A study of the parallel molecule–surface reaction
HCl + surface→H...surface + Cl: A comparison between quantum mechanical and quasi-classical trajectory results

Yaakov Shima and Michael Baer
Soreq Nuclear Research Center, Yavne 76000, Israel

(Received 17 April 1985; accepted 10 June 1985)

This work is devoted to the study of quantum effects as encountered in reactions of gas–solid–surface interactions. The reaction that was chosen is HCl (υ = 0, 1,...,4) + surface→H...surface + Cl where the HCl molecule was assumed to approach the surface while being parallel to it (i.e., γ = π/2). Results due to quantum mechanical and quasi-classical trajectory treatments were compared and sometimes large differences were encountered indicating the importance of quantum effects. The model assumed for this treatment inherently includes corrugation and part of the study was devoted to the influence of corrugation on the results.

I. INTRODUCTION

From the study of exchange processes between an atom and a diatomic molecule it is known that quantum effects are important whenever the following situations are encountered:

(a) Light atoms, such as hydrogen and its isotopic analogs, are involved in the process.
(b) The process takes place in the threshold region or in the vicinity of potential barriers.
(c) The process is governed by resonances of various types.
(d) Detailed information is required, such as state-to-state transition probabilities or differential cross sections.

However, it is not known to what extent quantum effects are important for chemical processes between two atoms and a solid surface (adsorption, desorption, exchange, etc.) We are currently interested in developing quantum mechanical approximations which will enable us to treat certain chemical processes occurring as a result of such interactions. In our first study a theory within the infinite order sudden approximation (IOSA) was presented which permits the study of the exchange reactions:

$$\begin{align*}
&AB + S \rightarrow \begin{bmatrix} AS + B \\ BS + A \end{bmatrix} \\
&\text{(I)}
\end{align*}$$

Here AB is a diatomic molecule and S stands for “surface.” The same theory with minor changes can be applied to desorption processes of Rideal$^{1,2,4}$ type:

$$\begin{align*}
&AS + B \rightarrow S + AB. \\
&\text{(II)}
\end{align*}$$

Moreover, with somewhat more radical changes the same theory can be applied for adsorption as well. Whereas we hope to treat Rideal-type desorption and eventually adsorption in subsequent publications, the present study is devoted to the exchange process (I). We chose to start the numerical study with such a reaction, and not with the more common ones, because the reactive IOSA which is employed was tested extensively with respect to gas phase reactions$^{5}$ and reaction (I) is of a similar type. Still, the changes in the proposed theory are significant enough that reaction (I) is a gas–solid–surface reaction and not a regular gas phase reaction.

At this stage it is important to emphasize that neither this study nor the next few ones of this type to follow are expected to yield results that can be compared with experiments. For instance, in this particular study we show that calculations within the reactive IOSA are feasible (all the details of how to carry out such a calculation are given) but no claims are made that the system chosen for this purpose bears any resemblance to a realistic case. On the contrary, we made the system as simple as possible not only for the sake of our own convenience but in order to present our new approach in most comprehensive way. Consequently, the surface is assumed to be rigid so that no energy is assumed to flow into the solid. We also assume the surface, to a certain extent, to be noncorrugated, which means that the potential depends only on the interatomic distance and on the distances of the two atoms from the surface. However, within the IOSA the horizontal distance between the two atoms is not allowed to be more than a given value p$_0$ (see text) and so a kind of corrugation is built into the theory, not through the potential but through the model. The potential chosen for the interaction is a LEPS surface, essentially of the kind used by McCrea and Wolken,$^6$ by Gelb and Cordillo,$^7$ and more recently by Tully.$^8$ Again no claims are made that this is a realistic potential, etc., but gross-modal a reasonable potential that can be applied in such treatment.

Although the emphasis in this work is on the quantum mechanical approach, a classical reactive IOSA$^6$ is also introduced for the sake of comparing the quantum results with the classical ones. Whereas both the quantum and classical theories are general, the calculations were performed for a single IOSA angle γ (see Fig. 1). We chose γ to be π/2 for the following reasons:

(a) This γ value is expected to be a typical one for the diatomic–solid–surface interaction.
(b) Since our aim is to apply the gas phase IOSA for the gas–solid–surface reaction, we decided to be as
The diatomic chosen for this study is the HCl molecule which is a light-heavy type diatomic. From a full classical trajectory study that we performed prior to the IOSA study in this paper, it was found that in the energy range for which results are presented here, the reaction

$$\text{HCl} + \text{S} \rightarrow \text{HS} + \text{Cl}$$

is the dominant process.

The energy range of our study is $1.95 < E_{\text{tot}} < 3.30$ eV. The lower value is close to the endothermicity of the reaction and therefore is also the threshold value. From the classical trajectory study it was established that the adsorption probability in this energy range does not exceed 0.3 and that dissociation does not occur.

The paper is arranged in the following way. The theory for both the quantum and the classical IOSA is presented in the next section, the details on the potential and the numerical treatment are given in the third section, results are shown in the fourth, and the conclusions summarized in the fifth section.

II. THEORY

In this section we treat the quantum and the classical IOSA. The general theory was given in a previous paper; here we concentrate on a fixed $\gamma$ situation. A description of the model is given together with details of how the calculations of the $S$ matrix elements and the classical trajectories are actually carried out.

A. The quantum mechanical treatment

To perform the quantum calculations we have to distinguish between two kinds of coordinates:

(i) The reagents coordinates which are characterized by the subscript $\lambda$. The reagents are best described by the three-polar coordinate $r_\lambda = (r, \gamma, \phi)$ for the interatomic vib-rotational motion and three Cartesian coordinates $R = (X_{\lambda}, Y_{\lambda}, Z_{\lambda})$ for the translational motion.

(ii) The products coordinates which are characterized by the subscript $\nu$. The products are best described in terms of two sets of Cartesian coordinates: $r_\nu = (X_\nu, Y_\nu, Z_\nu)$ for the bound atom and $R_\nu = (X_\nu, Y_\nu, Z_\nu)$ for the unbound atom.

The various coordinates are shown in Fig. 1.

The treatment can be simplified if the various vectors are scaled in the following:

$$R_\lambda = a_\lambda^{-1} R_\nu; r_\lambda = a_\lambda r_\nu \quad \alpha = \lambda, \nu,$$

where

$$a_\lambda = \left( \frac{m_A m_B}{m_A + m_B} \right)^{1/4}, \quad a_\nu = \left( \frac{m_B}{m_A} \right)^{1/4}.$$

Here $m_A$ and $m_B$ are the masses of the desorbed and adsorbed atoms, respectively. By employing these coordinates, the transformation from one system of coordinates to the other is given by (we dropped the primes)

$$\begin{pmatrix} R_\nu \\ r_\nu \end{pmatrix} = \begin{pmatrix} \cos \beta & \sin \beta \\ \sin \beta & -\cos \beta \end{pmatrix} \begin{pmatrix} R_\lambda \\ r_\lambda \end{pmatrix},$$

where

$$\cos \beta = \left( \frac{m_A}{m_A + m_B} \right)^{1/2}.$$

Within the IOSA we distinguish in each channel between two varying coordinates and four frozen ones. In the $\lambda$ channel the two varying ones are $r$ and $Z_\lambda$, whereas in the $\nu$ channel the corresponding two varying coordinates are $z_\nu$ and $Z_\nu$. The transformation from $(Z_\lambda, r)$ to $(Z_\nu, z_\nu)$ is, according to Eq. (3), as follows:

$$Z_\nu = Z_\lambda \cos \beta + r \cos \gamma \sin \beta,$$

$$z_\nu = z_\lambda \sin \beta - r \cos \gamma \cos \beta.$$

In what follows we assume the surface to be noncorrugated which means that the potential between the two atoms and the surface depends on their distances from the surface only. Consequently, the IOSA Schrödinger equation for the reagents becomes

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial Z_\lambda^2} + \frac{\partial^2}{\partial r^2} \right) + V(r, Z_\lambda; \gamma) - E \right] \psi(r, Z_\lambda; \gamma) = 0,$$

and for the products,

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial z_\nu^2} + \frac{\partial^2}{\partial Z_\nu^2} \right) + V(z_\nu, Z_\nu; \varphi) - E \right] \psi(z_\nu, Z_\nu; \varphi) = 0.$$

Here $\mu$ is the reduced mass of the system, i.e.,

$$\mu = (m_A m_B)^{1/2}$$

and $\rho$ is the horizontal distance between the two interacting atoms (see Fig. 1).

From Eq. (7) it can be seen that out of four "frozen" coordinates in the entrance channel only $\gamma$ becomes a parameter for which the calculations have to be repeated. In the exit channel also only one frozen coordinate is encountered, i.e., $\rho$, and in principle the calculations also have to be repeated for each value of $\rho$. However, as will be shown later, $\rho$ and $\gamma$ have to be related to each other through the equation

$$\rho = r_0 \sin \gamma \quad \text{and} \quad \gamma = \gamma_0,$$

to ensure the uniqueness of the potential along the line $r = r_0$. The meaning of $r_0$ is as follows. In the entrance channel the system is moving on a plane defined by the equation

$$\gamma = \gamma_0.$$
In the exit channel the system is also moving on a plane which is defined by the equation

$$\rho = \rho_0.$$  \hspace{1cm} (12)

The two planes intersect along a straight line. We have shown\textsuperscript{2} that the equation of the line in reagents coordinates is

$$r = r_0.$$  \hspace{1cm} (13)

If the process can be characterized by a single parameter $r_0$, then for each value of $\gamma$ the value of $\rho$ is uniquely determined and the calculations have to be carried out only as a function of one parameter (either $\gamma$ or $\rho$). The parameter $r_0$ is explicitly related to the corrugation of the surface. In Fig. 2(a) a (light heavy-type) molecule is seen approaching an $x$ directional corrugated surface. In Fig. 2(b) the equivalent IOSA model is shown in which the wavy potential is replaced by a step function potential. It is to be noted that the horizontal distance between the two atoms is limited to $\rho_0$ (as long as the $x$ component of the translational energy is smaller than the height of the potential barrier). 

In order to obtain the $S$ matrix elements and the corresponding transition probabilities, Eqs. (7) and (8) have to be solved. There are different methods for deriving the physical solutions, as determined by the asymptotic conditions. One way is to employ the usual propagation procedure as was done while treating collinear gas phase exchange collisions.\textsuperscript{10} In fact, the information given in Appendix A will suffice for carrying out such a calculation. Since the present calculation deals with a light heavy molecule, the ordinary methods become not only time consuming but numerically unstable; therefore we used a recent more stable method which employs polar coordinates as defined with respect to the origin.\textsuperscript{11,12} A description of the procedure for our particular case is given in Appendix B. Using these coordinates, which are also known as Delvès' or hyperspherical coordinates, the two Schrödinger equations given in Eq. (7) and (8) become

$$\begin{align*}
-\frac{\hbar^2}{2\mu} & \left( \frac{\partial^2}{\partial R^2} + \frac{1}{R} \frac{\partial}{\partial R} + \frac{1}{R^2} \frac{\partial^2}{\partial \gamma^2} \right) \\
+ V(R, \theta, \phi) & \psi(R, \theta, \phi) = 0, \hspace{1cm} (14)
\end{align*}$$

where the relation between $R$ and $\theta$ and the previous variables is as follows (see Appendix B):

(a) for reagents:

$$r = R \sin \theta,$$

$$Z_A = R \cos \theta - r_0 (1 - \cos \gamma) \cot \beta,$$  \hspace{1cm} (15)

(b) for products:

$$z_r = R \sin(\beta - \theta),$$

$$Z_r = R \cos(\beta - \theta) - r_0 (1 - \cos \gamma)(\sin \beta)^{-1}.$$  \hspace{1cm} (16)

It may be seen that for $\gamma = 0$, Eqs. (15) and (16) reduce to the ordinary collinear case.

We shall not go into more details of how Eq. (14) is solved as they were given several times on other occasions.\textsuperscript{11,12} We just mention that we follow the procedure by Shoemaker et al.\textsuperscript{12} and employ their computer program.

**B. The classical trajectory treatment**

In treating two atoms interacting with a surface we usually encounter 12 equations of motion: 6 for the coordinates and 6 for the momenta. The classical Hamiltonian given in terms of reagent coordinates is

$$\begin{align*}
H & = \frac{1}{2\mu_R} (p_{x_A}^2 + p_{y_A}^2 + p_{z_A}^2) + \frac{1}{2\mu_r} \times \\
& \left( \frac{\hat{p}_r^2}{r^2} + \frac{\hat{p}_\theta^2}{r^2 \sin^2 \gamma} + \frac{\hat{p}_\phi^2}{r^2 \sin^2 \gamma} \right) \\
& + V(X_A, Y_A, Z_A, r, \theta, \phi), \hspace{1cm} (17)
\end{align*}$$

where

$$\mu_R = m_A + m_B \hspace{0.5cm} \mu_r = \frac{m_A m_B}{m_A + m_B}. \hspace{1cm} (18)$$

Assuming the surface to be noncorrugated, the potential becomes

$$V = V(Z_A, r, \gamma) \hspace{1cm} (19)$$

and the corresponding relevant Hamiltonian equations are

$$\begin{align*}
\dot{Z}_A & = \frac{p_{z_A}}{\mu_R} \hspace{1cm} \dot{p}_{z_A} = -\frac{\partial V}{\partial Z_A}, \hspace{1cm} (20a) \\
\dot{r} & = \frac{p_r}{\mu_r} \hspace{1cm} \dot{p}_r = -\frac{\partial V}{\partial r}, \hspace{1cm} (20b) \\
\dot{\gamma} & = \frac{p_{y_A}}{\mu_r r^2} \hspace{1cm} \dot{p}_{y_A} = -\frac{\partial V}{\partial \gamma}, \hspace{1cm} (20c)
\end{align*}$$

where it was also assumed that at $t = 0$,

$$p_x = p_{x_A} = p_{x_A} = 0.$$  \hspace{1cm} (21)

Within the framework of the IOSA, Eqs. (20c) are ignored and we are left with four differential equations to be solved where $\gamma$ is a parameter.

In a similar way the classical Hamiltonian in terms of products coordinates is given in the form
\[ H = \frac{1}{2m_A}(p_{x_A}^2 + p_{y_A}^2 + p_{z_A}^2) + \frac{1}{2m_B}(p_{x_B}^2 + p_{y_B}^2 + p_{z_B}^2) \]
\[ + V(x_A, y_A, z_A, x_B, y_B, z_B), \]
(22)
where it is assumed that A is the desorbed atom and B the adsorbed one.

Assuming again the surface to be noncorrugated, the potential becomes
\[ V = V(Z_v, \varphi), \]
(23)
where
\[ \rho = (x_A - x_v)^2 + (y_A - y_v)^2 \]
(24)
and consequently the corresponding Hamiltonian equations are
\[ \dot{Z_v} = \frac{p_{Z_v}}{m_A}, \quad \dot{p}_{Z_v} = -\frac{\partial V}{\partial Z_v}; \]
(25a)
\[ \dot{z_v} = \frac{p_{Z_v}}{m_B}, \quad \dot{p}_{z_v} = -\frac{\partial V}{\partial z_v}; \]
(25b)
\[ \dot{\varphi} = \frac{p_{\varphi}}{\mu_r}, \quad \dot{p}_{\varphi} = -\frac{\partial V}{\partial \varphi}. \]
(25c)
It should be noted that \( \rho \) and \( r \) are related in each situation as
\[ \rho = [(r^2 - (Z_v - z_v)^2)^{1/2}. \]
(26)
Within the IOSA, Eqs. (25c) are ignored and we are left with four differential equations to be solved where \( \rho \) is the parameter.

The next subject to be handled is the transition from reagents to the products channel. The transition occurs along the line \( r = r_0 \), where, in order to continue a trajectory from the \( \lambda \) channel to the \( v \) channel, one has to transform \((Z_A, r, P_{Z_A}, P_r)\) to \((Z_v, z_v, P_{Z_v}, P_{z_v})\) variables in such a way that total energy and, as much as possible, the various momenta are conserved. This is done by assuming the validity of Eq. (3) or Eqs. (5) and (6). This guarantees that the potential is uniquely defined along the line if Eq. (10) is also fulfilled.

Differentiating Eq. (3) with respect to time and multiplying through by \( \mu \), one obtains the relation for the momenta, i.e.,
\[ \begin{pmatrix} P_{r_1} \\ P_{z_1} \end{pmatrix} = \begin{pmatrix} \cos \beta & \sin \beta \\ \sin \beta & -\cos \beta \end{pmatrix} \begin{pmatrix} P_{r_A} \\ P_{z_A} \end{pmatrix}. \]
(27)
Within the IOSA the only way to guarantee the conservation of kinetic energy (the uniqueness of the potential energy was already treated) is to assume the validity of Eq. (27) for the scalars (and not the vector). Thus in the present notation Eq. (27) becomes
\[ P_{z_v} = \cos \beta P_{z_A} + \sin \beta P_r, \]
\[ P_{z_A} = \sin \beta P_{z_A} - \cos \beta P_r, \]
(28)
and for ordinary (unscaled) variables we get
\[ P_{Z_v} = \cos \beta P_{Z_A} + P_r, \]
\[ P_{Z_A} = \sin \beta P_{Z_A} - P_r. \]
(29a)
Equations (5) and (6) together with Eqs. (28) form the transformations from reagents to products or vice versa.

As mentioned, the transition from reagents to products coordinates occurs whenever \( r \) becomes larger than \( r_0 \). However, not every trajectory that enters the products channel necessarily leads to products. The model permits some of the trajectories to return to the reagents channel. Such a trajectory is shown in Fig. 3. The condition for a trajectory to return is that the difference \( \Delta z \), defined as
\[ \Delta z = Z_v - z_v, \]
changes sign. The sign of \( \Delta z \) is determined at time \( t = t_c \) when the trajectory entered the products channel (at point \( L \)). From there on \( Z_v(t) \) and \( z_v(t) \) are known for any time and if it happens that at some time \( t \)
\[ \text{sign}(\Delta z(t)) \neq \text{sign}(\Delta z(t = t_c)) \]
(31)
this implies that the trajectory again reached the line \( r = r_0 \) (at the point \( K \) in Fig. 3). Consequently the inverse transformation has to be employed to allow the continuation of the trajectory into the reagents channel.

### III. NUMERICAL DETAILS

To perform the calculation a modified LEPS surface is employed:
\[ V = U_1 + U_2 + U_3 - [Q_1^2 + (Q_2 + Q_3)^2]^{1/2}, \]
(32)
where
\[ U_1 = \frac{D_1}{4(1 + \Delta_1)} [(3 + \Delta_1)\exp(-2\alpha(r - r_0)) - (2 + 6\Delta_1)\exp(-\alpha_r(r - r_0))], \]
(33a)
and
\[ Q_1 = \frac{D_1}{4(1 + \Delta_1)} [(1 + 3\Delta_1)\exp(-2\alpha(r - r_0)) - (6 + 2\Delta_1)\exp(-\alpha_r(r - r_0))], \]
(33b)
where \( D_1, \alpha_r, \alpha, \) and \( \Delta_1 \) are, respectively, the dissociation energy, the internuclear equilibrium distance, the characteristic Morse parameters and the Sato parameters used to ad-
TABLE I. Morse and Sato parameters for the HCl + surface systems studied in this work.

<table>
<thead>
<tr>
<th>Molecule*</th>
<th>$D$ (eV)</th>
<th>$r_0$(Å)</th>
<th>$\alpha$(Å$^{-1}$)</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH</td>
<td>2.74</td>
<td>1.65</td>
<td>1.025</td>
<td>0.03</td>
</tr>
<tr>
<td>HCl</td>
<td>4.613</td>
<td>1.277</td>
<td>1.865</td>
<td>0.147</td>
</tr>
<tr>
<td>SCl</td>
<td>1.5</td>
<td>2.014</td>
<td>1.887</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*S indicates "surface."

just the potential so it has desired features. The numerical values of these parameters are listed in Table I. From that table it is also seen that the exothermicity $\Delta H_0$ is

$$\Delta H_0 \sim D_{HCl} - D_{HS} = 4.613 - 2.740 = 1.873 \text{ eV}.$$ 

Some features of the potential energy are given in Fig. 4 where the adiabatic vibrational states of the Cl--H--S system are drawn as a function of $R$. These were derived for $\gamma = \pi/2$ and $r_0 = 4.5$ bohrs. Except for $v = 0$, all the other vibrational states exhibit relatively deep wells in the interaction region. The depths of these wells are sometimes larger than 1 eV. The figure shows four vibrational states, three of which belong to the asymptotic region of HCl + S and one to the asymptotic region of HS + Cl. It should also be emphasized that the sixth and seventh vibrational states interact very strongly and that the corresponding diabatic states cross each other twice, the first time at $R \sim 23.5$ bohrs and the second at 26.5 bohrs. Crossings of this type are also encountered for other pairs of vibrational states where one corresponds to an adiabatic reagent state and the other to an adiabatic product state.

In the actual calculation 30 states were included, of which 15 correspond asymptotically to the S + HCl system and 15 to the Cl + HS system. The main reason for the need for such a large number of states is due to the deep wells of the various vibrational states as encountered in the interaction region. These wells are not associated with any potential

well, as may be noticed from the behavior of the ground vibrational states.

**IV. RESULTS**

**A. The quantum mechanical results**

The reactive transition probabilities as a function of the total energy for various initial vibrational states are presented in Fig. 5 [see also Ref. 9(c)]. The calculations were carried out for $r_0 = 4.5$ bohrs. The main findings are

(i) for the lower vibrational states, namely $v_i = 0, 1, 2$ hardly any threshold is encountered, except for the endothermicity ($\sim 1.94 \text{ eV}$). The higher vibrational states exhibit a clear threshold behavior of at least 0.1 eV.

(ii) No systematic indication is given as to the importance of the distribution of the energy between the vibrational and translational modes of motion for promoting the reaction. In general, the highest reaction probabilities are found for $v_i = 0$ although along part of the energy axis higher probabilities are encountered for $v_i = 4$.

(iii) The probability functions oscillate in the low energy range but then become rather stable and only weakly dependent on the energy.

A comparison of calculated results for $r_0 = 4.5$ bohrs and $r_0 = 4.0$ bohrs given in Fig. 6 shows they are very sensitive to the value of $r_0$. For $v_i = 0$ the reaction transition probability decreased from $\sim 0.5$ to 0.3 [see Fig. 6(a)], for $v_i = 2$ it increased from $\sim 0.3$ to 0.55 [see Fig. 6(b)] and for $v_i = 4$ it decreased again from $\sim 0.7$ to 0.35 [see Fig. 6(c)]. Thus no regular behavior is found.

Some of these irregularities are also seen in Fig. 7. Here the reactive probabilities are presented as a function of the initial state for three different $r_0$ values, i.e., $r_0 = 4.0, 4.5,$
sition probabilities are encountered even with modest changes in this parameter. However, there are also some hints that the results seem to converge as \( r_0 \) becomes large. This is, in particular, confirmed by the results shown in Fig. 7.

**B. The classical trajectory results**

Classical trajectory results, shown in Figs. 8–10, were obtained in order to compare them with the quantum results. The transition probabilities as a function of total energy for different initial vibrational states and for \( r_0 = 4.5 \) bohrs and \( r_0 = 4.0 \) bohrs are compared in Figs. 8 and 9, respectively. In general the agreement is better for \( r_0 = 4.5 \) bohrs, especially for \( v_i = 1, 2, 4 \), with a somewhat less satisfactory fit for \( v_i = 3 \). Significant deviations are seen for \( v_i = 0 \). For \( r_0 = 4.0 \) bohrs the deviations between the quantal and classical results are much more severe, in particular for \( v_i = 0, 2, 3 \).

**FIG. 6.** Quantal reactive transition probabilities for the processes HCl(\( v_i \)) + surface\( \rightarrow \)H\( \rightarrow \)surface + Cl: a comparison between results obtained for \( r_0 = 4.5 \) bohrs (---) and \( r_0 = 4.0 \) bohrs (--). (a) \( v_i = 0 \); (b) \( v_i = 2 \); (c) \( v_i = 4 \).

4.75 bohrs, and for two energies, i.e., \( E_{\text{tot}} = 2.473, 3.073 \) eV. The vibrational distribution for \( r_0 = 4.5 \) bohrs differs significantly from the distribution for \( r_0 = 4.0 \) bohrs but is somewhat similar to the one for \( r_0 = 4.75 \) bohrs.

We made the ansatz that \( r_0 \) is a parameter related to the corrugation. Thus our study suggests that the results are very sensitive to the corrugation. Large changes in the transi...

**FIG. 7.** Initial vibrational distributions are calculated for different total energies and various \( r_0 \) values: (a) \( E_{\text{tot}} = 2.473 \) eV, (b) \( E_{\text{tot}} = 3.073 \) eV.

**FIG. 8.** A comparison between quantal and classical transition probabilities for the processes HCl(\( v_i \)) + surface\( \rightarrow \)H\( \rightarrow \)surface + Cl. The calculations were carried out for \( r_0 = 4.5 \) bohrs. (a) \( v_i = 0 \); (b) \( v_i = 1 \); (c) \( v_i = 2 \); (d) \( v_i = 3 \); (e) \( v_i = 4 \); (---) quantal results; (---) classical results.
effects (i.e., deviations between the quantum and the classical results) to be more pronounced for the smaller \( r_0 \) value. This result is not surprising as the smaller \( r_0 \) is, the larger the gap between eigenstates of the horizontal potential well on the surface. Although the calculations were carried out for high energy (1.94 < \( E_{\text{tot}} \) < 3.3 eV), significant deviations between the classical and the quantum results were found. These could sometimes be as large as 100% and not necessarily near threshold (in fact, the threshold region is excluded in this study). As mentioned, the discrepancy between the quantum and the classical results tends to decrease when \( r_0 \) increases, except for \( v_i = 0 \) where hardly any change is noticed. The source for the deviations for \( v_i = 0 \) can be explained if we consider a diatomic molecule for which, according to classical mechanics, the turning points are of highest probability and the equilibrium distance of smallest probability. The opposite is true in quantum mechanics. Here, for \( v_i = 0 \), the turning points are of lowest probability and the equilibrium distance is of highest probability. Thus, statistically, the relative positions of the two atoms in the close interaction region are significantly different and this is probably the source of the quantum effects. Support for this interpretation is given in Fig. 6, where results are compared for two different \( r_0 \) values. The change of \( r_0 \) from 4.5 to 4.0 bohrs is enough to reduce the transition probability from ~0.5 to ~0.3 (the same trend was observed for the classical results).

(b) The dependence on the initial vibrational states. Part of our study was devoted to this problem. For \( r_0 = 4.5 \) bohrs we found that for the first three vibrational states the translational energy is much more efficient in promoting the reaction. Thus along the entire energy range studied we have \( P(v_i = 0|E_{\text{tot}}) > P(v_i = 1|E_{\text{tot}}) > P(v_i = 2|E_{\text{tot}}) \). The next two vibrational states behave in an entirely different way. In the lower energy range the reactive probabilities were found

In Fig. 10 the transition probabilities are presented as a function of initial vibrational states for two different energies and two different \( r_0 \) values. Although, in general, the classical and the quantum results exhibit a similar functional shape, again we find the fit for \( r_0 = 4.5 \) bohrs to be much better than that for \( r_0 = 4.0 \) bohrs.

V. DISCUSSION

Before starting the discussion it is important to reiterate that the potential energy surface is independent of horizontal coordinates (in other words the potential is flat) as long as the horizontal distance between the two atoms is smaller than \( r_0 \). The conclusions drawn from this work would therefore mainly apply for similar realistic systems.

In this study we concentrated on three main subjects:

(a) Quantum effects. The main purpose of this work was to study the importance of quantum effects taking place in the gas–solid reactions. Two identical models, one quantum and one classical, were constructed and the derived results were compared. The models are characterized by a parameter \( r_0 \) which is closely related to the horizontal dimension of the corrugation. The calculations were done for two values of \( r_0 \), i.e., \( r_0 = 4.0, 4.5 \) bohrs, and we found the quantum

FIG. 9. As in Fig. 8, but for \( r_0 = 4.0 \) bohrs.

FIG. 10. A comparison between quantal and classical initial vibrational distributions for different total energy and \( r_0 \) values: (a) \( E_{\text{tot}} = 2.473 \) eV; \( r_0 = 4.5 \) bohrs; (b) \( E_{\text{tot}} = 3.073 \) eV; \( r_0 = 4.5 \) bohrs; (c) \( E_{\text{tot}} = 2.473 \) eV; \( r_0 = 4.0 \) bohrs; (d) \( E_{\text{tot}} = 3.073 \) eV; \( r_0 = 4.0 \) bohrs; (—) quantum results; (—) classical results.
to be of the same size as those encountered in the lower vibrational states; however, around $E_{\text{rot}} = 2.5$ eV the probabilities increased abruptly, behaving as if a suppressed mechanism is suddenly triggered. This feature was found in both frameworks, i.e., the classical and the quantum. A different situation is encountered when $r_0 = 4.0$ bohrs. Here $P(v_i = 0|E_{\text{rot}}) \sim P(v_i = 1|E_{\text{rot}})$ and the "suppressed" mechanism is triggered when $v_i$ becomes 2 and 3, and to a lesser extent for $v_i = 4$. Again the sudden rise in the probability functions happens in the vicinity of $E_{\text{rot}} \sim 2.5$ eV. The reason for this behavior is not yet known.

(c) The dependence on the corrugation. We have explained how corrugation is introduced through a coordinate $r_0$ (or $\rho$) and how it is related to the horizontal dimension of the corrugation. We found that the smaller the value of $r_0$ the more sensitive the results are to modest changes in $r_0$. However, it seems that the results tend to converge as $r_0$ increases. This is most clearly presented in Fig. 7; large changes in the initial vibrational distribution are noticed in the transition from $r_0 = 4.0$ bohrs to $r_0 = 4.5$ bohrs. However, they become less pronounced in the transition from $r_0 = 4.5$ bohrs to $4.75$ bohrs.

To summarize this work, quantum effects in the reactive interactions between a diatomic molecule and a solid surface are expected to be significant. Consequently, studies, and in particular predictions, based on classical trajectories should be considered with care.

ACKNOWLEDGMENT

We are indebted to Professor D. J. Kouri for sending us his collinear computer code which was used (following the relevant modifications) to derive the quantal $S$ matrix elements.


The transformation from the mass scaled reagents coordinates $(Z_x, r)$ to the mass scaled products coordinates $(Z_x, \nu)$ is given in the form

$$Z_\nu = Z_x \cos \beta + r \cos \gamma \sin \beta,$$

$$Z_x = Z_x \sin \beta - r \cos \gamma \cos \beta.$$  \hspace{1cm} (A1)

In order to simplify the discussion, we start with the case where $\gamma = 0$, which is the ordinary collinear case as encountered in atom–molecule collisions (see Fig. 11).

The border line between the reagents and products arrangement channels is defined as

$$r = r_0.$$  \hspace{1cm} (A3)

The segment $PQ$ is part of this line, where $Q$ is a point located on the $Z_\nu$ axis. It is easily seen that

$$|QP| = Z_{\lambda 0} - r_0 \cot \beta,$$

or also [see Fig. 11],

$$|QP| = |MP|/\sin \beta = z_{\lambda 0}/\sin \beta.$$  \hspace{1cm} (A4)

The same relation can be obtained from Eq. (A2) by substituting $(Z_{\lambda 0}, r_0)$ for $(Z_x, r)$.

In the noncollinear case when $\gamma \neq 0$ the value of $z_{\lambda 0}$ as obtained from Eq. (A2) becomes larger [the point $M$ moves to $M(\gamma)$ in Fig. 12]. This implies that the whole $Z_\nu$ axis is shifted away from $P(Z_{\lambda 0}, r_0)$ by the same amount. Since in the noncollinear case Eq. (A5) is still valid, we find that in general

$$|Q'P| = |Q(\gamma)P| = Z_{\lambda 0} - r_0 \cos \gamma \cot \beta,$$

where the meaning of $Q'$ is $Q' = Q(\gamma)$. This distance becomes equal to $Z_{\lambda 0}$ when $\gamma = \pi/2$ which also implies that the angle $\beta(\gamma)$ between $|Q(\gamma)P|$ and the $Z_\lambda$ axis is $\pi/2$ (see Fig. 12).

Unless the collinear case is considered the two planes, namely the reagents and the products planes, are two different planes. However, rotating the products plane around the

FIG. 12. The noncollinear arrangement. It is seen how $\beta$ becomes $\beta(\gamma)$ and how the points $Q$ and $M$ become $Q(\gamma)$ and $M(\gamma)$, respectively. The point $P(Z_{\lambda 0}, r_0)$ does not change due to variations in $\gamma$.

FIG. 13. The $\lambda$ and the $\nu$ arrangement channels for a nonzero $\gamma$. Notice the existence of two different origins for each arrangement $O_x$ and $O_\nu$.
$Q(\gamma)P$ line by an appropriate angle will cause the two planes to coincide. In this new situation we distinguish between two different origins, namely the origin for $(Z_{\lambda}, r)$ and the origin for $(Z_{\nu}, z_{\nu})$. They will be designated as $0_{\lambda}$ and $0_{\nu}$ (see Fig. 13).

Next we calculate $|00_{\lambda}|$ and $|00_{\nu}|$. To calculate $|00_{\lambda}|$ the point $N$ is introduced so that

$$|00_{\lambda}| = |0N| - |0_{\lambda}N|,$$  

(A7)

where

$$|0N| = r_0 \cot \beta$$  

(A8)

and

$$|0_{\lambda}N| = Z_{\lambda 0} - |Q(\gamma)P|.$$  

(A9)

Recalling Eq. (A6), we get for $|00_{\lambda}|$,

$$|00_{\lambda}| = r_0 \cot \beta (1 - \cos \gamma).$$  

(A10)

To obtain $|00_{\nu}|$ the following relation is used:

$$|00_{\nu}| = |Q(\nu)Q(\nu)| - |0, Q(\nu)|.$$  

(A11)

From Fig. 13 it can be seen that

$$|Q(\nu)| = r_0 / \sin \beta.$$  

(A12)

Regarding $|0, Q(\nu)|$, we recall that $Q(\nu)$ is a point on the $Z_{\nu}$ axis. If $Z_{\nu}$ is the coordinates of $Q(\nu)$ in the $\lambda$ arrangement, then $Z_{\nu}$ is given, according to Eq. (A1), as

$$Z_{\nu} = Z_{\nu 0} \cos \theta + r_0 \cos \nu \sin \beta.$$  

(B3)

But from Eq. (A6) we have that

$$Z_{\nu 0} = Z_{\lambda 0} - |Q(\gamma)P| = r_0 \cos \gamma \cot \beta,$$  

(A14)

and also

$$r_0 = r_0,$$  

(A15)

so that substitution of Eqs. (A14) and (A15) in Eq. (A13) yields

$$Z_{\nu} = |0, Q(\nu)| = r_0 \cos \gamma / \sin \beta.$$  

(A16)

Combining Eqs. (A11), (A12), and (A16), we obtain

$$|00_{\nu}| = r_0 (1 - \cos \gamma) / \sin \beta.$$  

(A17)

From Eqs. (A10) and (A17) an interesting relation is obtained, namely

$$|00_{\nu}| = |00_{\lambda}| \cos \beta,$$  

(A18)

or in other words the origin of the $\lambda$ arrangement $0_{\lambda}$ is a point on the $Z_{\nu}$ axis (see Fig. 13).

Another important relation is the value of $\beta(\gamma)$:

$$\tan \beta(\gamma) = r_0 / |0, N|$$  

(A19)

or [see Eqs. (A9) and (A6)],

$$\tan \beta(\gamma) = \tan \beta / \cos \gamma.$$  

(A20)

**APPENDIX B: THE APPLICATION OF POLAR COORDINATES**

Recently a new method of solving a reactive quantum mechanical system was introduced. This method is based on two polar coordinates defined with respect to a common origin. A common origin is encountered in the collinear case but, as we have shown in Appendix A, two different origins are encountered for all other arrangements. To overcome this problem a common origin can be formed by continuing the two $Z$ axes, i.e., $Z_{\lambda}$ and $Z_{\nu}$, until their intersection at point 0 (see Fig. 13). Consequently it is suggested to define polar coordinates $(R, \theta)$ with respect to this newly formed origin. However, the connection between $(R, \theta)$ and the two arrangements systems of coordinates $(Z_{\lambda}, r)$ and $(Z_{\nu}, z_{\nu})$ is somewhat more complicated than in the ordinary case.

The aim is to express $Z_{\lambda}$ and $r$, once $R$ and $\theta$ are given. From Fig. 14(a) it can be seen that

$$r = R \sin \theta,$$  

(B1)

$$Z_{\lambda} = R \cos \theta - |00_{\lambda}|.$$  

(B2)

The value of $|00_{\lambda}|$ is given in Eq. (A10), i.e.,

$$|00_{\lambda}| = r_0 \cos \beta (1 - \cos \gamma).$$  

(B3)

so that $Z_{\lambda}$ becomes

$$Z_{\lambda} = R \cos \theta - r_0 \cos \beta (1 - \cos \gamma).$$  

(B4)

Equation (B4) has to be applied with some care. If the angle $\theta_{\lambda}$ is defined as [see Fig. 14(a)]

$$\tan \theta_{\lambda} = r / Z_{\lambda} = \frac{R \sin \theta}{R \cos \theta - r_0 \cos \beta (1 - \cos \gamma)},$$  

(B5)

then the whole procedure is valid as long as

$$\theta_{\lambda} \leq \beta(\gamma).$$  

(B6)

A similar situation is encountered in the $\nu$ arrangement channel [see Fig. 14(b)]:

$$z_{\nu} = R \sin (\nu - \theta),$$  

(B7)

$$Z_{\nu} = R \cos (\nu - \theta) - |00_{\nu}|.$$  

(B8)

From Eq. (A17) we have

$$|00_{\nu}| = r_0 (1 - \cos \gamma) / \sin \beta,$$  

(B9)
and consequently Eq. (B8) becomes

$$Z_v = R \cos(\beta - \theta) - r_0(1 - \cos \gamma)/\sin \beta.$$  \hspace{1cm} (B10)

As can be seen, Eqs. (B1) and (B2) look similar to Eqs. (B7) and (B10).