

## **D<sub>2</sub>+Ni<sub>n</sub>(T), n=7 and 9, COLLISION SYSTEM**

Mustafa Böyükata, Perihan Durmuş and Süleyman Özçelik  
 Department of Physics, Gazi University, 06500 Ankara, Turkey

Ziya B. Güvenç\*  
 Department of Computer Engineering, Çankaya University, 06530 Ankara, Turkey

Julius Jellinek  
 Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA

**Abstract**—In this study the kinetics of reactions of Ni<sub>n</sub>, n=7 and 9, clusters with a deuterium (D<sub>2</sub>) molecule are studied via quasiclassical molecular dynamics. Dissociative chemisorption probabilities as functions of impact parameters, collision energies, and a vibrational state of a D<sub>2</sub> molecule are calculated. And the corresponding reactive cross sections are evaluated. Resonance formation in the low collision energy region is discussed.

### **1. INTRODUCTION**

Understanding the processes involved in the chemisorption (associative and dissociative) of molecules on the surface of small clusters is a research area of great interest and importance in basic science and catalysis. Chemisorption of hydrogen on transition metal catalysts is routinely used to estimate metal dispersion or surface areas from which the particle size may be inferred [1]. Small metal clusters have properties which can be highly dependent on cluster size and are different from the bulk metal [2]. Works on the chemisorption of hydrogen and deuterium on various metal clusters demonstrated that there can be large changes in cluster reactivity within a very narrow size range. In the study of iron cluster-hydrogen reactions the rate constants were found to change by nearly two orders of magnitude with the addition of one atom to Fe<sub>18</sub> and rate constants varied over three orders of magnitude between Fe<sub>8</sub> and Fe<sub>23</sub> [2]. For the reaction of deuterium with cobalt and niobium clusters the rate constants varied over two orders of magnitude [2]. In other experimental studies for reactions of palladium [3] and nickel [4] clusters with H<sub>2</sub> and D<sub>2</sub> molecules, these changes in the rate constants are also observed. Interestingly, both nine-atom Pd and Ni clusters exhibited a dramatic drop in reactivity towards D<sub>2</sub>.

Nickel, being studied heavily, is an important catalyst in hydrogenation reactions. In the last decade there have been experimental [5] and theoretical [6] examinations of the chemisorption of H<sub>2</sub> and D<sub>2</sub> on various Ni single crystal surfaces. The study of the reactivity of clusters has provided valuable information about the dependence of reaction

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\* Corresponding author. E-mail: guvenc@cankaya.edu.tr

rates on cluster size [7], variation of reactivity with isomer, and mode dependence i.e., cluster's internal energy and rovibrational state of the molecule [8-10]. Jellinek and Güvenç have pointed out a maxima in the reactive cross sections, about room temperature collision energy, of  $D_2 + Ni_{13}$  system resulting from indirect dissociation mechanism.

In this work we performed a quasiclassical trajectory study of reactions of the  $D_2(v,j)$  molecule with the  $Ni_7$  and  $Ni_9$  clusters and their isomers. A preliminary results pertaining to the reactive channel is presented. The dissociative chemisorption probabilities are calculated as functions of the impact parameter, collision energy and the rovibrational state of the  $D_2$ . The corresponding reactive cross sections are obtained from these probabilities. In the next Section an outline of the theoretical background and of the computational procedure are given. The numerical results and their discussions are presented in Sec. 3.

## 2. THEORETICAL BACKGROUND AND COMPUTATIONAL PROCEDURE

The total potential energy surface defining the forces acting on each atom in the entire collision system is represented as:

$$V = V_{EA} + V_{LEPS} \quad (1)$$

where  $V_{EA}$  is an embedded-atom potential describing the interactions between the atoms in the Ni-cluster and  $V_{LEPS}$  is a LEPS (London-Eyring-Polanyi-Sato) function accounting for D-D and  $D_2-Ni_n$  interactions.  $V_{EA}$  is used in the parameterization given by Voter and Chan; for details see [11], and for the LEPS potential see [7-10].

The time evolution of the molecule-cluster collision system is generated by solving numerically Hamilton's equations of motion for all atoms in the system. A fourth-order variable step-size predictor corrector propagator was employed. The maximal step size of  $5 \times 10^{-15}$  s is used and conservation of the total energy as well as of the total linear and angular momenta are within 0.03-0.15%. A nonrotating and nontranslating cluster was prepared at a given initial temperature  $T(K)$  defined as

$$T(K) = \frac{2 \langle E_k \rangle}{(3n - 6)k} \quad (2)$$

where  $E_k$  is the total kinetic energy of the cluster,  $k$  is the Boltzmann constant, and  $\langle \rangle$  stands for the long-time average, and  $n$  is the number of atoms in the cluster. The initial vibrational ( $v$ ) and rotational ( $j$ ) states of the  $D_2$  molecule are quantized using a quasiclassical prescription [12]. Time is set to zero at the beginning of each trajectory, and the molecule is sent towards the cluster starting from 8.5 Angstrom away from the center of mass of the  $Ni_n$  cluster with a specified collision energy  $E_{tr}$  (relative translational) and an impact parameter  $b$ . The D-D and D-cluster distances are monitored for each collision. The trajectory is terminated either when the D-D distance exceeds the value of 2.223

Angstrom (three times the equilibrium D-D bond length) or when the departing from the cluster  $D_2$  molecule reaches again the asymptotic region. The former one is counted as corresponding to a dissociative adsorption of the  $D_2$ , and the later one represents a nonreactive collision of the molecule. Possible recombination of the D atoms and subsequent desorption of the  $D_2$  molecule are neglected.

In order to determine the probability  $P_{v,j,T}(b, E_{tr})$  of dissociative chemisorption of the  $D_2(v,j)$  molecule, with specified  $E_{tr}$  and  $b$  on a  $Ni_n(T)$  cluster, we have run  $N=500$  trajectories for each set of initial conditions. These trajectories correspond to different initial relative orientations of the molecule and of the cluster, and to different initial phases of the  $D_2$  oscillator.  $P_{v,j,T}(b, E_{tr})$  is calculated as

$$P_{v,j,T}(b, E_{tr}) = \frac{\tilde{N}_{v,j,T}(b, E_{tr})}{N} \quad (3)$$

where  $\tilde{N}_{v,j,T}(b, E_{tr})$  is the number of reactive trajectories. The calculations were repeated on a grid of  $b$  and  $E_{tr}$  with intervals of  $\Delta b=0.25$  Angstrom and of  $\Delta E_{tr}=0.01$  eV up to 0.10 eV, and of  $\Delta E_{tr}=0.05$  eV until 1.0 eV, respectively. The cross section of the dissociative chemisorption is calculated in accordance with

$$\sigma_{v,j,T}(E_{tr}) = 2\pi \int_0^{b_{\max}} P(b, E_{tr}) b db \quad (4)$$

where  $b_{\max}$  is the largest impact parameter at which  $P_{v,j,T}(b, E_{tr})=0$ .

The minimum energy structures and energetics of the  $Ni_7$  and  $Ni_9$  clusters are given in Fig. 1 and Fig. 2, respectively. The lowest energy isomer of the  $Ni_7$  is a pentagonal bipyramid, and the second one has a capped octahedron configuration. The energy spacing of these two isomers is larger than that of two isomers of the  $Ni_9$ . The first isomer (lowest energy) of the  $Ni_9$  is formed by only triangular bipyramids. The second isomer is an aggregation of three square pyramids such that six-nickel atoms are shared by the pyramids. These isomers are almost degenerate. The reactive cross sections of the  $D_2 + Ni_n$  system are discussed in the next Section.

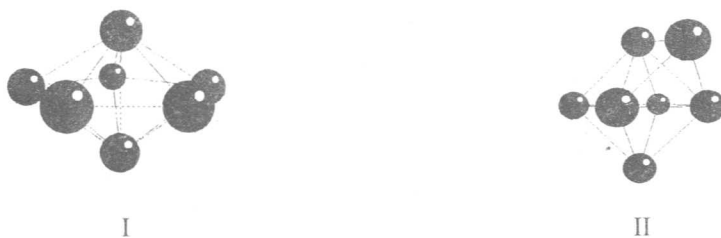


Figure 1. The minimum energy geometries of a  $Ni_7$  cluster. The energetics are -2.64 and -2.60 eV/atom, respectively.



Figure 2. The minimum energy geometries of a  $\text{Ni}_9$  cluster. The energetics are -2.81 and -2.80 eV/atom, respectively.

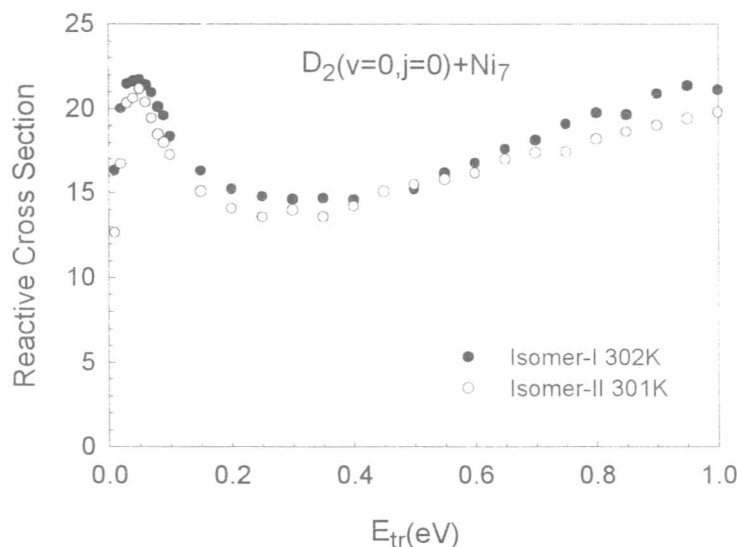


Figure 3. Reactive (dissociative chemisorption) cross sections of the  $\text{D}_2 + \text{Ni}_7$  system are calculated in units of  $\text{\AA}^2$ . The molecule is in the ground state and the internal energies of the isomers of a  $\text{Ni}_7$  cluster are near the room temperature.

### 3. RESULTS AND DISCUSSIONS

The reactive cross sections of the  $\text{D}_2$  molecule in the ground state with the isomers of a  $\text{Ni}_7$  cluster are presented in Fig. 3 as a function of the collision energy. The internal energies of the isomers are equivalent to the room temperature (302K and 301K). The first isomer of the  $\text{Ni}_7$  is slightly more reactive than the second isomer in the entire collision energy range, except one energy (0.45 eV) at which the curves cross each other. In the low energy region reactivity increases rapidly and reaches to a maximum value near 0.050 eV. As the collision energy increases further, the cross sections decrease and have minimum values near 0.30 eV. Beyond this energy, both curves increase monotonically. The peaks in the low energy region represent the complex formation of the  $\text{D}_2$  molecule with the  $\text{Ni}_7$  cluster; the molecule attaches itself to the surface of the cluster and then

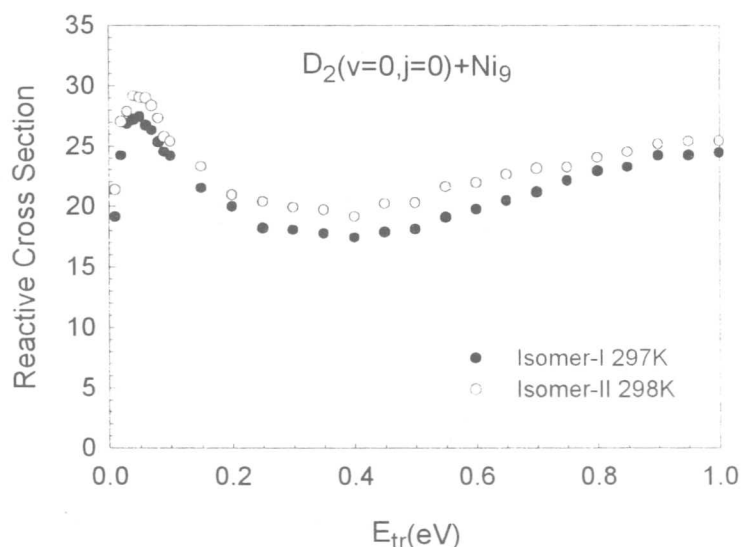


Figure 4. The same as in Fig. 3 with the isomers of a  $\text{Ni}_9$  cluster.

searches for the “active site” to break its bond. This “resonance” enhances the reactivity as seen from Figures 3 and 4. The life time of the complex decreases with increasing collision energy. For details see Ref. [8-10]. In Fig. 4 the reactive cross sections of the  $\text{D}_2(v=0,j=0) + \text{Ni}_9$  collision system are presented for both isomers of the clusters. In contrast to the  $\text{Ni}_7$ , the second isomer of the  $\text{Ni}_9$  is slightly more reactive at all energies. The internal energies of the isomers are also equivalent to the room temperature (297K and 298K). This system also displays complex formation in the low collision energy region. The behaviour of the curves are very similar to that of the  $\text{D}_2(v=0,j=0) + \text{Ni}_7$

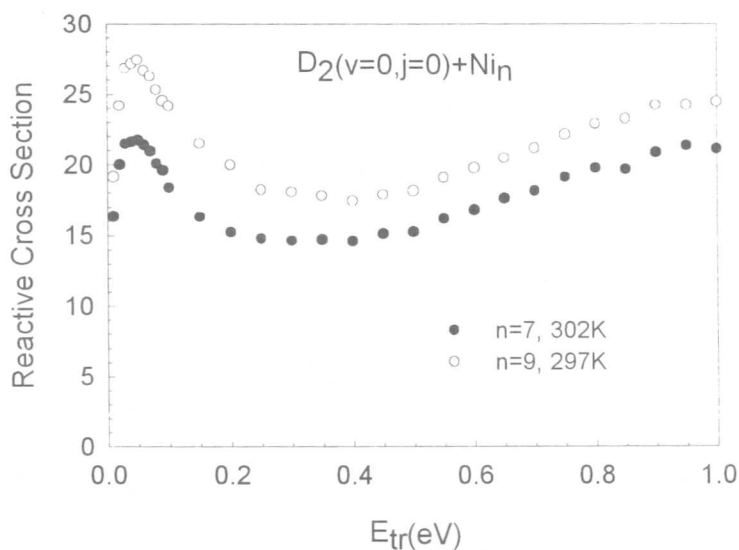


Figure 5. Reactive cross sections of the  $\text{D}_2 + \text{Ni}_7$  and  $\text{D}_2 + \text{Ni}_9$  collision systems. Here, only the first isomers of the clusters are considered.

system. The peak positions are also at the same collision energy. Both reactive cross sections, for the  $\text{Ni}_7$  and  $\text{Ni}_9$  clusters, are compared in Fig. 5. Each curve corresponds to the first isomer of the clusters. As seen clearly, at all energies the  $\text{Ni}_9$  cluster is more reactive than the  $\text{Ni}_7$ . This leads to larger rate constant for the  $\text{D}_2 + \text{Ni}_9$  system. In the experimental studies this system  $\text{D}_2 + \text{Ni}_9$ , however, exhibits a dramatic drop in the reactivity [4] compared to the  $\text{D}_2 + \text{Ni}_7$  and  $\text{D}_2 + \text{Ni}_8$  systems. Our theoretical results are consistent with the experimental data for the  $\text{D}_2 + \text{Ni}_7$ , but, inconsistent with that for the  $\text{D}_2 + \text{Ni}_9$  system.

Results of the systematic studies of the  $\text{D}_2 + \text{Ni}_n$ ,  $n=7-20$ , collision systems will be published elsewhere. All our findings, except the  $\text{D}_2 + \text{Ni}_9$  system, are in good agreement with the experimental data [4]. Detail studies are in progress to elucidate the "mysterious" drop of the reactivity.

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### REFERENCES

- 1- J.H. Sinfeld, Catalytic hydrogen analysis over supported metals *Catal. Rev.* **3**, 175-205 1969.
- 2- S.C. Richsmeier, E.K. Parks, K. Liu, L.G. Pobo, S.J. Riley, Gas phase reactions of iron clusters with hydrogen. I. Kinetics, *J. Chem. Phys.* **82**, 3659-3665, 1985; M.D. Morse, M.E. Geusic, J.R. Heath, R.E. Smalley, Surface reactions of metal clusters. II. Reactivity surveys with  $\text{D}_2$ ,  $\text{N}_2$  and  $\text{CO}$ , *J. Chem. Phys.* **83**, 2293-2304, 1985.
- P. Fayet, A. Kaldor, D.M. Cox, Palladium clusters:  $\text{H}_2$ ,  $\text{D}_2$ ,  $\text{N}_2$ ,  $\text{CH}_2$ ,  $\text{CD}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  reactivity and  $\text{D}_2$  saturation studies, *J. Chem. Phys.* **92**, 254-261, 1990.
- W.F. Hoffman III, E.K. Parks, G.C. Nieman, L.G. Pobo, S.J. Riley, The kinetics of reactions of nickel clusters with hydrogen and deuterium, *Z. Phys. D.* **7**, 83-89, 1987; L. Zhu, J. Ho, E.K. parks, S.J. Riley, Temperature dependence of the reaction of nickel clusters with deuterium, *J. Chem. Phys.* **98**, 2798-2804, 1993.
- H.J. Robota, W. Vielhaber, M.C. Lin, J. Segner, G. Ertl, Dynamics of interaction of  $\text{H}_2$  and  $\text{D}_2$  with  $\text{Ni}(110)$  and  $\text{Ni}(111)$  surfaces, *Surface Science* **155**, 101-120, 1985; A.V. Hamza, R.J. Madix, Dynamics of the dissociative adsorption of hydrogen on  $\text{Ni}(100)$ , *J. Phys. Chem.* **89**, 5381-5386, 1985; D.O. Hayward, A.O. Taylor, The variation of the sticking probability of hydrogen and deuterium on  $\text{Ni}(111)$  with energy and angle of incidence, *Chem. Phys. Lett.* **124**, 264-267, 1986.
- E.M. Seigbaum, M.R.A. Bloomburg, C.W. Bauschlicher, Jr., The dissociation of  $\text{H}_2$  on the  $\text{Ni}(100)$  surface, *J. Chem. Phys.* **81**, 2103-2111, 1984; C.Y. Lee, A.E. De sto, Dissociation dynamics of  $\text{H}_2$  on  $\text{Ni}(100)$ ,  $\text{Ni}(110)$ , and  $\text{Ni}(111)$  surfaces, *J. Chem. Phys.* **84**, 485-495, 1986.
- Raghaven, M.S. Stave, A.E. DePristo, Ni clusters: structures and reactivity with  $\text{H}_2$ , *J. Chem. Phys.* **91**, 1904-1917, 1989.

- 8- J. Jellinek, Z.B. Güvenç, Dissociative chemisorption of  $D_2$  on a  $Ni_{13}$  cluster, *Z. Phys. D*, **19**, 371-373, 1991.
- 9- J. Jellinek, Z.B. Güvenç, Mode Selectivity in cluster-molecule interactions  $Ni_{13}+D_2$ , in 'Mode Selective Chemistry', 153-164, Edited by J. Jortner et al. (eds.), Kluwer Academic Publishers, Netherlands, 1991.
- 10- J. Jellinek, Z.B. Güvenç, Collisions of molecules with clusters: a quasiclassical study, in 'Topics in Atomic and Nuclear Collisions', 243-256, Edited by B. Remaund et al., Plenum Press, New York, 1994; J. Jellinek and Z. B. Güvenç, Structure, Melting, and Reactivity of Nickel Clusters From Numerical Simulations, in 'The Senergy Between Dynamics and Reactivity at Clusters and Surfaces', Edited by L. J. Farrugta, Kluwer, Dordrecht, p.217-240, 1995; and references therein.
- 11- A.F. Voter, S.P. Chen, Accurate interatomic potentials for Ni, Al, and  $Ni_3Al$ , *Mater. Res. Soc. Symp.* **82**, 175-180, 1987.
- 12- R.N. Porter, L.M. Raff, W.H. Miller, Quasiclassical selection of initial coordinates and momenta for a rotating Morse oscillator, *J. Chem. Phys.* **63**, 2214-2218, 1975.