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Determination of Chemisorption Probabilities of Hydrogen Molecules on a Nickel Surface by Artificial Neural Network

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Dissociative chemisorption probabilities for $H_2(v, j)$ + Ni(100) collision systems have been estimated by using Artificial Neural Network (ANN). For training, previously determined probability values *via* molecular dynamics simulations have been used. Performance of the ANN, for predicting any quantities in the molecule-surface interaction, has been investigated. Effects of the surface sites and the rovibrational states of the molecule on the process are analyzed. The results are in good agreement with the related previous studies.

INTRODUCTION

The interaction mechanism of molecules with surfaces has been investigated extensively, due to its relevance to a number of industrial applications. Especially, hydrogen-metal systems have been studied in detail owing to their fundamental importance.[1–7] The main traditional approach of the problem is determination of the sticking coefficients for different experimental conditions.[1,2] Understanding of the dynamics and energetics factors of the dissociative chemisorption (DC) of the molecule on metal surfaces is also important for the elucidation of microscopic process involved in the DC mechanisms. In the reactivity of the surface with the molecule, *e.g.,* the modes, such as; rovibrational states of the molecule, collision energies, impact sites, *etc*., play important roles and also some of these factors are strongly coupled.[7] In our earlier works we studied, by molecular dynamics (MD) simulation, the reactive and inelastic channels of the $D_2(v, j)$ molecule (v and j are the vibrational and rotational states of the molecule, respectively) at topologically different three impact sites on the Ni(100) surface,[8] the reactive channels of the $D_2(v = 0, j = 0)$ on Ni(100), Ni(110), Ni(111) low-index surfaces,[9] and the reaction dynamics of $H_2(v, j)$ molecules at those three sites on the Ni(100) surface.[10] These investigations have provided valuable information about the reactivity of the surfaces and mode dependence of the DC. For instance, chemisorptions of the molecules on the metallic surfaces show that there can be large variations of the surface reactivities depending on the surface index, impact sites, and the modes of the molecules. In addition, indirect dissociation mechanism, at about room temperature collision en-

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ergy,[8–10] and its effect on the DC have been pointed out. Similar trends were observed for different sites of the surfaces.[11–13]

In Ref. (10) a detailed quasiclassical trajectory study of reactions of the $H_2(v, j)$ molecule with the Ni(100) surface was reported at three target sites on the surface and with different selected rovibrational states of the molecule in order to reduce the scarcity in the literature. In that work, DC probabilities have been computed for the (v = 0, j = 0, 1, 3, 10) and (v = 1, j = 0) modes. Additionally, the DCs have been calculated for the j = 0 to j = 18 states, for the $H_2(v = 0)$ at collision energies of 0.05, 0.10, 0.20, 0.30, 0.50, 0.75 and 1.00 eV. Detailed search for the DC calculations, for all the rovibrational states of the molecule at all the sites and within the full range of 0.0–1.0 eV collision energy, can not be realized due to very long computation time. Therefore, the previously calculated DC values, using the conditions mentioned above[10] *via* MD simulation, have been used for training of the artificial neural network (ANN). In the present work, our goal is to use this trained ANN to estimate the DC probabilities of the $H_2(v, j)$ + Ni(100) collision systems for the entire »spectrum« mentioned above which include v = 0, j = 0–18 and v = 1, j = 0–18 rovibrational states, and the entire range of the collision energies (0.0–1.0 eV) for the atop, bridge and center sites of Ni(100). In our previous work we have also successfully applied the ANN, a nonlinear parameterized method, for evaluation of the reactive cross sections of the collisions of the D_2 molecule with Ni_{19} and Ni_{20} clusters.[14] In spite of much wider parameter space considered for the ANN than the DC**,** after the training of the ANN**,** the ANN modeling can determine them much more quickly than the MD simulations.

The deterministic nature of a nonlinear system allows extracting its functional structure from a time series using appropriate nonlinear techniques.[15] The ANN is a nonlinear technique which extracts relationships between the input variables and the output of the system. By analogy with the human brain, neural network (NN) is a massively parallel system that relies on the simple processors and dense arrangements of the individual interconnections of the processing units through which information is passed.[16] The NN can be trained efficiently with random data. These networks have demonstrated their ability to deliver simple and powerful solutions in the areas that have challenged conventional computing. Due to their proven ability to fit any data set, the ANNs have become very popular.[17] In the recent decade, the ANNs have been widely and successfully used in many fields.[17–22] This area has been developed to solve demanding pattern processing problems, which were intractable or extremely cumbersome when implemented using the traditional approaches.[23]

In this paper the performance of the ANN for predicting the DC probabilities in the molecule-surface interaction (its scope is mentioned above) has been investigated. The ANN results are compared to the previous MD studies. In the next Section, outlines of the theoretical background and that of the ANN procedure are given. The analysis of the findings are presented in Section Results and Discussion, and we conclude with a summary.

COMPUTATIONAL BACKGROUND AND ARTIFICIAL NEURAL NETWORKS

The computational details of the MD simulations (to be used here to train the ANN), and the concept of the ANN are previously described in Refs. (10) and (14). Therefore we will omit details of these here. However, for the sake of completeness of the present paper we briefly mention them here. In Ref. (10), the H_2 bombardment of the surface at various impact sites has been performed using a constant energy MD computer simulation. Hamilton's equations of motion were solved using Hamming's modified 4th order predictor-corrector variable step size propagator. The potential energy surface (PES) used in that simulation was formed by a four-body LEPS (London-Eyring-Polanyi-Sato) function accounts for the H-H and H-Ni interactions (for details see Ref. (24)). The surface consists of 74 rigid atoms. For each set of initial conditions; the specified collision energy and impact site on the surface, and a fixed rovibrational state of the molecule, 1000 trajectories, corresponding to different initial relative orientations of the molecule with respect to the surface, were run in order to determine the DC probabilities of the molecule.

The ANN is an important information processing paradigm that was inspired how biological nervous system works. In the biological systems, learning involves adjustments of the synaptic connections that exist between the neurons. This is true for the ANN's training process as well. The NN is represented by weighted interconnections between processing elements (PEs). These synaptic weights are the parameters that actually define the non-linear function performed by the NN. The process of determining such parameters is called training or learning,[25] relying on the presentation of many training patterns. The ability to find correlation among apparently disconnected data and the tolerance to noisy data are the main features of the ANN. For a real problem, any ANN must be trained at the beginning. Here, we have employed Back-Propagation (BP) training algorithm.[23,26] Thus, the NN is inherently adaptive; conforming to the imprecise, ambiguous and faulty nature of the real-world data. The BP algorithm is the most widely used NN because of its relative simplicity and universal approximation capacity.[27] The BP algorithm defines a systematic way to update the synaptic weights of multi-layer perceptron (MLP) networks. The supervised learning is based on the gradient descent method, mini-

mizing the global error on the output layer. The learning algorithm is performed in two stages:[28] feed-forward and feed-backward. In the first phase, the inputs are propagated through the layers of the processing elements, generating an output pattern in response to the input pattern presented. In the second phase, the errors calculated in the output layer are then back propagated to the hidden layers where the synaptic weights are updated to reduce the error. This learning process is repeated until the output error value, for all patterns in the training set, are below a specified value. The definition of the network size (the number of hidden layers and of neurons in each layer) is a compromise between the generalization and convergence. The convergence is the capacity of the network to learn the patterns on the training set, and the generalization is the capacity to respond correctly to the new patterns. The idea is to implement the smallest network possible, so it is able to learn all patterns, and at the same time, provide good generalization. However, a very long training process with problems such as; local minima and the restriction of learning only with the static input-output mappings are two limitations of the BP.[28]

In this study a four-layer ANN is used and trained with the BP algorithm.[29] Detailed information about the ANNs procedure has been given in Refs. (28)–(30) and readers can find the related references therein. For the training and the test MATLAB NN functions[31] were used.

RESULTS AND DISCUSSIONS

The BP network used is composed of an input layer, two hidden layers and an output layer (Figure 1). The number of neurons in the hidden layers has been determined *via* experimentation. The experimental results show that

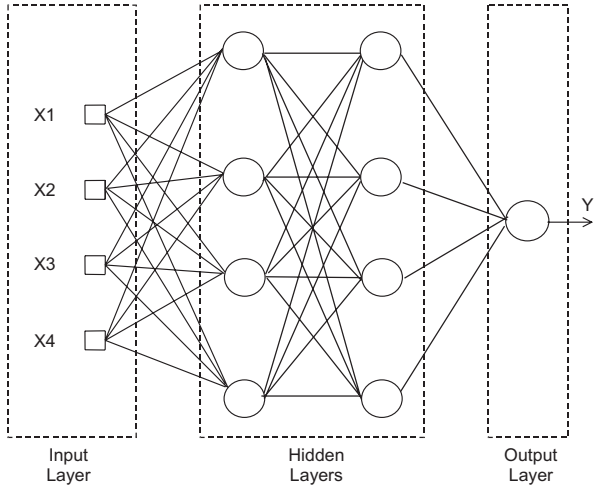

Figure 1. General structure of MLP neural network architecture (X1 is the surface site, X2 and X3 are the vibrational and rotational states, respectively, and X4 is the collision energy in eV, and Y is the DC probability).

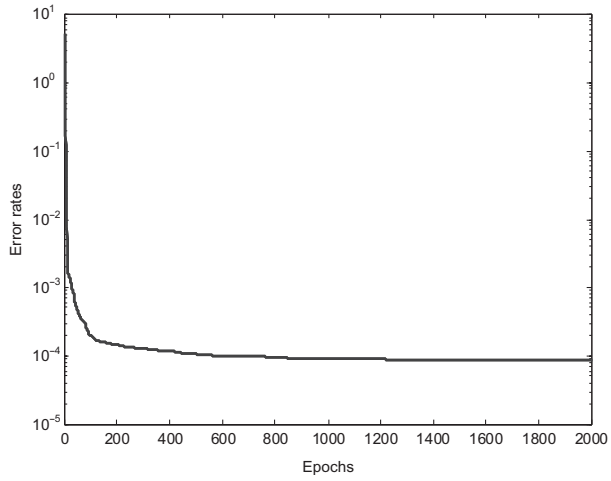

Figure 2. Changing training error-rate *versus* epoch number.

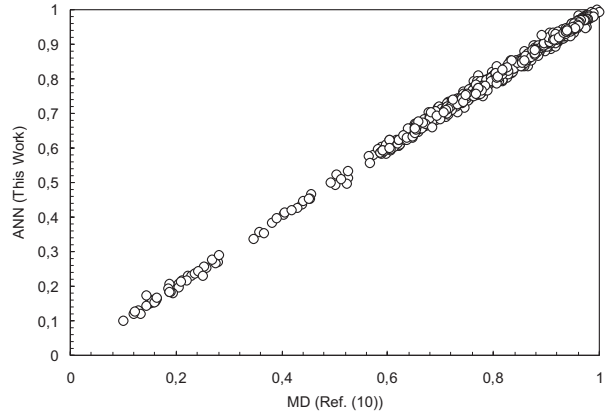

Figure 3. Estimated ANN results *versus* used MD data[10] of DC probabilities for training.

optimum numbers of the hidden neurons were ten and fifteen in the first and in the second hidden layers, respectively. In the present work the number of neurons is equal to 1 in the output layer. The stopping criteria for the network training are the sum of squared error (8.658×10^{-5}) and the maximum number of epochs is 2000. As shown in Figure 2 the error rate is lower than 10^{-4} for the number of epochs greater than 1000.

In order to see the agreements of the ANN estimated DC probabilities with the MD data, they are compared in Figure 3. As seen in the figure, the ANN can learn perfectly the relationships between the input variables (X1: surface site, X2 and X3: vibrational and rotational states, respectively, and X4: collision energy), and the output (Y: DC probability). The number of MD data[10] and their ranges that are used as input for the training of the ANN are presented in Table I. For each of the three X1 values (atop, center, bridge) 246, 264 and 266 data, respectively, have been used for two different vibrational states (0 and 1) with the corresponding rotational states of the molecule at various collision energies (X4), up to 1.0 eV. Totally 776 data members (features) have been

TABLE I. The MD data ranges[10] that used as input to train the ANN

X1	X2	X3	X4	Number of data
Atop	0	0–18	0.01–1.0	223
	1	0	0.01–1.0	23
Center	0	0–18	0.01–1.0	242
	1	0	0.01–1.0	22
Bridge	0	0–18	0.01–1.0	243
	1	0	0.01–1.0	23

considered to develop the ANN and test with the same MD data. It is understood, in this particular analysis, the ANN is able to produce reliable values with 0.25 % mean error, which was calculated over the deviation of the linear regression slope from the ideal value 1. The implemented ANN model can estimate the DC probabilities within much less computation time with a good performance.

The contour graphs in Figure 4 present the ANN predicted DC probabilities of the $H_2(v, j)$ molecule with the

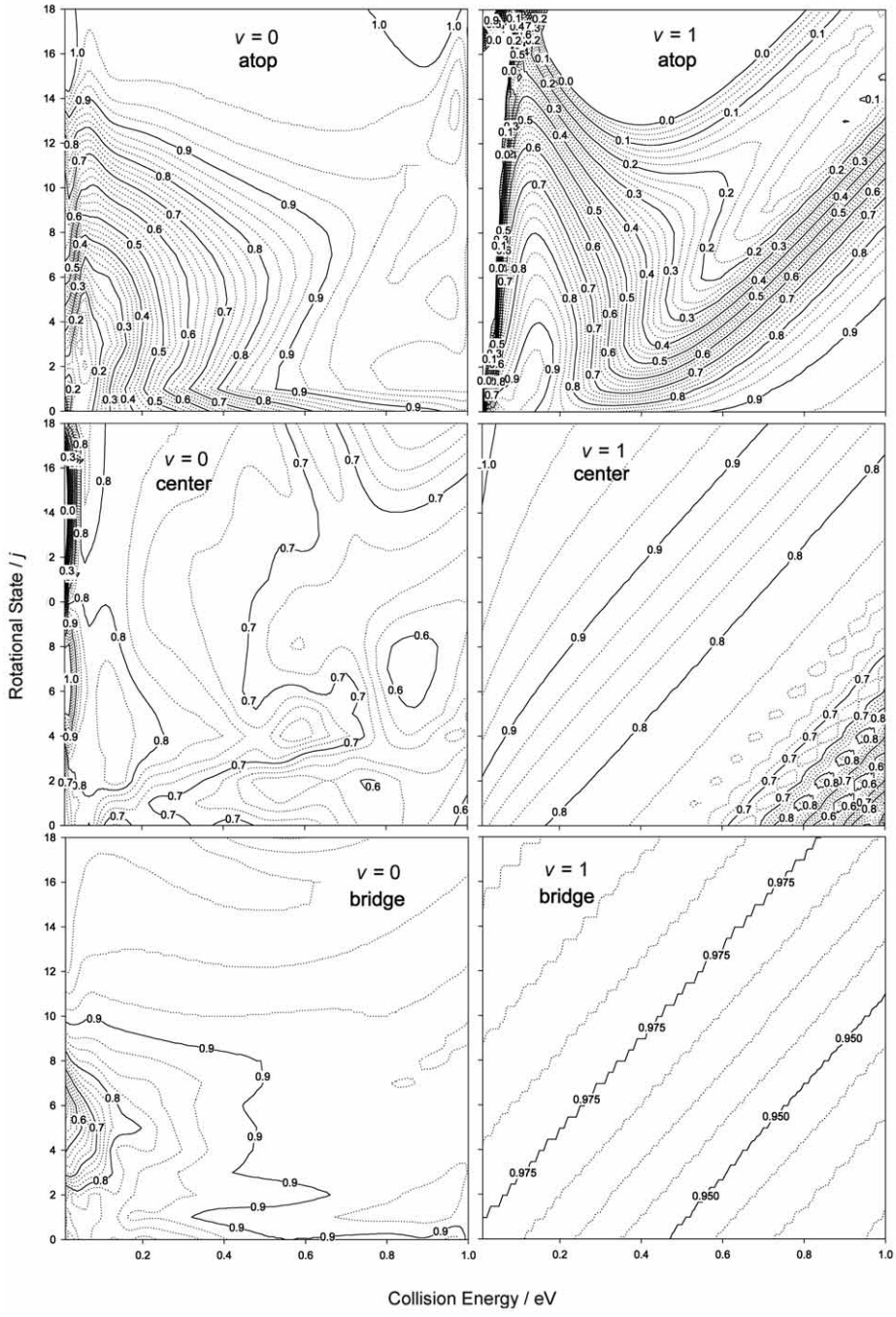

Figure 4. Dissociative chemisorption probabilities for $H_2(v,j)$ + Ni(100) as functions of rotational states and collision energies for two vibrational modes at three surface sites.

Ni(100) surface as a function of the collision energy (up to 1.0 eV) and rotational states (j = 0–18), for two vibrational modes (v = 0 and 1) and for three surface sites. The DC probabilities at the atop-site have quite different behavior compared to those of the other two sites. No threshold energies are necessary to observe the reactivity at almost all sites for the v = 0 state. This means that the H_2 (v = 0, j = 0) molecule is able to break its bond at all energies. However, the threshold energy region is observed for the v = 1 to break the bond of the H_2 at very low impact energies, *i.e.*, in this energy range the rotational excitation enhances the back scattering of the molecule after the collision. In fact, this is the rotational hindering of the DC, a well known effect in the dissociation of an H_2 on the metal surfaces.[32–36] However, this rotational hindering is observed for the v = 0 state. In the contrary (for the v = 0 state) the steering of the molecules[37] to more favorable orientations is playing a role to enhance the DC. At the lower collision energies and j values, the steering of the molecule to a more favorable orientation is much easier than that at higher j values. This is the source which forms the indirect mechanism.[9] At the higher j values, the steering effect for the molecule becomes less effective since rapidly rotating molecule cannot be guided easily by the PES to a more favorable geometry for the reaction. At the bridge-site, this phenomenon is clearly seen below 0.1 eV, especially for the v = 0 state case. There is another effect at the higher j values which is the loss of the rotational energy to the translational motion to help overcome the reaction barrier in the entrance channel.

This effect becomes significant for the higher j values. Therefore the rotational hindering is better visible for the lower j values (3–6) (especially at the bridge-site for the v = 0). On the other hand, the rotational hindering is not seen at the higher collision energies since they are much higher than the rotational energies. At the higher collision energies, v and j dependences are much less pronounced, however one may still say that the higher j value, the higher the DC. However, vibrational excitation of the impinging hydrogen molecule always promotes dissociation at the bridge and center sites on the low index Ni surface, and the DC probabilities are higher almost at all energies than those of the rotationally exited H_2. However, the atop-site behaves very differently for the v = 1 state, *e.g.*, $j \geq 2$ and v = 1 at $E \leq 0.1$ eV, and at $E \geq 0.2$ eV with high j and v = 1 the DC is zero. This typical region has not been calculated with the MD simulation.

At the lower collision energies, about 0.1 eV, the bridge and centre sites, for the v = 0, have a little bit similar reactivity. At higher energies the bridge-site is always more reactive than the other two sites. The DC probability gradually increases and reaches to a threshold value of 0.9 on the bridge. In contrast, the DC probabilities are decreasing slowly at the centre-site as the collision energy increases.

SUMMARY

The main goal of this study is to test the performance of ANNs for predicting any quantities in any molecule surface interaction studies. It has been observed that it can be used as an efficient tool to estimate the DC probabilities for the H_2 + Ni(100) collisions within much shorter run time. The DC probabilities strongly depend on the impact sites, the collision energies, and on the rovibrational states of the molecule. At the higher energies this dependence is weaker. The dynamics of the DCs as functions of the v, j, and impact sites are complicated in the low collision energy region. In general, the rotational excitations and the surface sites hinder the reactivity. This is more pronounced especially at the lower energies on the atop-site. The initial vibrational excitations of the molecule increase the probabilities more efficiently than the initial rotational excitations. In addition, the strong dependence of the DC probabilities on the low collision energies is also observed within the ANN estimations. Hence, the ANN results are in good agreement with the previous MD studies.

It can be noticed that no extra effort is necessary to compute the DCs for all the rovibrational states and the initial collision energies. After getting a sufficient set of data for the training process, the ANN can be used to predict all the interested initial conditions of the system. In conclusion, we believe that the ANN introduces new ideas that may help researchers to tackle optimization problems that, so far, have not been conveniently investigated.

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SAŽETAK

Određivanje vjerojatnosti kemisorpcije molekula vodika na površinu nikla pomoću umjetne neuronske mreže

Mustafa Böyükata, Yücel Koçyiğit i Ziya B. Güvenç

Disocijativne vjerojatnosti kemisorpcije za sudarne sustave $H_2(v, j)$ + Ni su procijenjene korištenjem ANN (Artificial Neural Network; umjetna neuronska mreža). Za treniranje mreže su se koristile prethodno (simulacijama molekulske dinamike) određene vrijednosti za vjerojatnosti. Istraživano je koliko je ANN dobra u predviđanju raznih veličina u međudjelovanju molekula s površinom. Analizirani su učinci raznih mjesta na površini i utjecaj rovibronskih stanja molekule. Postignuti rezultati se dobro slažu s prethodnim srodnim istraživanjima.