

MD SIMULATION STUDY THE COLLISION OF A DIATOMIC HYDROGEN ($v=0, j=0$) MOLECULE WITH A NANOSIZE COPPER ATOMIC CLUSTER (Cu_9)

M. A. AWAD^a, N. E. EISA^b, A. S. A. MAHGOUB^c, A. A. HENDI^d,
K. M. O. ORTASHI^e

^aKing Abdullah Institute for Nanotechnology, King Saud University, Riyadh 11321, Saudi Arabia

^bDepartment of Physics, University of Dammam, P.O. Box 1982, Dammam 31441, Saudi Arabia

^cPhysics Department, Khartoum University, Khartoum, Sudan

^dPhysics Department, Faculty of Science, King Saud University, Riyadh 11321, Saudi Arabia

^eDepartment of Chemical Engineering, King Saud University, Riyadh 11421, Saudi Arabia

In this study, the kinetics of a diatomic hydrogen molecule's impact with an atomic copper cluster (Cu_9) is studied via quasi-classical molecular dynamics, utilizing the technique of molecular dynamics (MD) simulations. The minimum geometry of the cluster was obtained by the thermal quenching method. The embedded potential expresses the interaction between atoms of the cluster, while the LEPS (London-Eyring-Polanyi-Sato) potential studies the interaction between gas atoms and the cluster. The reaction pathway, (dissociative adsorption of the molecule on the cluster) is considered. The probability of dissociative chemisorption, and reaction cross-section, were computed as a function of the hydrogen molecule's initial rovibrational states (v_i, j_i), the collision energy, impact parameter, and the cluster's temperature.

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1. Introduction

One of the most exciting challenges in present-day surface science is the task of developing detailed pictures of reactions at surfaces. The motivation to develop this understanding is simple: catalysis in the chemical industry contributes greatly to the global economy. Understanding the atomic structure, properties, and optimum reaction conditions of catalysts facilitates the control and optimization of the reaction products, and enables the design of new, cheap, and effective catalysts for industrial processes [1].

Heterogeneous catalysis is one process over which control may be greatly enhanced through the understanding of molecular clusters, especially metal cluster-molecule interactions [2]. In recent years, a variety of experimental studies have been performed to probe the kinetics and energetics of metal cluster-molecule reactions. This focus on reactivity should be distinguished from the vast amount of research that has focused on the structure and energetics of pure metal and semiconductor clusters.

Hydrogen is the most abundant element in the universe, making up 90% of the universe by weight and the only stable neutral two body system which has special

*Corresponding author: a.manalawad@googlemail.com

significance in quantum mechanics, all this make it one of the highest fertile ground for experimentalists[4].

Hydrogen chemisorptions play a very important role in understanding of various catalytic reactions, in metal dispersion, and in metal imbrittlement.

The interaction of hydrogen with copper cluster is still poorly characterized in both of theoretical and experimental studies. Because of the differences in the potential energy models selected to describe these interactions, the results was equivocal in determining the dissociation activation barrier, and the adsorption positions of the hydrogen atoms on Cu cluster sides.

The advent of high-speed computers has altered the picture, by providing a new perspective between experiment and theory. Computers enable the simulation of experiments that may be expensive, or impossible to perform in the laboratory (for example, those requiring extreme conditions), and they successfully fill the gap between experimental observations and theoretical modelling. One of these techniques is molecular dynamics (MD), which involves the integration of the equations of motion for a set of interacting atoms in order to follow their evolution over time. This integration is solved numerically using a computer, following the laws of classical, quasi-classical or quantum mechanics [5]. Before the collision, the copper cluster was prepared at desired temperatures T (0K), and the H₂ molecule is prepared at specific initial vibrational (v_i) and initial rotational (j_i) states.

2. Methodology

2.1. Geometries

In recent years, several studies have shown that the properties of small clusters show a sensitive dependence on the geometrical structure of the cluster. This means that the cluster's coordinates and momentum must be carefully identified for each selected temperature, using molecular dynamics and thermal quenching simulations [6]. In the model chosen by our work, the H-H bond was taken to be perpendicular to the line in which the Cu atoms were located. The initial separation between the diatomic molecule and the cluster was chosen to be 8.5 Å, and the initial moment and coordinates were chosen in accordance with a quasi-classical prescription developed by R. N. Porter [7], shown in table (1) below. Calculations were done for 500 trajectory in a grid of translation energy E_{tr} and impact parameter b with $\Delta E = 0.01\text{eV}$ and $\Delta b = 0.25\text{Å}$.

2.2 Potential energy surface (PES) representation

The force acting on each atom in the entire collision system is defined by the total potential energy surface which is represented by:

$$V = V_{EA} + V_{LEPS}$$

The energy of each atom is computed from the energy needed to embed the atom in the local $-$ electron density as provided by the other atoms of the metal.

The Embedded Atom potential is developed by Baw and Baskes:

$$V_{EAM} = \sum_i^n F_i(\bar{\rho}_{h,i}) + \frac{1}{2} \sum_i^n \sum_{j(\neq i)}^n \phi_{ij}(r_{ij})$$

here, $F_i(\bar{\rho}_{h,i})$ represents the energy of the embedding i molecule in the back ground host electron density ρ , and $\phi_{ij}(r_{ij})$ is the core-core pair repulsion between atoms i and j separated by the distance (r_{ij}) the derivation and detailed discussions of EAM appeared in the literature [8,9,10,11,12].

$$\phi_{ij}(R_{ij}) = D_{eq} \left(1 - e^{-a(r_{ij} - r_{eq})} \right)^2$$

D_{eq} , r_{eq} are the potential depth, minimum distance at equilibrium and "a" represent parameter controlling the width of potential well (Morse parameter).

The interaction between gas atoms A, B and the cluster C and among the gas interaction of the diatomic molecule is represented by a modified four-body LEPS potential (London-Eyring-Polyani-Sato) is:

$$V_{LEPS}(X_A, X_B, [X_C]) = Q_{AB} + Q_{AC} + Q_{BC} - [j_{A,B}^2 + (j_{A,C} + j_{B,C})^2 - j_{A,B}(j_{A,B} + j_{B,C})]^{1/2}$$

Where Q and j are the coulomb and exchange integrals respectively [13,14].

In the simulation studies for the collision the probability of dissociation chemisorptions for a particular incident energies of function of the impact parameter and translation energy will be calculated using the formula:

$$P_{v,j,T}(b, E_{tr}) = \bar{N}_{v,j,T}(b, E_{tr}) / N$$

Where $\bar{N}_{v,j,T}(b, E_{tr})$ is the number of effective trajectories, "N" is a number of trajectory (N=500).

The reaction cross section of the dissociative chemisorption was calculated from.

$$\sigma_{v,j,T}(E_{tr}) = 2\pi \int_0^{b_{max}} P(b, E_{tr}) b db$$

Where b_{max} is the longest impact parameter at which $P_{v,j,T}(b, E_{tr}) = 0$

3. Results and Discussion

The time was set to zero at the beginning of each trajectory and the H-H and H-cluster distance were monitored for each collision. The trajectory terminated either when the H-H distance exceeded the value of 2.233 Å (three times the equilibrium length) or when the hydrogen molecule reached approximately the same region after departing from the cluster.

To study the reactivity of H molecules with copper clusters we calculated the reaction cross-section for the reaction at Cu9 at temperature T (T = 0 K). From the calculated data, three types of reaction process were observed. The first type was classified as molecules reaching the cluster with relatively high translational energy and then dissociating immediately upon reaching the cluster surface; this was called Direct Dissociation, as shown in Fig. 1(a). The second reaction type involved molecules reaching the cluster with low collision energy such that they could not dissociate. These molecules instead attached themselves to the surface of the cluster. Once attached, the molecules showed rotation and vibration as they explored until either reaching the active site of the cluster and their intramolecular bond breaking, or until they gained enough energy from the cluster atoms to allow them to dissociate. This pathway caused a resonance for some period at the surface of the cluster, and was called Indirect Dissociation, as in Fig. 1(b). The third type occurred for all translation energies where molecules reached the cluster and were inelastically back scattered, as shown from Fig. 1(c). This reaction type is referred to as Inelastic Scattering. Following back scattering, the molecule rotates and vibrates while retuning back to its initial distance. The reaction type observed is independent of both the translation energy of the impinging molecule as well as upon the reaction impact parameter.

We investigated the reactive cross-section of the H₂ molecule (in the ground state) with the (non-rotating, non-translating) Cu₉ cluster (at 0 K) as function of collision energy. We found that in the low energy region (starting from 0.01 eV), reactivity increased rapidly and reached a maximum value near 0.05 eV Fig (2). As the collision energy increased further, the cross-section

decreased, having a minimum value near 0.35 eV, beyond which the reaction cross-section increased monotonically. The peak in the low energy region represents complex formation between the H₂ molecule and the cluster. In this region, the molecule attaches itself to the surface of the cluster and then explores the surface until either reaching an active site that can break its bond, or till it gains enough energy to dissociate. This resonance enhances the reactivity. The minimum area ($E_{tr}=0.25\text{eV}$) confirm the existence of the activation barrier associated with this type of reactions. This results was tend to be in a good correspondence with that reached before in the Cu + H₂ [15,16,17] and Ni + H₂ [18,19] dissociative adsorption reaction.

The dissociation probability of the molecule as a function of the impact parameter for a small range of molecule translation energies ($0.01 < E_{tr} < 1.0\text{eV}$) was investigated. As seen in Fig (3), the molecules that reach the cluster with high translation energy (for example 0.8eV) will have greater dissociation probability when interacting with atoms near the center of mass of the cluster i.e. at impact parameter $b=0 \text{ \AA}$. This probability decrease successively with the increase in the impact parameter till it reach its minimum value at 4.25 \AA . The molecule interact at lower translation energy (as example 0.01eV) have the lowest probability of dissociation, but they dissociate at larger impact parameter than for the previous case, which clearly supports the explanation for the area of indirect dissociation given above.

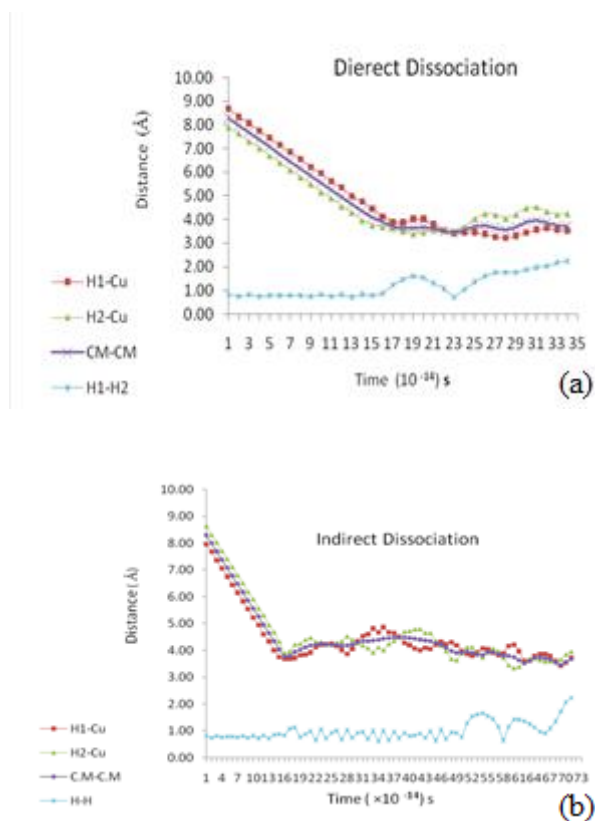


Fig. 1. (a) Direct Dissociation in the collision of the Cu₉ + H₂; ($E_{tr}=0.5 \text{ eV}$),
(b) Indirect Dissociation in the collision of the Cu₉ + H₂; ($E_{tr}=0.05 \text{ eV}$),

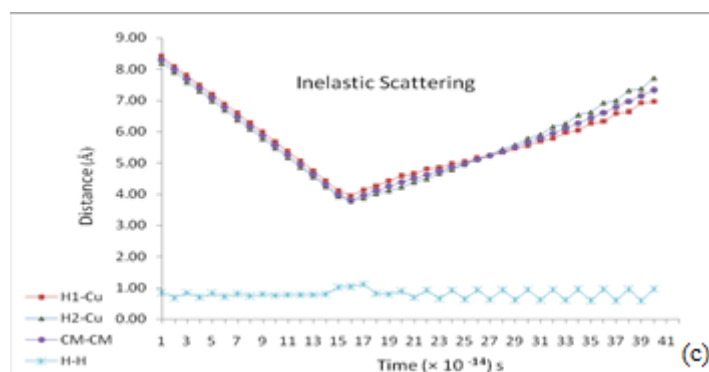


Fig. 1. (c) Inelastic scattering in the collision of the $\text{Cu}_9 + \text{H}_2$; ($E_{tr} = 0.5 \text{ eV}$), CM-CM the distance between center of mass of the molecule and the center of mass of the cluster.

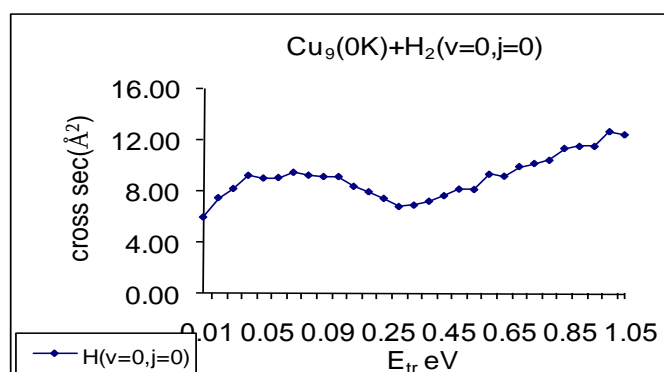
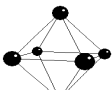

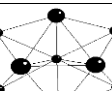
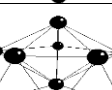


Fig.2 .Dissociative chemisorptions reaction cross section of $\text{H}_2(v=0, j=0) + \text{Cu}_9(0K)$.

Table(1) $\text{Cu}(6,7,8,9,10)$ Geometrics, structures, bond lengths, and the Minimum energy of the most stable . Cu_n (6, 7, 8, 9, 10).

Cluster size	The most stable isomers	Structure Symbol	Name	Average bond length (Å)	Min. energy (eV)
Cu_6		(O_h)	Octahedron	2.400	-12.813
Cu_8		(C_{2v})	Bicapped octahedron	2.412	-18.239
Cu_9		(C_{2v})	Double capped octahedron	2.446	-21.009
Cu_{10}		(C_{3v})	tricapped tetrahedron	2.455	-23.884

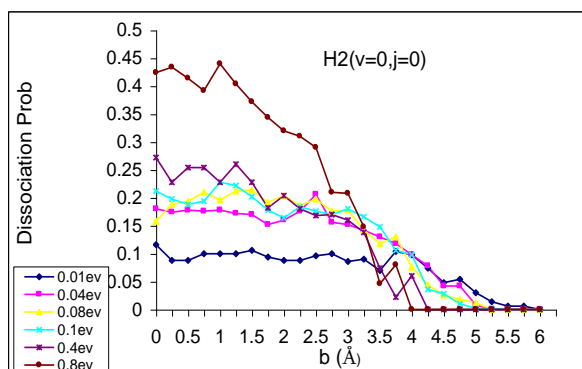


Fig. (3) Reaction probability as function of impact parameter for different value of E_{tr} (eV) for Cu_9 atomic cluster at (0K) at $(v=0, j=0)$

4. Conclusion

We report the results of a quasi-classical simulation study of the interaction of an H_2 molecule with a Cu_9 cluster. Both the reactive (dissociative adsorption of the molecule on the cluster) and non-reactive (scattering of the molecule from the cluster) reaction pathways were considered. The processes were examined as a function of the initial quantum rovibrational state of the hydrogen molecule, the collision energy, and the impact parameter. For hydrogen molecules in the low translation energy region, the reaction cross-section increased rapidly and reached a maximum value. Further increase of the collision translation energy caused a dramatic decrease in reaction cross-section to a minimum value, demonstrating the existence of a reaction threshold. As the energy increased yet further, the reaction cross-section started to increase monotonically again. We also found that dissociation adsorption increases monotonically with the increase in molecule translational energy, E_{tr} .

Acknowledgements

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