
**MONTE CARLO QUASICLASSICAL TRAJECTORY STUDY
OF A 2D MODEL OF CHEMISORPTION OF H₂
ON A METALLIC CLUSTER SURFACE**Jan VOJTÍK^a, Jiří ŠAVRDA^a and Jiří FIŠER^b^a *J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
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Dynamics of a 2-dimensional model of chemisorption of H₂ on a metallic surface is studied by quasiclassical trajectory Monte Carlo approach. The process is governed by a H₂-cluster potential energy surface based on the diatomics-in-molecules potential for H₂ on a planar Li₈ cluster. The probabilities of dissociative adsorption of H₂ on the surface and some additional characteristics of the collision process for a selected set of initial vibrational and translational conditions are presented. The effect of the initial vibrational and translational energy on the outcome of the H₂-surface collision events is discussed.

In a recent communication¹ we have reported preliminary results of our classical trajectory study of the dynamics of a two-dimensional (2D) model of dissociative chemisorption of H₂ on a lithium cluster surface. The potential energy surface (PES) used to govern the model process was an analytical representation of the H₂-Li₈ ground electronic state potential generated by the semiempirical valence-bond technique of diatomics-in-molecules²⁻⁵ (DIM). The DIM PES's have recently become very popular in theoretical description of gas-phase collision systems⁶⁻⁸, including those which exhibit electronically nonadiabatic behaviour⁹⁻¹³ and Penning ionization¹⁴⁻¹⁶.

A use in the molecule-surface dynamical studies of a PES based on the DIM approach is far from being standard at present, mainly because the systems involved are much more complicated than the colliding systems studied to date in the gas phase. In fact, in order to be able to employ this rather sophisticated approach, we were forced to represent the (cluster) surface by a relatively small number (8) of metal atoms and, furthermore, to consider explicitly only two degrees of freedom, one corresponding to adsorption and the other to dissociation. On account of this small size of the cluster, one must expect that the model is influenced by the edge effects.

On the other hand, the DIM scheme is much more flexible than the extended LEPS formula¹⁷⁻²¹ usually employed in dynamical studies to generate molecule-

-surface interactions. Because of the increased flexibility of our DIM approach we have obtained a two-dimensional cut through the molecule-surface PES which exhibits such a combination of basic features which has not as yet been reported¹⁷⁻²¹. The form of our 2D PES of a DIM quality was used in our recent work¹ to gain some insight into the way in which the dissociative chemisorption of H₂ on the surface is promoted by an energy conversion in the colliding system. The study was limited to H₂ initially excited to at most the fourth vibrational state and the results obtained are quite interesting.

The purpose of the present paper is to describe some aspects of the model in more detail, extend the study to H₂ excited to the fifth vibrational level and to present some additional characteristics of the H₂-surface colliding system which appear to be useful for the discussion of the mechanism of the model H₂-surface collision event.

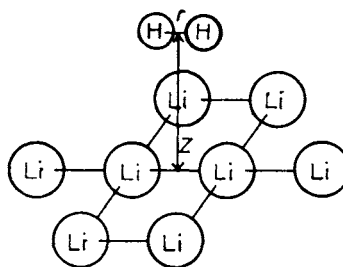
THEORETICAL

The 2D model potential used in the present study is based on the DIM calculation of the interaction between the H₂ molecule and a planar Li₈ cluster. The restriction of the number of degrees of freedom of the system to just two was accomplished according to Moffat²² and is illustrated by Fig. 1. The rigid surface assumption was invoked in the model, the nearest neighbour Li-Li internuclear distance being taken to be 3.51 Å. Further, the H-H molecular axis is oriented so as to become parallel to the Li(1)-Li(4) axis of the cluster and the H-H centre is restricted to vary along the line which is perpendicular to the Li₈ cluster surface and is drawn through the midpoint of the cluster central Li-Li axis. The remaining, explicitly considered degrees of freedom of the model are then the internuclear separation in the H₂ molecule (r) and the distance from the H₂ midpoint to the cluster surface, denoted by z .

A quasiclassical picture of the dynamical behaviour of the H₂-surface (H₂-S) model is obtained through the calculation of a very large number of classical trajec-

FIG. 1

Configuration of the H₂-Li₈ system used in the generation of the 2-dimensional model potential. The nearest-neighbour Li-Li separation is fixed at 3.51 Å. Distances are expressed as relative quantities $R = R'/R_0$, where R' are given in SI units and $R_0 = 0.1$ nm, throughout the paper. In the text this quantity is referred to as Å



tories, *i.e.* functions of time of the variables $r(t)$, $z(t)$ determined by classical mechanics (Hamilton equations) for a large number of different initial conditions chosen according to Monte Carlo sampling method. During the time span of any single trajectory one has to calculate the H_2-S potential and its derivatives a large number of times. Because of this, a direct use of the DIM scheme in the dynamical calculations is prohibitively expensive in terms of computer time.

Accordingly, we had to look for an analytical representation of the 2D H_2-S PES which besides being sufficiently computationally efficient, would be capable of representing quite faithfully a 2D PES of a DIM quality. A type of a 2D function amenable for this purpose is that of bivariate cubic splines²³.

According to the nature of the interactions in the model system, and in view of the configuration and size of the cluster, the physically relevant range of the r , z variables, in which the H_2-S PES was constructed, was chosen to be $0.1 \text{ \AA} \leq z \leq 8.0 \text{ \AA}$, and $0.3 \text{ \AA} \leq r \leq 15.0 \text{ \AA}$.

In this region of the model configuration space, an irregular rectangular grid consisting of 1 780 (20×89) geometries of the system was chosen. At each of these points, the lowest singlet electronic Born–Oppenheimer eigenenergies of the system were calculated using the DIM model described in some detail previously²⁴. It should be stressed that in the whole region of the H_2-Li_8 configuration space considered in these calculations, the ground electronic state of the system was well separated in energy from the first excited singlet state. In fact, the lowest energy difference between these states we arrived at was greater than ~ 0.8 eV. Hence within the model adopted here, there are no regions of configuration space exhibiting significant non-adiabatic coupling between the lowest two singlet potential energy surfaces of the type recently reported for the $H-Li_9$ clusters^{25,26}. Put another way, the nuclear motion considered in this model is predicted not to produce break-downs of the Born–Oppenheimer approximation and not to induce transitions from the ground-state PES to the excited ones. In view of this, the dynamical behaviour of the model system could be pictured as being governed by a single, ground state PES.

Once the DIM values of the ground singlet state of the system for all the grid points were computed, the desired spline representation of the PES for the whole 2D region mentioned above was obtained by our FORTRAN program based on the algorithm designed by de Boor^{27,28}. In addition to the ground state DIM eigenvalue for each of the 1 780 mesh points, the input to the program requires knowledge of the first or second derivatives of the PES at the boundaries of the region. These were obtained, following refs^{23,29} by a four-point Lagrange interpolation.

A contour diagram for the bivariate cubic spline representation of the ground state DIM PES of the model is given in Fig. 2. A comment on the main features of this 2D PES appears to be required here. There is a barrier (I) to adsorption of about 0.17 eV in the entrance channel which is a cause of an elastic recoil of those molecules, the H_2-S translational energy of which is relatively low. On the other hand,

conjugated momenta:

$$\begin{aligned}
 \dot{z} &= P_z/M, \\
 \dot{r} &= P_r/\mu, \\
 \dot{P}_z &= -\partial V(r, z)/\partial z, \\
 \dot{P}_r &= -\partial V(r, z)/\partial r.
 \end{aligned}
 \tag{1}$$

Here, P_z and P_r are the conjugated momenta corresponding to the H_2 —S distance and the H—H internuclear separation, respectively, M is the total mass of the H_2 molecule, while μ is the reduced mass of the H—H pair; $V(r, z)$ is the H_2 —S potential. Of the methods for numerical solution of the set of Eqs (1) tested, we have finally chosen to use the Hamming method which proved to be most efficient, accurate, and stable for the present problem. A typical value of numerical integration time step required to insure the desired accuracy ranged between 1.0×10^{-17} s and $7.0 \cdot 10^{-17}$ s.

RESULTS AND DISCUSSION

The trajectories were run in batches labeled by the initial H_2 —S translational energy E_T^0 and the H_2 vibrational level v (or, equivalently, the vibrational energy E_v^0 , taken from refs³⁰). Details of the way in which the trajectories were started, including the initial choice of the Monte Carlo variable corresponding to the H_2 vibrational phase are described in ref.¹. Each batch contained about 100 trajectories, which number is, for one Monte Carlo variable involved here, sufficiently large. The calculations were carried out for quite a large number of translational energies, distributed in the energy range from 0.162 eV (slightly below the barrier height in the entrance channel) to 0.465 eV.

For the batch with $E_T^0 = 0.162$ eV all trajectories were elastically recoiled from the barrier I . Of all the other trajectories computed, no one led to such a behaviour of the H_2 —S system which corresponds to dynamically stable molecular (nondissociative) adsorption. Accordingly, the H_2 molecules were found to either dissociatively adsorb or recoil (elastically or inelastically) from the surface. This feature of the dynamical behaviour of our model is at first sight surprising, but understandable, in terms of the 2D character of the model (including the rigid surface approximation) and the shape of our H—H—S PES (Fig. 2).

In Fig. 3 we show a schematic plot of a trajectory which is classed as leading to dissociative adsorption of H_2 on the model surface. The trajectory corresponds to H_2 initially excited to the 5th vibrational state, *i.e.*, $v = 5$ and $E_v^0 = 2.563$ eV. The H_2 —S translational energy at the beginning of the trajectory was 0.2 eV. It is to be noted that the initial amount of energy in the H—H vibrational degree of freedom in this

vibrational state is well above the barrier IV separating the (H₂—S) well from the immediate region of the (H—H—S) minimum (Fig. 2). In spite of this, the trajectory is more complicated than one would expect on the basis of a chemical intuition. The classical behaviour of the system depicted in Fig. 3 serves also to indicate that the outcome of a single classical H₂—S collision is¹, especially for $v = 4$ and $v = 3$, very sensitive to the way in which the trajectory enters the region at the mouth of the valley leading from the (H—H—S) minimum to the (H₂—S) one. This, in turn, implies that a sizable $T \rightarrow v$ energy conversion which is necessary for a trajectory (with $v = 4$ and especially with $v = 3$) leading to a dissociative adsorption on the surface requires a favourable relationship between the initial H₂—S velocity, E_v^0 and the randomized variable which determines the initial vibrational phase of H₂. It should be mentioned that the term $T \rightarrow v$ conversion in the H₂—S colliding system is used in precisely the same way as in ref.¹.

Returning to the trajectory shown in Fig. 3 we remark that out of the batch of the 100 trajectories with the $E_T^0 = 0.2$ eV and $v = 5$, 85 trajectories were found to lead to dissociative adsorption of the system. Another point to be noted is that of these 85 trajectories, the time span of the trajectory of Fig. 3 was one of the shortest. On a technical point, it should be perhaps interesting to mention that 15 852 numerical integration time steps were required for the trajectory of Fig. 3 to reach the final configuration.

For $v \leq 2$, no trajectories were found to lead to dissociative adsorption on the surface. Taking into account the height of the (H₂—S) \rightarrow (H—H—S) barrier, the corresponding initial vibrational energies for the lowest $1^1\Sigma_g^+$ H₂ state ($E_0 = 0.270$ eV, $E_1 = 0.786$ eV, $E_2 = 1.273$ eV) and the range of H₂—S translational energies considered, the result is not surprising. For higher initial vibrational states, the situation is in general different. In Fig. 4 we show the approximate dissociation probabilities P_d corresponding to different E_T^0 and $v = 3, 4, 5$. The probability

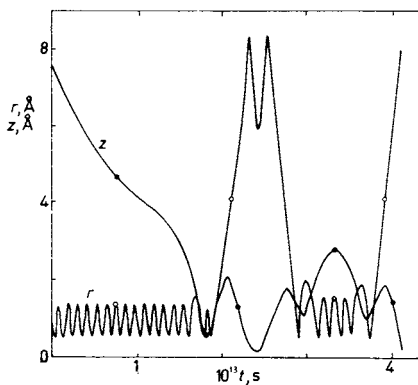


FIG. 3

H₂-surface trajectory leading to dissociative adsorption. Initial kinetic energy 0.2 eV, initial vibrational state of H₂: $v = 5$. (○) H—H internuclear separation, (●) H₂—S distance

for a batch of trajectories was determined according to the relation

$$P_d = N_d/N, \quad (2)$$

where N is the number of the trajectories run in the batch and N_d is the number of those trajectories in the batch which led to dissociative adsorption. The curves presented in the figure are the "taut" cubic spline interpolants^{2,3} to the P_d values computed. As expected, the dissociation probability increases in going from $v = 3$ to $v = 5$. What is more interesting is that the $P_d(E_T^0)$ dependence has, for all the three vibrational states, a quite pronounced oscillatory shape and, more surprisingly, that at some E_T^0 , the dissociation probability for the $v = 3$ case vanishes. A large portion of the main features of each of the $P_d(E_T^0)$ curves can be connected with the dependence on E_T^0 of the corresponding temporary trapping probability P_t which, according to ref.¹, is a fraction of the trajectories in a batch which remain in the (H_2 -S) well region for at least one (complete) H_2 -S vibrational period. The $P_t(E_T^0)$ dependences for $v = 3, 4$, and 5 are given in Fig. 5. The curves were obtained in much the same way as those for $P_d(E_T^0)$. Even a cursory examination of Figs 4 and 5 reveals that the zero P_d values for the $v = 3$ trajectories and the whole structure of the $P_d(E_T^0)$ dependence for the $v = 4, 5$ cases have their origin in the $P_t(E_T^0)$ curves. Most important is the fact that the E_T^0 values for which the dissociation probability in the $v = 3$ case vanishes are just those initial H_2 -S translational energies at which the trajectories do not get (temporarily) trapped on the surface. This supports the idea¹ that sufficiently large $T \rightarrow v$ energy conversion, which is required for dissociation in the $v = 3$ case, can only be achieved during several favourable passages of the

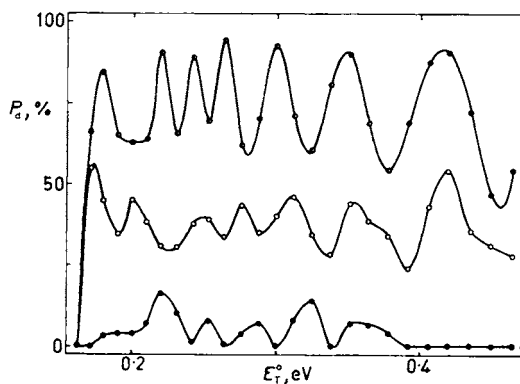


FIG. 4

Dissociation probabilities P_d for $v = 3$ (●), $v = 4$ (○), and $v = 5$ (●) as functions of the initial H_2 -surface kinetic energy E_T^0

system through the (H₂—S) well region. However, it is seen from Figs 4 and 5 that only a relative small fraction of the $v = 3$ trajectories trapped on the surface happens to dissociate. An example of a trapped trajectory with $v = 3$ which was recoiled from the surface is shown in Fig. 6. The trajectory corresponds to $E_T^0 = 0.253$ eV, i.e., to the region of smaller E_T^0 , where the difference between $P_t(E_T^0)$ and $P_d(E_T^0)$ is

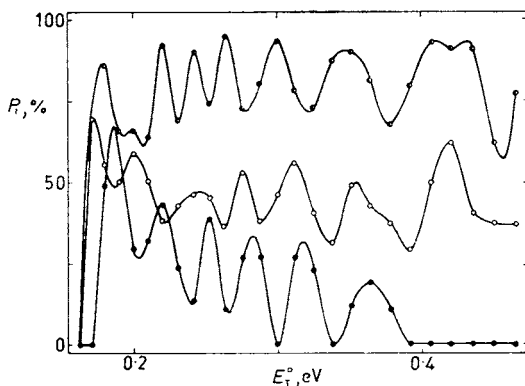


FIG. 5

Temporary trapping probabilities P_t for $v = 3$ (●), $v = 4$ (○), and $v = 5$ (◐) as functions of the initial H₂-surface kinetic energy E_T^0

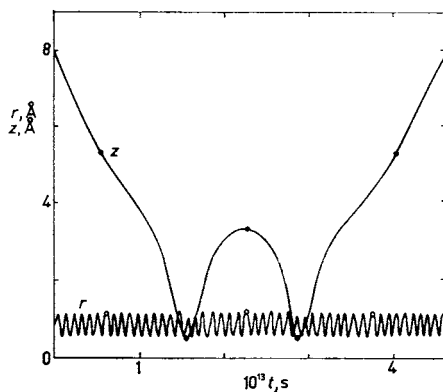


FIG. 6

H₂-surface trajectory of H₂ recoiled from the surface. Initial H₂-S kinetic energy 0.253 eV, initial vibrational state of H₂: $v = 3$. (○) H—H internuclear separation, (●) H₂—S distance

quite significant. The reason for this profound difference is that a sufficiently large increase of the vibrational energy of the system during the $\text{H}_2\text{—S}$ collision is, besides the factors mentioned above, influenced by the amount of energy initially available in the $\text{H}_2\text{—S}$ translational degree of freedom. As opposed to the $v = 3$ case, the difference between $P_i(E_T^0)$ and $P_d(E_T^0)$ is rather small for the $v = 4$ and $v = 5$ trajectories. This dramatic change of the relationship between $P_i(E_T^0)$ and $P_d(E_T^0)$ in going from $v = 3$ to $v = 4, 5$ can be understood by taking into account that the pertinent initial H_2 vibrational levels are $E_3^0 = 1.731$ eV, $E_4^0 = 2.161$ eV, $E_5^0 = 2.563$ eV and that the $(\text{H}_2\text{—S}) \rightarrow (\text{H—H—S})$ barrier height is 2.22 eV, the corresponding saddle point having the energy 1.52 eV relative to the asymptotic $\text{H}_2\text{—S}$ minimum.

Summarizing, we conclude that with a type of potential used here, the dissociative adsorption of a H_2 molecule on the surface is influenced quite markedly by the translational-vibrational energy conversion. The effect is most pronounced in the third vibrational state which is, within the present model, physically most interesting. For higher vibrational levels of H_2 , this effect is considerably smaller but significant. However, starting from $v = 4$ the effect does not seem to alter considerably with increasing v . It is difficult to assess at present to what extent are these results influenced by the model itself, namely by the rigid surface approximation and the 2D character of the PES. Of interest is the fact that the outcome of the $\text{H}_2\text{—S}$ collision events is essentially determined by subtleties of the behaviour of the system in a relatively small portion of the $(\text{H}_2\text{—S})$ well region lying around the entrance part of the $(\text{H}_2\text{—S}) \rightarrow (\text{H—H—S})$ valley. The primary information on the behaviour of the system in this region is condensed in the (temporarily) trapping probabilities $P_t(E_T^0)$ and, further, in the relation between the dissociation probability $P_d(E_T^0)$ and $P_t(E_T^0)$. These $P_d(E_T^0)$ dependences are of principal importance in dynamical studies of molecule-surface systems. In an attempt to get an additional information on what is going on in this critical region of the H—H—S surface, we turned our attention to the elastic and inelastic recoil of H_2 from the surface, which takes place in the system in addition to dissociative adsorption. As already mentioned, the model did not lead to any molecular adsorption. Further, penetration of H_2 through the surface was quite negligible especially for $v = 3$ and $v = 4$. Hence, the probability estimates for the recoil of H_2 from the surface for all initial E_T^0 and $v = 3, 4, 5$ can easily be deduced from Fig. 4.

This probability represents the primary characteristic of the system in the recoil channel. Because of the 2D feature of the present model (including the rigid surface approximation) and the initial scattering conditions considered, the system in this channel is completely characterized by the distribution of the vibrational energy of the recoiled molecules. The corresponding fractions of the recoiled H_2 molecules ending in individual vibrational levels v' for initial vibrational states $v = 3, 4, 5$ and the whole range of E_T^0 considered are given in Figs 7, 8, and 9, respectively. In calculating these quantities, the vibrational level of the recoiled trajectory was deter-

mined using the standard histogram method described in refs^{31,32}. Note that the trajectories which did not overcome the barrier in the entrance channel, *i.e.* those with $E_T^0 \leq 0.17$ eV, were excluded from the analysis.

It is seen from Fig. 7 that in the H₂—S system with H₂ originally in the third

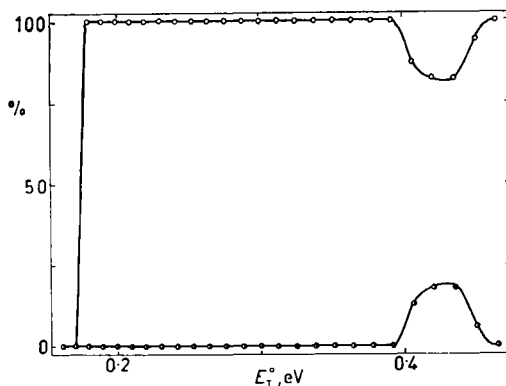


FIG. 7

Distribution to vibrational states of the H₂ molecules recoiled from the surface. Initial vibrational state of H₂: $v = 3$. Initial H₂—S translational energy E_T^0 is in eV. Final states: $v' = 3$ (○), $v' = 2$ (●)

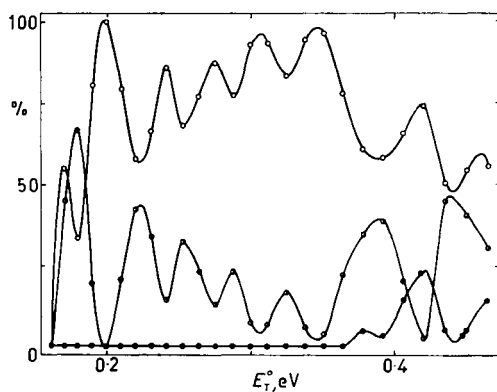


FIG. 8

Distribution to vibrational states of the H₂ molecules recoiled from the surface. Initial vibrational state of H₂: $v = 4$. Initial H₂—S translational energy E_T^0 is in eV. Final states: $v' = 5$ (●), $v' = 4$ (○), $v' = 3$ (●)

vibrational state, the recoil of the H_2 molecules from the surface is elastic in the whole range of E_T^0 except for a small interval of initial translational energies close to the upper limit. For this interval, a relatively small fraction of recoiled H_2 molecules was found to be in the $v' = 2$ vibrational level. It should be noted that the E_T^0 interval just mentioned corresponds to those E_T^0 for which no trapping of molecules occurred (Fig. 4).

For the $v = 4$ case (Fig. 8) the situation is already more complicated. Besides the elastic recoil which prevails in the whole range of E_T^0 (except for an immediate region of $E_T^0 = 0.18$ eV), less probable, but quite significant vibrational deexcitation of the H_2 molecules occurs. Another interesting feature of the $v' = 5$ and $v' = 4$ fractions in the $v = 4$ case is that the corresponding dependences oscillate quite markedly with the change in E_T^0 . This feature is consistent with the shape of the corresponding ($v = 4$) dissociative adsorption (Fig. 4) and temporary trapping (Fig. 5) dependences on E_T^0 . However, no simple connection between the structures of the $P_d(E_T^0)$ and $P_i(E_T^0)$ curves and those exhibited by the dependences of Fig. 8 appears to exist. As a final comment concerning this figure: For $E_T^0 = 0.378$ eV, the channel leading to $v' = 5$ becomes effectively (histogram method) open. Accordingly, starting from this E_T^0 a certain fraction of the recoiled H_2 molecules was excited from $v = 4$ to $v' = 5$.

It is seen from Fig. 9 that most of these considerations apply (with appropriate modification) to the $H_2(v = 5)$ —S collisions. The only significant difference with respect to the $v = 4$ case is that practically in the whole E_T^0 region considered, the fraction of elastically recoiled H_2 molecules is substantially smaller than that cor-

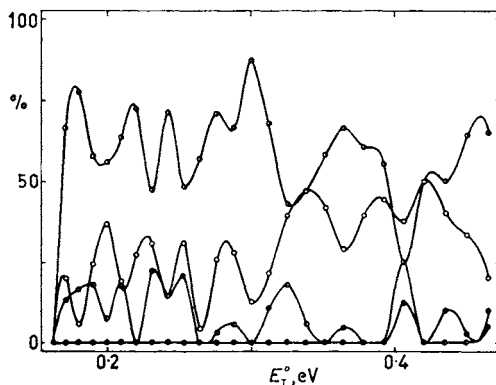


FIG. 9

Distribution to vibrational states of the H_2 molecules recoiled from the surface. Initial vibrational state of H_2 : $v = 5$. Final states $v' = 6$ (●), $v' = 5$ (○), $v' = 4$ (●), $v' = 3$ (○)

responding to H₂ recoiled in the $v' = 4$ level. It appears likely that this profound difference between the $v = 5$ and $v = 4$ H₂—S collisions may be explained by that in the $v = 5$ case, the initial H₂ vibrational energy (2.563 eV) is already greater than the barrier to dissociative adsorption (2.22 eV). This relatively large energy difference, (and increased vibrational amplitude of H₂ with $v = 5$) seems to diminish the fraction of the H₂ molecules which can be elastically recoiled.

In concluding this communication we note that the classical trajectory study of the dynamics of the present H₂-surface model provides a rather interesting information on the details of the model H₂-surface collision process. Some of the results are surprising and can be only partially understood at present. One of the most challenging features of our results is the oscillatory dependence on the initial H₂—S translational energy of most of the quantities we calculated. There are some indications^{33,34} that a conclusive attitude to some aspects of the dynamics of the present H₂—S model can be taken up only on the basis of a quantum mechanical treatment of the dynamical behaviour of the system. Because of the 2D-character of our model, at least sample calculations of this type appear to be feasible. The work on the quantum mechanical time dependent description of the dynamics of the model is in progress.

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