QUANTUM-MECHANICAL STUDY
OF THE PARALLEL MOLECULE-SURFACE REACTION HCl + S → HS + Cl

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Quantum-mechanical transition probabilities are presented for the molecule HCl($v_1$) reacting with a solid surface S, i.e. HCl($v_1$) + S → HS + Cl: $v_1 = 0,\ldots, 4$. The calculations were done for a fixed parallel approach ($\gamma = \pi/2$) of the molecule. Results are shown as a function of total energy $E_{\text{tot}}$ for the energy range $1.95 \leq E_{\text{tot}} \leq 3.3$ eV.

1. Introduction

Quantum effects occurring in a reactive exchange process between an atom and a diatomic molecule are known to be important in the vicinity of potential barriers and are responsible for resonance processes [1]. It is not known if these effects are equally important for the exchange process between a diatomic molecule AB and a surface S, i.e.

AB + S → AS + B,

→ BS + A ,

but it is expected that they are.

Recently a quantum-mechanical theory was presented for treating these processes [2]. This theory is based on the infinite order sudden approximations (IOSA). Within this approach only processes given in (I) can be treated whereas other “bond breaking” processes which may occur, namely adsorption and dissociation, have to be ignored. Consequently for the theory to be relevant it has to be applied only in those cases (or situations) where these two additional processes do not occur. In another study [3] employing classical trajectories, we have shown that this requirement is fulfilled when a diatomic molecule with one light and one heavy atom (LH) interacts with the surface while moving with an energy in a well defined region. Two typical cases were studied, HCl and HI. The proper energy region for HCl was $2.7-5.0$ eV and for HI, $1.5-4.0$ eV. (It is very likely that the upper value is much larger.) The IOSA calculation consists of solving fixed angle ($\gamma$) Schrödinger equations and calculating reactive $\gamma$-dependent probabilities. In this communication we present results of a calculation for one fixed angle, namely $\gamma = \pi/2$ (see fig. 1). This value of $\gamma$ was chosen for three reasons:

(a) In the proposed energy range there is almost no adsorption (or dissociation) [3].

(b) This angle is of highest probability because it is weighted by $\sin \gamma$ when a total probability is required.

![Fig. 1. The coordinates of the interacting particles: (a) reagents; (b) products.](image-url)
(c) It was shown that in the vicinity of this angle the reaction is not less probable than in other $\gamma$ regions [3].

The calculations here are done for a rigid and to a certain extent non-corrugated surface. This means that the potential was assumed to depend on the interatomic distance and the distances of the two atoms from the surface. This assumption significantly reduces the amount of computation. However within the IOSA, the horizontal distance between the two atoms is not allowed to be larger than a given value $\rho$, thus a kind of corrugation is built into the theory, not through the potential but through the model [4].

In this work the reaction studied is

$$\text{HCl}(v*) + S \rightarrow \text{HS} + \text{Cl, } v_i = 0, ..., 4.$$  \hspace{1cm} (11)

A short description of the theory is given in section 2 while the results are presented in section 3.

2. Theory

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

(a) The reagent's coordinate: here the translational coordinate $R$ is the distance from the center of mass of the diatomic molecule to the surface and the internal coordinate $t$ is the interatomic distance (see fig. 1a).

(b) The product's coordinates: here the translational coordinate $Z$ is the distance of the desorbed atom from the surface and the internal coordinate $z$ is the distance from the adsorbed atom to the surface (see fig. 1b).

The transformation from the reagent to product coordinates for mass-scaled magnitudes is given in the form

$$Z = R \cos \beta + r \cos \gamma \sin \beta,$$  \hspace{1cm} (1a)

$$z = R \sin \beta - r \cos \gamma \cos \beta,$$  \hspace{1cm} (1b)

where $\gamma$ is the IOSA angle (see fig. 1a) and $\beta$ is defined as

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

Here $m_A$ is the mass of the desorbed atom and $m_B$ the mass of the adsorbed atom. The scaling factors $a_\lambda$ and $a_\nu$ for the two channels are

$$a_\lambda = \left[ m_A m_B / (m_A + m_B) \right]^{1/4}, \quad a_\nu = (m_B/m_A)^{1/4}.$$  \hspace{1cm} (3)

The Schrödinger equation to be considered in the reagent channel is

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial t^2} \right) + V(r, R; \gamma) - E \right] \psi(r, R; \gamma) = 0,$$  \hspace{1cm} (4)

and in the product channel

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial t^2} \right) + V(z, Z; \rho) - E \right] \psi(z, Z; \rho) = 0.$$  \hspace{1cm} (5)

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

$$\mu = (m_A m_B)^{1/2}$$  \hspace{1cm} (6)

and $\rho$ is the horizontal distance (see fig. 1b) between the two interacting atoms. In ref. [2] we have shown that in the case of a non-corrugated surface the reagent channel is characterized by the angle $\gamma$ and the product channel by the distance $\rho$. In other words, in the entrance channel the interacting system is moving on a fixed $\gamma$ plane and in the exit channel on a fixed $\rho$ plane. (In the gas-phase case we had two fixed $\gamma$ angles, one, $\gamma_h$, for the entrance channel and one, $\gamma_v$, for the exit channel [5].) In order for a reaction to take place the system has to move from the fixed $\gamma$ plane to the fixed $\rho$ plane by crossing the intersection line of the two planes (see fig. 2). This line

$$\rho = \left[ m_A m_B / (m_A + m_B) \right]^{1/2}.$$  \hspace{1cm} (7)

The available configuration space is marked by the full heavy lines. The point O is the origin for the reagents system of coordinates and O' for the products system of coordinates. The line OQ defined by the angle $\beta_\gamma$ for $\gamma = 0$, is a section along the Z axis. Thus, for $\gamma = 0$, $\beta_\gamma$ equals $\beta$. Also shown is the line $\Gamma$ defined by $r = r_0$. 

Fig. 2. The two arrangement channels of the system. The available configuration space is marked by the full heavy lines. The point O is the origin for the reagents system of coordinates and O' for the products system of coordinates. The line OQ defined by the angle $\beta_\gamma$ is for $\gamma = 0$, a section along the Z axis. Thus, for $\gamma = 0$, $\beta_\gamma$ equals $\beta$. Also shown is the line $\Gamma$ defined by $r = r_0$. 

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was shown [2] to be \( r = r_0 \). For a given value of \( \gamma \) and a fixed value of \( r_0 \), the system of coordinates is entirely determined. Among other magnitudes \( \rho \) is also obtained from the relation

\[
\rho = r_0 \sin \gamma.
\]

(7)

It is noticed that \( \rho \) is equal to zero for \( \gamma = 0 \) which is the collinear case.

To derive the \( S \) matrix elements and the transition probabilities, eqs. (4) and (5) have to be solved. A description of the numerical procedure will be given elsewhere [4]. Here we point out the fact that a solution was obtained by employing an efficient available collinear program [6] which was especially devised for treating a heavy–light–heavy mass combination (the HCl + S is such a system) but was modified for our particular purpose.

3. Results

To perform the calculation a modified LEPS surface [7] is employed,

\[
V = U_1 + U_2 + U_3 - \left[ Q_1^2 + (Q_2 + Q_3)^2 \right] - Q_1 (Q_2 + Q_3)]^{1/2},
\]

(8)

where

\[
U_i = [D_i/4(1 + \Delta_i)] \left\{ (3 + \Delta_i) \exp \left[ -2\alpha_i (r_i - r_{i0}) \right] - (2 + 6\Delta_i) \exp \left[ -\alpha_i (r_i - r_{i0}) \right] \right\}
\]

(9)

and

\[
Q_i = [D_i/4(1 + \Delta_i)] \left\{ (1 + 3\Delta_i) \exp \left[ -2\alpha_i (r_i - r_{i0}) \right] - (6 + 2\Delta_i) \exp \left[ -\alpha_i (r_i - r_{i0}) \right] \right\},
\]

(10)

where \( D_i, r_{i0} \) and \( \alpha_i \) are the dissociation energy, the internuclear equilibrium distance and the characteristic Morse parameters, respectively. The coefficients \( \Delta_i, i = 1, 2, 3 \), are the usual Sato parameters used to adjust the overall potential so that it has certain features. The numerical values for the various parameters are listed in ref. [3].

As was mentioned in section 1 the calculations were carried out for \( \gamma = \pi/2 \). We originally intended to show results for \( \gamma = 0 \) also (the usual collinear case) but it was soon realized, as in fact expected, that the transition probabilities are negligibly small unless the initial vibrational state of HCl is high enough to match the endothermicity, i.e. \( v_i \gg 5 \). The second parameter of the calculation is \( r_0 \) which was assumed to be 4.5 bohr.

To check convergence the calculations were repeated three times (except for other minor tests) for a different number of vibrational states, i.e. \( n = 25, 28, 30 \). In general, only minor changes were encountered except for \( v_i = 0 \), where deviations as large as 30% were found for certain energies when \( n \) was varied from 25 to 28.

In fig. 3 are given the reactive transition probabilities as a function of the total energy for five initial vibrational states of HCl. The following are the main findings of this preliminary work:

1. Hardly any threshold is obtained. The reaction probability does not gradually decrease to zero as in ordinary cases but become zero at the moment the total energy is below the products vibrational ground state.

2. The translational energy is found to be, in general, more efficient in promoting the reaction than the vibrational energy. For example, it is noticed that reactive probabilities from \( v_i = 0 \) are usually much

\[ \text{Fig. 3. Reactive transition probabilities for the processes HCl}(v_i) + S \rightarrow HS + Cl, \ v_i = 0, \ldots, 4, \text{as a function of total energy.} \]
larger than those from excited states (except for \( v_1 = 4 \)).

(3) While studying the heavy—light—heavy (HLH) systems in the gas phase it was established that the dynamics of these systems are governed by the conservation of translational energy [8]. This rule was also found to be valid for the collinear case, i.e. \( \gamma = 0 \), but seems to break down entirely when other configurations are considered. The implication of this rule in our case is that no exchange would take place unless \( v_1 \geq 5 \). As is noticed, large transition probabilities are encountered for any initial vibrational state.

A more extensive study, which will include a comparison with classical trajectory results, will be published at a later date [4].

References