A THEORETICAL STUDY OF EXOTHERMIC REACTIONS

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The Born approximation is applied to the Marcus equation in order to reveal the main factors that lead to strong vibrational nonadiabatic transitions. It is found that the necessary conditions for a reaction process to be accompanied by vibrational transitions are: (a) \( \alpha = K_0 \bar{\rho} > 0.5 \) (\( K_0 \) is the curvature and \( \bar{\rho} \) is half the width of the oscillator, both calculated in the interaction region); (b) \( K_2 = (1/K_0) \left( \frac{d^2k(s)}{ds^2} \right) \) is at least of the order of the exothermicity. \( (d^2k(s)/ds^2) \) is calculated in the interaction region; \( s \) is the reaction coordinate.) A simple model for calculating the curvature in the interaction region is presented as well. Several systems for which exact quantum mechanical and classical transition probabilities exist are analyzed according to this model.

1. Introduction

Although much numerical work has been devoted to the study of collinear reactive exothermic systems [1] only a limited number of theoretical studies has been performed to reveal the main factors which lead to highly vibrational excited products. Two studies directed towards this goal were based on the concept of the reaction coordinate as introduced by Hofacker [2] and both attributed the vibrational transitions to the centrifugal term which is obtained while treating the kinetic part of the hamiltonian. Hofacker and Levine [3] suggested that nonadiabatic transitions occur mainly due to a dynamic (energy dependent) displacement of the equilibrium position in the interaction region. Their main requirement for a strong vibrational coupling between the \( i \)th and the \( j \)th state is

\[
g_{ij} = \left( \frac{E_{K_i} - E_{K_j}}{\Delta E_{ij}} \right) k(s) \bar{\rho} > 1, \tag{1.1}
\]

where \( E_{K_i} \) is the kinetic translational energy, \( \Delta E_{ij} \) is the vibrational spacing in the interaction region, \( k(s) \) is the curvature and \( \bar{\rho} \) is half the width of the harmonic oscillator. Basilevsky [4] followed a different approach. By examining the Marcus equation [5] which uses curvilinear coordinates as well, he reached the conclusion that vibrational transitions are due to a centrifugal term which is obtained when expanding the kinetic term in the Marcus equation. Applying the Born approximation he was able to furnish a condition for a strong vibrational transition from an initial state \( i \) to a final state \( j \)

\[
g_{ij} = \left( \frac{E_{K_i}}{\Delta E_{ij}} \right) k(s) \bar{\rho} > 1, \tag{1.2}
\]

where \( \Delta E_{ij} \) is the energy spacing between the two states. The disadvantage of Basilevsky's treatment is that the centrifugal term, to which he attributed the strong vibrational coupling, cannot be evaluated for systems with large curvatures due to the strong singularity in it. Since these are the only systems which undergo strong vibrational transitions, his treatment is incomplete.

A different point of view was taken by Baer [6] who, while analyzing his exact quantum mechanical
results related to the H(D) + Cl₂ system, assumed a Franck–Condon type model which relates the initial vibrational state of the reagents to the final vibrational state of the products. With this simple model most of the features found in the calculations could be explained. Berry [7] and later Halavee and Shapiro [8] formulated their models along the same lines. In Berry’s model the Franck–Condon factor was calculated for the final product state and a intermediate state in the interaction region, whereas Halavee and Shapiro coupled together the initial reagent state with a final intermediate state. In all three cases the overlap was calculated between two shifted harmonic oscillator wavefunctions. In the first two the shift was assumed to be a parameter and in the third it was correlated with the classical turning point in the entrance channel.

In the present work the Marcus equation is again considered, but the treatment of the kinetic term is different. The strong vibrational coupling is not attributed to the centrifugal term, but rather to another term which arises due to sharp variations in the curvature with respect to the translational coordinate s.

2. The Schrödinger equation

The collinear reactive collision of atom A with molecule BC will be described in terms of the curvilinear coordinates ρ and s. Here s is the reaction coordinate leading smoothly from the translational reagents coordinate to the translational products coordinate defined along the minimum energy path. ρ, the vibrational coordinate, is assumed to be perpendicular to s.

According to Marcus [5] the Schrödinger equation takes the form:

\[
\begin{align*}
[H(n) - E] \psi(s, \rho) &= \left\{ -\frac{\hbar^2}{2\mu} \left[ \frac{1}{\eta} \frac{\partial}{\partial s} \frac{1}{\eta} \frac{\partial}{\partial s} + \frac{1}{\eta} \frac{\partial}{\partial \rho} \frac{1}{\eta} \frac{\partial}{\partial \rho} \right] + V(s, \rho) - E \right\} \psi(s, \rho) = 0,
\end{align*}
\]

where \( E \) is the energy, \( \mu \) is the reduced symmetric mass
\[
\mu = \frac{m_A m_B m_C}{(m_A + m_B + m_C)^{1/2}}.
\]
\( \eta \) is a function of s and ρ of the form:
\[
\eta = 1 + k(s) \rho,
\]
k(s) is the curvature of the reaction path and \( V(s, \rho) \) is the potential that governs the collision process. \( V(s, \rho) \) is written as
\[
V(s, \rho) = V_1(s) + V_2(\rho, s),
\]
where \( V_2(\rho, s) \) is a “Morse like” potential which coincides with the diatomic potentials of the reagents and the products for \( s = \pm \infty \), respectively, and fulfills the condition:
\[
V_2(0, s) = 0.
\]

Let us make the substitution
\[
\psi(s, \rho) = \eta^p \chi(s, \rho),
\]
where \( p \) is a given number. Then it can be shown that:
\[
T_\rho(s) = \frac{1}{\eta} \frac{\partial}{\partial \rho} \eta \frac{\partial}{\partial \rho} \psi(s, \rho)
\]
\[
= \eta^p \left\{ \frac{\partial^2 \chi}{\partial \rho^2} + \frac{2p-1}{\eta} \frac{\partial \eta}{\partial \rho} \frac{\partial \chi}{\partial \rho} + \frac{p^2}{\eta^2} \left( \frac{\partial \eta}{\partial \rho} \right)^2 \right\},
\]
and
\[
T_\rho(s) = \frac{1}{\eta} \frac{\partial}{\partial \rho} \eta \frac{\partial}{\partial \rho} \psi(s, \rho)
\]
\[
= \eta^p \left( \frac{\partial^2 \chi}{\partial \rho^2} + \frac{2p+1}{\eta} \frac{\partial \eta}{\partial \rho} \frac{\partial \chi}{\partial \rho} + \frac{p^2}{\eta^2} \left( \frac{\partial \eta}{\partial \rho} \right)^2 \right).
\]

Defining \( T(s, \rho) \) as:
\[
T(s, \rho) = -\left( \frac{\hbar^2}{2\mu} \right) [T_\rho(s) + T_\rho(s)],
\]
we obtain
\[
T(s, \rho) = -\frac{\hbar^2}{2\mu} \eta^p \left[ \frac{1}{\eta^2} \frac{\partial^2 \chi}{\partial s^2} + \frac{\partial^2 \chi}{\partial \rho^2} + \frac{1}{\eta^2} \tilde{W}_\chi \right],
\]
where
\[
\tilde{W} = (2p+1) \frac{\rho \frac{dk}{ds} \frac{\partial}{\partial s}}{\eta} + p(2p-2) \frac{\rho \frac{\partial k}{\partial s} \frac{\partial^2 k}{\partial s^2}}{\eta^2} + \frac{1}{\eta^2} \tilde{W}_\chi.
\]

Since \( k(s) \) becomes zero as \( s \rightarrow \pm \infty \), we see that \[
\lim_{s \rightarrow \pm \infty} \tilde{W}(s, \rho) = 0.
\]

The equation to be solved is:
\[
\eta^p \left\{ \frac{\hbar^2}{2\mu} \left[ \frac{1}{\eta^2} \frac{\partial^2 \chi}{\partial s^2} + \frac{\partial^2 \chi}{\partial \rho^2} + \frac{1}{\eta^2} \tilde{W}_\chi \right] + [V(s, \rho) - E] \right\} \chi = 0.
\]
Expanding $\chi(s, \rho)$ in the usual way

$$\chi(s, \rho) = \sum_n \xi_n(s) \phi_n(\rho; s), \quad (2.14)$$

where $\{\phi_n(\rho; s)\}$ is a local basis set that follows from the equation

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{ds^2} + V_2(\rho, s) - e_n(s) \right] \phi_n(\rho; s) = 0, \quad (2.15)$$

and substituting eq. (2.14) in eq. (2.13) leads to

$$\eta^{p-2} \left\{ \sum_n \left[ -\frac{\hbar^2}{2\mu} I_n \frac{d^2}{ds^2} \xi_n + U_n \xi_n \right] + \sum_n \left[ -\frac{\hbar^2}{2\mu} W_n \right]ight\} = 0, \quad (2.16)$$

where

$$I_n = |\phi_n|,$$

$$U_n = U|\phi_n| = [V_1(s) + e_n(s) - E]|\phi_n|,$$

$$G_n = (1-\eta^2)|\phi_n|,$$

$$W_n = W|\phi_n| = \left[ p(p-2) \left( \frac{p}{\eta} \right)^2 \frac{d^2k}{ds^2} \right] + p \frac{\rho \frac{d^2k}{ds^2}}{\eta} + (2p+1) \eta k \frac{\partial}{\partial \rho} + p^2 k^2 \right] |\phi_n|,$$

$$f_n^{(2)} = f^{(2)}|\phi_n| = \left[ \frac{d^2}{ds^2} + (2p-1) \frac{p \frac{d^2k}{ds^2}}{\eta} \right] |\phi_n|,$$

$$f_n^{(1)} = f^{(1)}|\phi_n| = \left[ \frac{d}{ds} + (2p-1) \frac{p \frac{dk}{ds}}{\eta} \right] |\phi_n|.$$  

Eq. (2.16) is valid for every value of $p$ as long as $\eta$ is different from zero in the region of interest. The final results of exact treatments are then expected to be independent of $p$. In most treatments $p$ was taken to be either $-1/2$ [4,5] or $4$ [9-11] and recently it was also suggested to be $1/2$ [12]. If however, $\eta$ becomes zero (when $k(s)$ is large enough), then the choice of $p$ is limited. In the appendix it is shown that $p$ can be taken in the range $1 \leq p \leq 3$, with a preferential choice of $p=2$. If $p$ is chosen in this way then $\eta^{p-2}$ in eq. (2.16) is well defined and has an inverse.

Multiplying eq. (2.16) from the left by $\langle \phi_m | \eta^{-(p-2)}$ and integrating over $\rho$ one obtains a system of coupled differential equations of second order:

$$-\frac{\hbar^2}{2\mu} \frac{d^2\xi_n}{ds^2} + U\xi_n = \left[ \frac{\hbar^2}{2\mu} W + Z \right] \xi_n, \quad (2.18)$$

where $U$ is a diagonal matrix:

$$U_{nm} = [V_1(s) + e_n(s) - E] \delta_{nm}. \quad (2.19)$$

The elements of $W$ are defined as:

$$W_{nm} = \langle \phi_n | W | \phi_m \rangle, \quad (2.20)$$

and $Z$ is a matrix of the form:

$$Z = U G - \left( \frac{\hbar^2}{2\mu} \right) \left( f^{(2)} + f^{(1)} \right) \frac{d}{ds}. \quad (2.21)$$

Here:

$$G_{nm} = \langle \phi_n | G_m \rangle,$$

$$f_{nm}^{(2)} = \langle \phi_n | f_m^{(2)} \rangle, \quad f_{nm}^{(1)} = \langle \phi_n | f_m^{(1)} \rangle.$$  

In general there are no difficulties in evaluating the elements of any of the matrices except the one which contain $\eta^{-1}$ and $\eta^{-2}$. As can be seen from eq. (2.17) the first two terms of $W$ and the last terms of $f^{(1)}$ and $f^{(2)}$ become singular when $\eta$ become zero. This usually happens on the concave side of the reaction coordinate because $k(s)$ is always positive and $p$ on this side is negative. Therefore, in order to avoid this singularity the coordinate $s$ has to be chosen in such a way that the $|\phi_n(\rho; s)\rangle = n=1,\ldots$, are small enough in this region to permit the evaluation of the integrals. Practically, this amounts to choosing the curve $s$ with a smaller curvature so that it will not follow the minimum energy path. However, we will still assume the coordinate $s$ to be defined along the minimum energy path and in this way maintain the physical picture of the reaction process.

3. The Born approximation

In order the study the way vibrational transitions occur during a rearrangement process, we consider the Born approximation [10,13]. The Born approximation is not intended to give quantitative results, but rather to determine qualitatively which are the dominant transitions. Therefore we prefer to relate the following discussion to the potential matrix elements $V_{nm}$ (rather than to the transition amplitude matrix elements):
\[ V_{nm} = \int_{-s_1}^{s_2} \xi_n^*(s) \tau_{nm}(s) \xi_m(s), \quad (3.1) \]

where \( \xi_n(s) \) is the solution of the adiabatic equation [cf. eq. (2.18)]:
\[ -\left( \frac{\hbar^2}{2\mu} \right) \frac{d^2 \xi}{ds^2} + U_0 - 0, \quad (2.18') \]
and \( \tau_{nm} \) are the matrix elements of \( \tau \) defined as
\[ \tau = \left( \frac{\hbar^2}{2\mu} \right) \imath + \mathcal{Z}. \quad (3.2) \]

In order to estimate the \( V \) matrix elements [using eq. (3.1)] the \( \tau \) matrix elements will be considered, employing the following two assumptions:
(a) The vibrational eigenfunctions \( \{ \phi_n(\rho; s) \} \) are assumed to vary slowly enough as a function of \( s \) to ignore any contributions due to the derivatives of \( |\phi_n| \) with respect to \( s \).
(b) The interaction that leads to vibrational transitions is localized in a narrow interval of \( s \) where \( k(s) \) reaches its maximum value.

If \( s=0 \) is chosen as the coordinate for which this happens, then \( k(s) \) can be written
\[ k(s) = K_0(1 - \frac{1}{2} K_2 s^2), \quad (3.3) \]
so that
\[ \frac{dk}{ds}|_{s=0} = 0. \quad (3.4) \]

Deleting the terms in \( \tau \) that either contain derivatives of \( |\phi_n| \) with respect to \( s \) or the term \( dk/ds \) and substituting eq. (3.3) in \( \tau \) we finally obtain
\[ \tau(s \approx 0) = U(1 - \eta_0^2) + \frac{\hbar^2}{2\mu} \left[ (2p+1) K_0 \frac{\partial}{\partial \rho} + p^2 K_0^2 - p \frac{\eta_0 - 1}{\eta_0} K_2 \right], \quad (3.5) \]
where
\[ \eta_0 = 1 + K_0 \rho. \quad (3.6) \]

In forming the \( \tau_{nm} \) elements and inserting them in eq. (3.1), it can be seen that the only term which may yield vibrational transitions with \( |\Delta n| > 2 \) is the last term (the third term in the brackets).

If \( q_{nm} \) is defined as the matrix element
\[ q_{nm} = \langle \phi_n | 1/\eta_0 | \phi_m \rangle - \delta_{nm}, \quad (3.7) \]
then the \( V_{nm} \) matrix elements with \( |n-m| > 2 \) are estimated to be
\[ V_{nm} \approx p\lambda q_{nm} \int_{-s_1}^{s_2} \xi_n^*(s) \xi_m(s) ds, \quad (3.8) \]
where
\[ \lambda = \left( \frac{\hbar^2}{2\mu} \right) K_2, \quad (3.9) \]
and \( s_1 \) and \( s_2 \) are small and restricted by the condition [see eq. (3.3)]:
\[ s_i < \left( \frac{2}{K_2} \right)^{1/2}. \quad (3.10) \]

To complete the derivation, the integral in eq. (3.8) has to be solved. Assuming that the surface is an early barrier type surface such that \( \xi_i(s) \) behaves like a product (free) wavefunction in the interaction region, \( \xi_i(s) \) can be approximated by
\[ \xi_i(s) = (\mu/k_i \hbar^2)^{1/2} \exp \left[ i (k_i s + \phi_i) \right], \quad (3.11) \]
where \( \phi_i \) is the phase shift and \( k_i \) is the wave number. The phase shift \( \phi_i \) can be written
\[ \phi_i = x_i + iy_i \quad (y_i > 0), \quad (3.12) \]
where \( y_i \) is related to the transmissivity of \( V_1(s) \) [see eq. (2.4)], namely through the definition of the transmission coefficient \( T_i \):
\[ T_i = \exp (-y_i). \quad (3.13) \]

The wave number \( k_i \) is in general written
\[ k_i = \left( \frac{2\mu}{\hbar^2} \right) \left[ E - V_1(s) - \epsilon_i(s) \right]^{1/2}. \quad (3.14) \]
However, assuming the barrier to be far enough from the interaction region in the reagent channel, both \( V_1(s) \) and \( \epsilon_i(s) \) can be approximated by:
\[ V_1(s) \approx V_1 \quad (s = \infty), \quad (3.15) \]
\[ \epsilon_i(s) \approx \epsilon_i \quad (s = \infty), \quad (3.15) \]
so that \( V_1 \) is a negative constant (equal to the exothermicity) and \( \epsilon_i \) are the products vibrational eigenstates measured with respect to \( V_1 \) \( (s = \infty) \). Substituting eq. (3.11) in eq. (3.8) leads, for \( n = 0 \), to
\[ V_{0m} = A_{0m} \exp \left[ - (y_0 + y_m) \right] \left[ (k_m + k_0)/2(k_m k_0)^{1/2} \right] \]
\[ \times [\alpha_{0m} (\epsilon_m - \epsilon_0)] \left[ 1 - \exp \left[ -i \Delta k_{0m}(s_1 + s_2) \right] \right], \quad (3.16) \]
where \( \Delta k_{0m} = k_0 - k_m \) and
\[ A_{0m} = \exp \left[ i (\Delta k_{0m} s_2 + \frac{1}{2} \pi - \phi_0 + \phi_m) \right]. \quad (3.17) \]
From eq. (3.16), it is seen that the coupling term $V_{0m}$, which is a measure of the intensity of the vibrational transition $0 \to m$ $(m > 2)$, is proportional to $\lambda q_{0m}$. Large values of $\lambda$ make the fourth term in eq. (3.5) the main term that is responsible for vibrational transitions. If $\lambda$ is large enough then the final vibrational distribution is determined by $q_{0m}$. In many exothermic reactions the major transitions from reagent ground state to the $m$th state of the products are for $m > 2$. Therefore the two necessary conditions for $m > 2$ are:

(i) The value of $\lambda$ has to be the same or larger than the $U$ matrix elements $^*$. Since the largest term in $U$ for small initial translational energies is equal to the exothermicity $D$ of the reaction, we find that

$$\lambda \geq D.$$  

(3.18)

(ii) $q_{0m}$ for $m > 2$ has to be larger than $q_{0m}$ for $m \leq 2$. Both $\lambda$ and $q_{0m}$ are estimated in the following sections.

4. The $q_{nm}$ term

From the definition of $q_{nm}$ it can be seen that the integrand has a pole at $\eta_0 = 0$. This difficulty was previously encountered and discussed to a certain extent by Rankin and Light [15]. The appearance of the pole is related to the definitions of the coordinates $s$ and $p$. Already in the classical treatment, where these coordinates were first proposed, it was suggested that they not be used unless the points are not "too far" from $s$ (on the concave side) $^*$.

In all exact treatments in the past this difficulty was avoided either by assuming that the curvature is not large [15] or by choosing a curve $s$ which does not follow the minimum energy path. In one of the more efficient methods $^*$ the minimum energy path is approximated by circular arcs with varying radii, all defined with respect to the same center which is located in the plateau region. In these cases the singularity usually appears in the nonphysical region (where $\phi_n(\rho)$; $n = 0, 1, \ldots$ are negligibly small) and therefore can be ignored. Here we are interested in systems with large curvatures and since it is important for the present study to follow the route of the wavepacket (at least in the low energy region) we are forced to choose the coordinate $s$ as the minimum energy path.

The equation $\eta = 0$ defines a line (as a function of $s$) which is a branch cut such that for values of $\rho$ which are smaller than $-k^{-1}(s)$ the wavefunction is no longer uniquely defined. One way to overcome this difficulty is to replace $H(\eta)$ [cf. eq. (2.1)] by $H(\eta + i\epsilon)$ and let $\epsilon$ approach zero after completing the algebra. In this way the singularity is removed and the close coupling expansion is justified because the Riemann sheet on which the wavefunction is calculated is uniquely defined. This procedure yields

$$q_{nm}(\epsilon) = \langle \phi_n | \eta_0 + i\epsilon \rangle^{-1} \langle \phi_m \rangle,$$  

(4.1)

where for simplicity $\delta_{nm}$ is deleted and will be added at the end of this treatment. Since $q_{nm}(\epsilon)$ exists, $q_{nm}$ is defined as:

$$q_{nm} = \lim_{\epsilon \to 0} q_{nm}(\epsilon).$$  

(4.2)

Evaluating eq. (4.1) we obtain for $q_{nm}$:

$$q_{nm} = \mathcal{P} \langle \phi_n | \eta_0 | \phi_m \rangle + (\epsilon/k_0)^{n+1} \phi_n(k_0^{-1}) \phi_m(k_0^{-1}),$$  

(4.3)

where the first term is the principal value of $q_{nm}$.

From eq. (4.3) it also becomes clear under what conditions this singularity can be ignored.

In order to calculate the principal value of $q_{nm}$ we introduce the matrix

$$P_{nm} = \langle \phi_n | \eta_0 | \phi_m \rangle.$$  

(4.4)

It can be shown that the principal value of $q$ namely $q_p$ is:

$$q_p = P^{-1},$$  

(4.5)

where the order of $P$ has to be large enough to obtain converged results for the $q_p$ matrix elements of interest. Assuming harmonic oscillator wavefunctions the $P$ matrix elements are equal to

$$P_{nm} = \delta_{nm} + K_0 \bar{\rho} d_{nm},$$  

(4.6)

where $d_{nm}$ is given by:

$$d_{nm} = 2^{-1/2} [m+1]^{1/2} \delta_{nm+1} + (n+1)^{1/2} \delta_{nm-1},$$  

(4.7)

and $\bar{\rho}$ is equal to

$$\bar{\rho} = (\hbar/\mu \omega)^{1/2}.$$  

(4.8)

* The second term in eq. (3.5) which may cause vibrational transition with $|\Delta n| \leq 1$ is usually much smaller than the fourth term.
In a recent publication Atabek et al. [18] analytically derived the matrix elements of $q_p$ for a similar case:

$$q_{nn} = \frac{Q_{n}Q_{n}}{Q_{N}^{2}} \prod_{i=s}^{t-1} \{-\alpha[(j+1)/2]^{1/2}\}, \quad m \neq n;$$

$$= Q_{m}Q_{n}/Q_{N}, \quad m = n. \tag{4.9}$$

where $s = \min (m, n), t = \max (m, n); N$ is the order of the matrix. $Q_{s}$ and $Q_{t}$ are polynomials defined by the recurrence relations:

$$Q_{0} = Q_{1} = 1, \quad Q_{j+1} = Q_{j} - \frac{1}{2} \alpha^{2} j Q_{j-1}. \tag{4.10}$$

$$\tilde{Q}_{N-1} =\tilde{Q}_{N-2} = 1, \quad \tilde{Q}_{j-1} =\tilde{Q}_{j} - \frac{1}{2} \alpha^{2} (j+1) \tilde{Q}_{j+1}, \tag{4.11}$$

and

$$\alpha = K_{0} \beta. \tag{4.12}$$

It has been shown [18] that

$$Q_{N} = \tilde{Q}_{-1}. \tag{4.13}$$

5. The curvature

In order to calculate the curvature of the minimum energy path we approximate it by a hyperbola of the form:

$$1/r = u = -K(1 + e \cos \theta), \tag{5.1}$$

where

$$K = a/b^{2}. \tag{5.2}$$

$a$ is the semitransverse axis, $b$ is the semiconjugate axis and $e$ is the eccentricity. The curvature is defined as [19]:

$$k = \frac{u + d^{2}u/d\theta^{2}}{[1 + [1/u] (d^{2}u/d\theta^{2})^{2}]^{3/2}}. \tag{5.3}$$

Substituting eq. (5.1) for $u$ leads to:

$$k = K \left(\frac{1 - e \cos \phi}{(1 - 2 e \cos \phi + e^{2})^{3/2}}\right)^{3/2}, \tag{5.4}$$

where

$$\phi = \pi - \beta. \tag{5.5}$$

It can be shown that for small values of $\phi$, $k(s)$ becomes

$$k = K(1 - \frac{3}{2} e^{2}K^{2} s^{2}), \tag{5.6}$$

where

$$s = r(\phi)\phi. \tag{5.7}$$

The eccentricity $e$ is related to the angle between the two asymptotes [20]:

$$e^{2} = \cos(\beta/2), \tag{5.8}$$

where $\beta$ is related to the masses of the three-atom system:

$$\beta = \arctan \left(\frac{m_{B} M/m_{A} m_{C}}{1/2}\right); \tag{5.9}$$

$m_{B}$ is the mass of the central atom and $M$ is the sum of the three masses. Also since

$$e = (a^{2} + b^{2})^{1/2}/a, \tag{5.10}$$

by combining eqs. (5.2), (5.8) and (5.9) we obtain

$$K = a^{-1} \cotan^{2}(\beta/2). \tag{5.11}$$

Substituting $s = 0$ in eq. (5.6) yields

$$k(s=0) = K_{0} = a^{-1} \cotan(\beta/2), \tag{5.12}$$

which is the maximal value of the curvature, i.e.

$$K_{0} = K. \tag{5.7}$$

The second derivative $d^{2}k/ds^{2}$ at $s=0$ can be obtained at once by using eq. (5.6):

$$d^{2}k/ds^{2} = -3 e^{2} K^{2}. \tag{5.13}$$

Therefore using eqs. (3.3), (5.8) and (5.11) we obtain for $K_{2}$

$$K_{2} = (3/a^{2}) \sin^{-4}(\beta/2). \tag{5.14}$$

From eqs. (5.12) and (5.14) it is seen that for $a$ smaller than 1 au, $K_{2} \gg K_{0} > K$. In fig. 1 $a$ and $\beta$ are shown for a system which is close to the F + H$_{2}$ system [25].

6. Results and discussion

The transition probabilities of four exothermic reactions:

$$\text{HeH}^{+} + \text{H} \rightarrow \text{H}_{2}^{+} + \text{He}, \tag{1}$$

$$\text{Cl}_{2} + \text{H} \rightarrow \text{HCl} + \text{Cl}, \tag{2}$$

$$\text{H}_{2} + \text{F} \rightarrow \text{HF} + \text{H}, \tag{3}$$

$$\text{HI} + \text{Cl} \rightarrow \text{HCl} + \text{I}, \tag{4}$$

determined by exact quantum and classical calcula-
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Fig. 1. Potential energy surface in skewed mass scaled coordinates. The minimum energy path (along which the coordinate s is defined) is drawn by a heavy line. Q is the intersection point of the two asymptotes that go through the equilibrium distances of the reagent and the product molecules. β is the angle between the two asymptotes and a is the closest distance between Q and the minimum energy path.

Several converged results of $q_{nm}$ (the subscript p is dropped) as a function of m for different values of α (α is dimensionless):

$$\alpha = K_0 \beta,$$

are presented in fig. 2. Preferential population of low vibrational states for small values of α (< 0.5) is seen, but as α increases the distribution becomes more even, so that high vibrational states (m ≥ 2) can also become populated. Thus an essential requirement for having highly excited vibrational states is that

$$\alpha \geq 0.5.$$  

If α is smaller, the possibility of obtaining highly excited vibrational states is completely ruled out regardless of whether or not additional requirements are fulfilled.

Calculated values of $K_0$ and $K_2$ obtained using eqs. (5.12) and (5.14) are presented in table 1 for reactions (1) – (4). In order to calculate α, the value of $q_{nm}$ can be determined from

$$\alpha = \frac{q_{nm}}{q_{nm,0}}.$$  

Table 1

<table>
<thead>
<tr>
<th>System</th>
<th>α (au)</th>
<th>β (deg)</th>
<th>$K_0$ (au)</th>
<th>α</th>
<th>$K_2$ (au$^{-2}$)</th>
<th>$\mu$ a)</th>
<th>$\lambda$ (eV) b)</th>
<th>D (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HeH$^+$ + H</td>
<td>1.47</td>
<td>50.76</td>
<td>2.62</td>
<td>0.79</td>
<td>32.6</td>
<td>0.82</td>
<td>0.28</td>
<td>0.8</td>
</tr>
<tr>
<td>Cl$_2$ + H</td>
<td>1.00</td>
<td>83.23</td>
<td>1.27</td>
<td>0.38</td>
<td>15.4</td>
<td>4.13</td>
<td>0.03</td>
<td>1.55</td>
</tr>
<tr>
<td>H$_2$ + F</td>
<td>0.80</td>
<td>46.43</td>
<td>6.79</td>
<td>2.04</td>
<td>194.0</td>
<td>0.95</td>
<td>1.46</td>
<td>1.4</td>
</tr>
<tr>
<td>HI + Cl</td>
<td>1.29</td>
<td>11.50</td>
<td>76.81</td>
<td>23.04</td>
<td>17,900</td>
<td>4.91</td>
<td>26.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>

a) Calculated from eq. (2.2). b) Calculated assuming $p = 1$. 

Fig. 2. The principal value of $q_{nm}$ as a function of n for different values of α as defined in eq. (6.1). ∙ α = 0.14, α = 0.28, α = 0.35, α = 0.42, α = 0.56.
\( \tilde{\rho} \) is also needed. Although in principle \( \tilde{\rho} \) can be calculated for any system once the masses and the potential are known, in practice only an estimate can be given. It is found that the value of \( \tilde{\rho} \) is approximately independent of the system and equals \( \approx 0.3 \) au. The value of \( \lambda \) given in table 1 is based on this value of \( \tilde{\rho} \).

6.1. The \( \text{HeH}^+ + \text{H} \) system

The \( \text{HeH}^+ + \text{H} \) system was exposed to both quantum mechanical and classical treatments. Kouri and Baer [21] found that in the low energy range almost no high vibrational states are formed. This somewhat unexpected result was later confirmed by Adams [22] and by classical trajectory calculations performed by Santhyamurthy et al. [23] and by Kuntz and Whitton [24].

From table 1 it can be seen that \( \alpha \) is large enough, but \( \lambda \) is much smaller than \( D \). Thus, the fact that no inverted population is found for this system is, according to the theory, due to the weak dependence of the curvature \( k(s) \) on \( s \).

6.2. The \( \text{Cl}_2 + \text{H} \) system

The \( \text{Cl}_2 + \text{H} \) system was studied quantum mechanically by Baer [6a] using a LEPS surface. He found that by far the most populated state is \( m=4 \). Similar results were also found by quasiclassical calculations by Essen et al. [25] and by Truhlar et al. [26]. These findings cannot be supported by the present theory due to the fact that the value of \( \alpha \) [see eq. (5.2)] cannot be estimated. From fig. 1 in ref. [6a] it can be seen that \( \alpha \) can be anywhere between zero and 0.5 au. Since a value of 0.5 au yields a \( \lambda \) which is more than an order of magnitude smaller than \( D (=1.95 \text{ eV}) \), it is concluded that \( \alpha \) has to be smaller than 0.15 au (\( \lambda \) varies as \( \alpha^{-2} \)).

More definite conclusions can be drawn for the two surfaces recently taken by Duff and Truhlar [27] in their classical trajectory study. Among other mass combinations they also treated the \( L + \text{HH} \) case and no vibrational transitions were encountered. In their surfaces the value of \( \alpha \) can be estimated more accurately and it was found to be \( \approx 1 \) au. The values of \( \alpha, K_0, K_2, \lambda \) and \( D \) given in table 1 refer to this case. As can be seen no inversion is expected for this system.

To summarize this case the following general conclusion can be drawn: any \( L + \text{HH} \) system is characterized by two features which are closely related

\begin{align*}
(1) & \quad \beta \approx \pi/2, \\
(2) & \quad \mu \gg 1.
\end{align*}

Therefore in order to obtain a \( \lambda \) which is about \( 1-2 \) eV, the value of \( \alpha \) has to be around 0.1 au. In other words the minimum energy path has to be tangential to the asymptotes of the hyperbola "almost" everywhere.

6.3. The \( \text{H}_2 + \text{F} \) system

The \( \text{H}_2 + \text{F} \) system was exposed to various quantum mechanical [28–30], quasiclassical [28] and semi-classical [28] calculations. In most cases it was found that the \( m=3 \) state (the highest) is the most populated. This result is in agreement with the theory as can be seen from the data given in table 1. Recently Manz [31] compared results from two different surfaces for the same system. For one no population of the higher states was observed, whereas for the other the most populated states were \( m=2,3 \). We have estimated the relative values of \( \alpha \) for the two surfaces and found the first one to be twice as large as the second. This difference is enough to explain his results because due to it \( \alpha \) becomes 0.40 and \( \lambda \approx 0.37 \text{ eV} \), namely values for which population of higher states is avoided.

6.4. The \( \text{HI} + \text{Cl} \) system

The \( \text{HI} + \text{Cl} \) system was studied quantum mechanically by Baer [32] and recently also classically by Kafri [33]. In both cases the highest vibrational state was found to be by far the most populated one. As is noticed from table 1 this result is expected due to the favorable values of \( \alpha \) and \( \lambda \). The \( \text{HI} + \text{Cl} \) system is a typical \( \text{HLH} \) system, characterized by the feature that \( \beta \approx 0 \). Therefore \( \alpha \) and \( \lambda \) will always be large enough irrespective of whether \( \alpha \) is small or large. Thus, a large vibrational inversion is always expected in such systems.

7. Summary

In this work we applied the Born approximation to the Marcus equation in order to extract the term which leads to the large vibrational nonadiabatic
transition probabilities encountered in exothermic reactions. It is found, by assuming that the transition is a one-step process localized in a small region along the minimum energy path, that three conditions have to be fulfilled: (i) The surface is an early barrier type surface and attractive to permit population of all open (product) states when maximum curvature is reached. This condition, formulated by Polanyi [14], was assumed to be valid throughout this study. (ii) The product $\alpha = K_0 \beta$ has to be larger than 0.5. ($K_0$ is the maximum curvature and $\beta$ is equal to half the oscillator width in the interaction region.) (iii) The value of $K_2$ (which is equal to $(d^2k/ds^2)/K_0$) has to be greater than or equal to the exothermicity. These conditions were tested against exact quantum mechanical and classical trajectory calculations. The values of $K_0$ and $K_2$ were derived by approximating the minimum energy path by a hyperbola:

$$K_0 = a^{-1} \cot^2(\beta/2), \quad K_2 = 3a^{-2} \sin^{-4}(\beta/2),$$

where $\beta$ is the angle between the skewed axes and $a$ is the semi-transverse axis of the hyperbola.

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Appendix: Determination of $p$

Eq. (2.16) can be written:

$$\eta^{(p-2)} F \phi_{n} = 0, \quad (A.1)$$

where $F$ is an operator defined by eqs. (2.16) and (2.17). If the matrix $\eta^{(p)}$ is defined as:

$$\eta^{(p)}_{mn} = \langle \phi_{m} | \phi_{n} \rangle, \quad (A.2)$$

eq (A.1), in matrix notation, becomes:

$$\eta^{(p)} F = 0, \quad (A.3)$$

where $F_{mn}$ are defined as:

$$F_{mn} = \langle \phi_{m} | F | \phi_{n} \rangle. \quad (A.1')$$

Eq. (A.3) leads to the equation

$$F = 0,$$

if $\eta^{(p)}$ is a regular matrix. If $\eta$ is different from zero in the integration interval then $\eta^{(p)}$ is a regular matrix for any value of $p$. If however $\eta$ becomes zero for some value of $p$ [cf. eq. (2.3)] then the choice of $p$ is limited. $\eta^{(p)}$ is well defined for $p=2$ because it reduces to the unity matrix. It will also be well defined as long as $p$ is not smaller than 1 or larger than 3. If $p$ is smaller than 1 the integral in eq. (A.2) does not converge, and if $p$ is larger than 3 the inverse of $\eta^{(p)}$ depends on the order of the matrix and no convergence (with respect to the order) is obtained.

References

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[18] O. Atabek, J.A. Beswick, R. Lefebvre, S. Mukamel and J. Jortner, Mol. Phys. 31 (1976) 1. This procedure could be used for small values of $\alpha(< 0.2)$. For larger ones we had to invert the matrix and take out the required elements.