH_2 and CH_3 . This explains the higher (~ 100 kJ/mol) free energy barrier for the diffusion of CH groups on the cluster than that for CH_2 and CH_3 groups (~ 60 kJ/mol) at 1273.

3. Comparison of different pathways and implications for graphene growth

The pathway, via the formation of C_2H_2 , is hypothesised to lead to the formation of larger hydrocarbons on the Cu surface.⁸ Further addition of CH to C_2H_2 was also observed to be thermodynamically favourable with an activation energy barrier of ~ 105 kJ/mol.⁸ However, there is another report which suggests that C_2H_5 is the key intermediate species in the formation of larger hydrocarbons, which subsequently dehydrogenates to form graphene on copper surface.⁸³ Based on our calculations, the free energy barrier for the dissociation of methane and of the formation of chemisorbed CH_3 on the larger clusters is around 100 kJ/mol and can be easily overcome at temperatures over 1000 K. However, for a surface mediated and restricted growth of larger hydrocarbons, which could eventually serve as precursors for nano-carbon growth, direct coupling of two CH_3 groups may not be the likely pathway. The pathway via C_2H_5 involves barriers in excess of 160 kJ/mol and the pathway via C_2H_2 involves barrier between 160 and 190 kJ/mol. Formation of C_2H_2 also entails greater surface saturation of small clusters compared to C_2H_5 due to the presence of four surface hydrogens and C_2H_2 being bound to the cluster through both carbons. Thus, considering the free energy barriers involved in the formation process and the surface limitations of small clusters, we believe the C_2H_5 pathway would be dominant in growth of larger hydrocarbon precursors on the clusters. Extending this to graphene growth on copper surfaces, we believe the C_2H_5 pathway would be dominant in the growth conditions with high hydrogen partial pressure. This is due to the competitive saturation of surface sites by chemisorbed hydrogen from the carrier gas, which, along with the possibility of the competitive recombination, makes it more likely to leave a higher concentration of CH_3 on the surface, compared to CH_2 and CH. This is in agreement with reports which claim CH_3 to be a more dominant species compared to CH in graphene growth on Cu(100) surface at high partial pressure of hydrogen.⁸⁴ An exhaustive investigation of other hydrocarbon intermediates that may be involved

in the formation of larger hydrocarbons via coupling of various CH_x surface species is beyond the scope of this report.

IV. SUMMARY AND CONCLUDING REMARKS

We investigated the collision induced dissociation of methane on Cu clusters of different sizes and also the further dissociation of the chemisorbed CH_3 to form carbon, using first-principles molecular dynamics and metadynamics simulations. The claims of copper vapour assisting direct CVD growth of graphene on inert substrates have been validated as Cu atoms can also dissociate methane to CH_3 which would be a precursor for further reactions. Collision induced vibrational activation of stretching and bending modes along with lattice relaxation of the clusters significantly reduces the free energy barrier for the dissociation of methane on Cu clusters. An increase in the cluster size and the order of dimension (1D, 2D, and 3D) of the cluster makes available higher number of sites for the chemisorption of the dissociated fragments (CH_3 and H) and thereby reduces the free energy barrier for the dissociation of methane. Additionally, it also increases the probability of favourable alignment of the C–H stretching vibration which represents the reaction coordinate, to the regions of high electron localization, bringing down the barrier for dissociation. The available sites are typically the regions along the axis of every Cu–Cu pair, and as a consequence, hydrogen adsorbs at these sites, unlike metal surfaces, where the hollow sites are preferred. Changes in the geometry and the morphology of the cluster result in significant changes to the electron localisation within the cluster; an effect more prominent in small planar clusters like Cu_6 , and increases the free energy barrier for the dissociation of methane.

Dehydrogenation of chemisorbed CH_3 has significantly higher free energy barrier compared to the collision induced dissociation of methane on the same cluster and decreases with increase in the cluster size. Formation of carbon is a very high barrier process (> 190 kJ/mol), with each elementary step of dissociation leading towards it having progressively increasing barriers. The corresponding barriers increase with cluster size. The cluster size dependence is attributed to the increasingly difficult reorganisation of the clusters required to accommodate the CH and C species, which retain the sp^3 hybridisation of carbon through Cu atoms of the cluster. Chemisorbed hydrogen resulting from the successive dehydrogenation steps does not inhibit or instigate further dissociation. Surface saturation with hydrogen may however severely affect further dissociation both by increasing the free energy barrier for dissociation and by competitive recombination.

Direct coupling of CH_x ($x = 1-3$) fragments on the clusters are facile processes with free energy barriers lower than 80 kJ/mol. The resulting C_2H_n species, with the exception of ones with $n = 4$ and 6, remain bound to the cluster. For the formation of larger hydrocarbon precursors bound to the cluster, CH_3 groups with high mobility (free energy barrier for movement on the cluster is less than 70 kJ/mol) are likely to be the key species, under conditions of saturation of the cluster with chemisorbed hydrogen. However, under low cluster saturation, pathways involving the CH group are equally possible on these clusters at the temperatures considered.

Extensive experimental investigations of the collision induced dissociation of methane on surfaces (primarily Ni and Pt) have been carried out by the state resolved molecular beam techniques.⁶⁶ These methods rely on laser excitation of specific vibrational states of methane to ascertain their efficacy in promotion of reaction and have been reviewed by Juurlink *et al.*⁶⁶ Both vibrational mode specificity and bond selectivity have been observed in methane and its isotopes in these kinds of experiments, and C–H stretching vibrations have been shown to be more effective than the bending vibrations in promoting the reaction.⁶⁶ To complement these experimental observations, computational studies have also been performed to investigate the mode and bond selectivity observed in these experiments. Recent investigations using first principles molecular dynamics simulations,^{64,85} quasiclassical trajectory (QCT) method based MD simulations,^{52,86} multidimensional quantum dynamics simulations,⁴⁹ and quantum dynamics via the reaction path Hamiltonian approach^{50,51} have all given significant insights into the mode selectivity, collision site, orientation, and lattice motion/reconstruction dependence of methane dissociation on metal surfaces in addition to dependencies on translation and rotational energies. The quantum dynamics based approaches require accurate PES with all molecular degrees of freedom and also the models to treat the molecule surface interactions and lattice motion. In CPMD-metadynamics simulations, the potential energy is calculated on the fly and all degrees of freedom of methane and lattice motion are inherently accounted for. With a careful choice of collective variables resembling the exact reaction coordinate, the CPMD-metadynamics derived free energy barriers are estimates of the actual free energy barriers for the reaction at the desired temperatures, averaging effects of thermal/collision induced vibrational activation, collision site, and lattice motion/reconstruction. Various dynamics parameters like collision angle, collision site morphology, lattice reconstruction, and their influence on the free energy barriers for the dissociation of methane via a precursor mediated pathway have been estimated. The investigation in the present paper is relevant to the thermal bulb kind of experiments and to the dissociation of methane in an actual CVD reactor and these simulations may not be an exact computational representation of the molecular beam experiments. Additionally, the CPMD-metadynamics technique samples reactive trajectories and thus direct estimation of the relative efficacies of individual molecular degrees of freedom in promoting the reaction may not be possible here.

ACKNOWLEDGMENTS

We acknowledge the financial support provided by Nanyang Technological University, Singapore.

¹P. Wu, W. Zhang, Z. Li, and J. Yang, *Small* **10**, 2136 (2014).

²C. Mattevi, H. Kim, and M. Chhowalla, *J. Mater. Chem.* **21**, 3324 (2011).

³X. Li, W. Cai, J. An, S. Kim, J. Nah *et al.*, *Science* **324**, 1312 (2009).

⁴C. M. Seah, S. P. Chai, and A. R. Mohamed, *Carbon* **70**, 1 (2014).

⁵S. J. Blanksby and G. B. Ellison, *Acc. Chem. Res.* **36**, 255 (2003).

⁶K. Li, C. He, M. Jiao, Y. Wang, and Z. Wu, *Carbon* **74**, 255 (2014).

⁷S. Yuan, L. Meng, and J. Wang, *J. Phys. Chem. C* **117**, 14796 (2013).

⁸W. Zhang, P. Wu, Z. Li, and J. Yang, *J. Phys. Chem. C* **115**, 17782 (2011).

⁹G. Gajewski and C. W. Pao, *J. Chem. Phys.* **135**, 064707 (2011).

¹⁰X. Li, W. Cai, L. Colombo, and R. S. Ruoff, *Nano Lett.* **9**, 4268 (2009).

¹¹P. Y. Teng, C. C. Lu, K. Akiyama-Hasegawa, Y. C. Lin, C. H. Yeh *et al.*, *Nano Lett.* **12**, 1379 (2012).

¹²H. Kim, I. Song, C. Park, M. Son, M. Hong *et al.*, *ACS Nano* **7**, 6575 (2013).

¹³C. Zhang, B. Y. Man, S. Z. Jiang, C. Yang, M. Liu *et al.*, *Appl. Surf. Sci.* **307**, 327 (2014).

¹⁴C. Zhang, B. Y. Man, C. Yang, S. Z. Jiang, M. Liu *et al.*, *Nanotechnology* **24**, 395603 (2013).

¹⁵Y. Song, J. Liu, L. Quan, N. Pan, H. Zhu, and X. Wang, *J. Phys. Chem. C* **118**, 12526 (2014).

¹⁶H. Q. Yang, Y. Q. Chen, C. W. Hu, M. C. Gong, H. R. Hu *et al.*, *Chem. Phys. Lett.* **355**, 233 (2002).

¹⁷Y. Wang, Q. Wang, Z. Geng, L. Lv, Y. Si *et al.*, *J. Phys. Chem. A* **113**, 13808 (2009).

¹⁸D. Troya, *J. Phys. Chem. A* **109**, 5814 (2005).

¹⁹J. D. Beckerle, Q. Y. Yang, A. D. Johnson, and S. T. Ceyer, *J. Chem. Phys.* **86**, 7236 (1986).

²⁰J. D. Beckerle, A. D. Johnson, Q. Y. Yang, and S. T. Ceyer, *J. Chem. Phys.* **91**, 5756 (1989).

²¹C. T. Rettner, H. E. Pfür, and D. J. Auerbach, *Phys. Rev. Lett.* **54**, 2716 (1985).

²²M. B. Lee, Q. Y. Yang, S. L. Tang, and S. T. Ceyer, *J. Chem. Phys.* **85**, 1693 (1985).

²³M. B. Lee, Q. Y. Yang, and S. T. Ceyer, *J. Chem. Phys.* **87**, 2724 (1987).

²⁴H. Ueta, M. Saida, C. Nakai, Y. Yamada, M. Sasaki, and S. Yamamoto, *Surf. Sci.* **560**, 183 (2004).

²⁵Z. J. Zuo, L. Wang, P. D. Han, and W. Huang, *Comput. Theor. Chem.* **1033**, 14 (2014).

²⁶G. H. Guvelioglu, P. Ma, X. He, R. C. Forrey, and H. Cheng, *Phys. Rev. Lett.* **94**, 026103 (2005).

²⁷R. C. Forrey, G. H. Guvelioglu, P. Ma, X. He, and H. Cheng, *Phys. Rev. B* **73**, 155436 (2006).

²⁸X. Yuan, L. Liu, X. Wang, M. Yang, K. A. Jackson, and J. Jellinek, *J. Phys. Chem. A* **115**, 8705 (2011).

²⁹L. Padilla-Campos, *J. Mol. Struct.: THEOCHEM* **815**, 63 (2007).

³⁰M. Yang, K. A. Jackson, C. Koehler, T. Frauenheim, and J. Jellinek, *J. Chem. Phys.* **124**, 024308 (2006).

³¹V. A. Ukraintsev and I. Harrison, *J. Chem. Phys.* **101**, 1564 (1994).

³²A. Laio and M. Parrinello, *Proc. Natl. Acad. Sci. U. S. A.* **99**, 12562 (2002).

³³R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

³⁴CPMD V. 3.15.3, Copyright IBM Corp. 1990-2008, Copyright MPI für Festkörperforschung, Stuttgart, 1997-2001, <http://cpmd.org/>.

³⁵V. Van Speybroeck and R. J. Meier, *Chem. Soc. Rev.* **32**, 151 (2003).

³⁶A. Laio and F. L. Gervasio, *Rep. Prog. Phys.* **71**, 126601 (2008).

³⁷S. Zheng and J. Pfendner, *Mol. Simul.* **41**, 55 (2015).

³⁸X. J. Kuang, X. Q. Wang, and G. B. Liu, *J. Chem. Sci.* **123**, 743 (2011).

³⁹M. Kabir, A. Mookerjee, and A. K. Bhattacharya, *Eur. Phys. J. D* **31**, 477 (2004).

⁴⁰P. B. Balbuena, P. A. Derosa, and J. M. Seminario, *J. Phys. Chem. B* **103**, 2830 (1999).

⁴¹P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

⁴²W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

⁴³J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

⁴⁴D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).

⁴⁵S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).

⁴⁶S. Nosé, *J. Chem. Phys.* **81**, 511 (1984).

⁴⁷W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).

⁴⁸W. Humphrey, A. Dalke, and K. Schulten, *J. Mol. Graphics* **14**, 33 (1996).

⁴⁹B. Jiang, R. Liu, J. Li, D. Xie, M. Yang, and H. Guo, *Chem. Sci.* **4**, 3249 (2013).

⁵⁰B. Jackson, F. Nattino, and G. J. Kroes, *J. Chem. Phys.* **141**, 054102 (2014).

⁵¹S. Nave, A. K. Tiwari, and B. Jackson, *J. Phys. Chem. A* **118**, 9615 (2014).

⁵²B. Jiang and H. Guo, *J. Phys. Chem. C* **117**, 16127 (2013).

⁵³See supplementary material at <http://dx.doi.org/10.1063/1.4919948> for further details regarding the computational methodology, additional supporting results, brief discussions, and video clips of the simulation trajectories corresponding to various reactions discussed in the manuscript.

⁵⁴A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.* **92**, 5397 (1990).

⁵⁵N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).

⁵⁶M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb *et al.*, GAUSSIAN 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2009.

⁵⁷P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82**, 270 (1985).

- ⁵⁸R. Dennington, T. Keith, and J. Millam, GaussView 05, Semichem, Inc., Shawnee Mission, KS, 2009.
- ⁵⁹E. Dombrowski, E. Peterson, D. Del sesto, and A. L. Utz, *Catal. Today* **244**, 10 (2015).
- ⁶⁰I. Alstrup, I. Chorkendorff, and S. Ullmann, *Surf. Sci.* **264**, 95 (1992).
- ⁶¹E. D. German and M. Sheintuch, *J. Phys. Chem. C* **117**, 22811 (2013).
- ⁶²R. Bisson, M. Sacchi, and R. D. Beck, *Phys. Rev. B* **82**, 121404 (2010).
- ⁶³P. M. Holmblad, J. Wambach, and I. Chorkendorff, *J. Chem. Phys.* **102**, 8255 (1995).
- ⁶⁴M. Sacchi, D. J. Wales, and S. J. Jenkins, *J. Phys. Chem. C* **115**, 21832 (2011).
- ⁶⁵R. R. Smith, D. R. Killelea, D. F. Delsesto, and A. L. Utz, *Science* **304**, 992 (2004).
- ⁶⁶L. B. F. Juurlink, D. R. Killelea, and A. L. Utz, *Prog. Surf. Sci.* **84**, 69 (2009).
- ⁶⁷L. Halonen, S. L. Bernasek, and D. J. Nesbitt, *J. Chem. Phys.* **115**, 5611 (2001).
- ⁶⁸B. Jackson and S. Nave, *J. Chem. Phys.* **138**, 174705 (2013).
- ⁶⁹B. Silvi and A. Savin, *Nature* **371**, 683 (1994).
- ⁷⁰P. Fuentealba, E. Chamorro, and J. C. Santos, in *Theoretical and Computational Chemistry—Theoretical Aspects of Chemical Reactivity* (Elsevier, 2007), Vol. 19, pp. 57-85.
- ⁷¹A. Savin, R. Nesper, S. Wengert, and T. F. Fassler, *Angew. Chem., Int. Ed. Engl.* **36**, 1808 (1997).
- ⁷²B. Silvi, *J. Mol. Struct.* **614**, 3 (2002).
- ⁷³R. Rousseau and D. Marx, *Chem.-A Eur. J.* **6**, 2982 (2000).
- ⁷⁴B. L. Yoder, R. Bisson, and R. D. Beck, *Science* **329**, 553-556 (2010).
- ⁷⁵B. L. Yoder, R. Bisson, P. M. Hundt, and R. D. Beck, *J. Chem. Phys.* **135**, 224703 (2011).
- ⁷⁶B. Jiang and H. Guo, *J. Chem. Phys.* **138**, 234104 (2013).
- ⁷⁷X. Zhang, L. Wang, J. Xin, B. I. Yakobson, and F. Ding, *J. Am. Chem. Soc.* **136**, 3040 (2014).
- ⁷⁸Q. Sun, Z. Li, M. Wang, A. Du, and S. C. Smith, *Chem. Phys. Lett.* **550**, 41 (2012).
- ⁷⁹I. Vlassiouk, M. Regmi, P. Fulvio, S. Dai, P. Datskos, G. Eres, and S. Smirnov, *ACS Nano* **5**, 6069 (2011).
- ⁸⁰M. Losurdo, M. M. Giangregorio, P. Capezzuto, and G. Bruno, *Phys. Chem. Chem. Phys.* **13**, 20836 (2011).
- ⁸¹M. Kalbac, O. Frank, and L. Kavan, *Carbon* **50**, 3682 (2012).
- ⁸²Y. Shibuta, R. Arifin, K. Shimamura, T. Oguri, F. Shimojo, and S. Yamaguchi, *Chem. Phys. Lett.* **610-611**, 33 (2014).
- ⁸³J. Zhang, Z. Wang, T. Niu, S. Wang, Z. Li, and W. Chen, *Sci. Rep.* **4**, 4431 (2014).
- ⁸⁴K. Li, C. He, M. Jiao, Y. Wang, J. Liu, and Z. Wu, *J. Phys. Chem. C* **118**, 17662 (2014).
- ⁸⁵M. Sacchi, D. J. Wales, and S. J. Jenkins, *Phys. Chem. Chem. Phys.* **14**, 15879 (2012).
- ⁸⁶F. Nattino, H. Ueta, H. Chadwick, M. E. van Reijzen, R. D. Beck *et al.*, *J. Phys. Chem. Lett.* **5**, 1294 (2014).