DYNAMICS OF HYDROGEN ATOM AND PROTON TRANSFER REACTIONS. SIMPLIFIED ANALYTIC TWO-STATE FORMULAE ✫

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Analytical formulae for the threshold region of the reaction probability curve for a nearly degenerate H-atom transfer are given and shown to yield good agreement with exact results for a two-state model system. Application to H and H^+ transfer in complex systems is discussed.

1. Introduction

The exchange dynamics of hydrogen atom and proton transfer reactions between two heavy particles has been studied recently [1–13]*. For the case of exact degeneracy of the reactant and product vibrational states which occurs in symmetric exchange reactions a new kind of vibrationally adiabatic approximation in reactive collisions was introduced [1] and used to derive analytical formulae for the reaction probability [1]. Subsequent accurate numerical calculations [6,7] on symmetric H-atom exchange demonstrated both the high degree of vibrational adiabaticity of the symmetric H-transfer reactions postulated in ref. [1] and the high accuracy** of the analytical formulae. The vibrationally adiabatic analysis in ref. [1] has been extensively applied in exploring various aspects of the dynamics of H-atom transfer reactions [6–10] as well as to indicate the possibility of forming molecules on repulsive potential energy surfaces [14–16].

The symmetric exchange treatment [1] was recently extended [11] to the closely related problem of the dynamics of H-atom exchange between two nearly degenerate vibrational states in an asymmetric reaction AH + B → A + HB ★. It was shown [11] that for this case the reaction dynamics can be represented in terms of two suitably distorted nearly degenerate vibrational states between which the exchange occurs. The resulting two coupled differential equations [1], which simulate the dynamics, were solved numerically [12] for a model BrH + Cl → Br + HCl reaction and were shown to yield results in good agreement with accurate multichannel calculations [12] for the same problem.

A perturbative (DWBA) approximate treatment of the two coupled equations valid in the reaction threshold region was also developed [11]. For reactions with some (at least few kcal/mol) activation energy the threshold region determines the kinetics of low and moderate temperature reactions. In section 2 we calculate a

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* The analogy of the coordinates used in electron transfer in atomic collisions with those for H-transfer between heavy atoms was discussed in ref. [2]. The same coordinates were used in ref. [3] to study the tunneling in $H + H_2$.

** The shift of the results of eq. (4.10) in ref. [1] relative to the accurate coupled channel ones [6] was misprinted in ref. [11] as 0.5 kcal/mol. It should read 0.5×10^{-3} kcal/mol.

★ The Sato parameters, listed as 0.02, 0.02, and 0.00 in ref. [11], refer to HBr, HCl, and BrCl, respectively.

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Boltzmann-weighted reaction probability $P_{ij}(T)$ obtained from the DWBA results in ref. [11] and compare it with the one obtained from accurate numerical solution of the two-state approximation for the BrH + Cl model system. A $P_{ij}(T)$ is useful for testing these DWBA results since it is more representative than $P_{ij}(E)$ of the accuracy which they can be expected to yield when used for calculations of reaction rates in actual physical processes.

An outline of a possible application of the formulae developed here and in ref. [11] to reactions of H and H^+ transfer between two complex molecules and to reactions in condensed phases is given in section 3. Vibrational adiabaticity is discussed in section 4. An approximate analytical expression for the reaction probability $P_{ij}(E)$, accurate over the whole energy range where the two-state approximation is valid, is given in a later paper [13].

2. Test of the relevant aspects of the "exponentiated" DWBA formula for evaluating reaction rates

It was shown earlier that the treatment of the reactive exchange dynamics in a collinear AH + B → A + HB reaction can, in the presence of an HB vibrational state nearly degenerate with the initial AH one, be represented approximately by a pair of coupled ordinary differential equations [1,11]

$$[-\tfrac{1}{2}\,\mathrm{d}^2/\mathrm{d}\rho^2 + \epsilon_i(\rho) - E + Q_{ii}]\,\varphi_i(\rho) = \mathrm{i}A_{ij}\,\mathrm{d}\varphi_j(\rho)/\mathrm{d}\rho\,,$$

$$[-\tfrac{1}{2}\,\mathrm{d}^2/\mathrm{d}\rho^2 + \epsilon_j(\rho) - E + Q_{jj}]\,\varphi_j(\rho) = \mathrm{i}A_{ji}\,\mathrm{d}\varphi_i(\rho)/\mathrm{d}\rho\,, \tag{1}$$

where the notation is that of refs. [1,11] (with A replacing P), ρ being the slow coordinate defined there, and where the negligible "centrifugal" diagonal term $-1/\rho^2$ on the left-hand side of both equations has been omitted.

It was shown in ref. [11] that instead of solving eq. (1) directly (e.g. ref. [17]) it is more appropriate to utilize the diagonal elements in eq. (1) for generating a pair of closely related but not exactly equivalent coupled equations in the diabatic representation:

$$[-\tfrac{1}{2}\,\mathrm{d}^2/\mathrm{d}\rho^2 + V_{ii}(\rho) - E]\,\Psi_i(\rho) = V_{ij}\Psi_j(\rho),$$

$$[-\tfrac{1}{2}\,\mathrm{d}^2/\mathrm{d}\rho^2 + V_{jj}(\rho) - E]\,\Psi_j(\rho) = V_{ij}\Psi_i(\rho) \tag{2}$$

($V_{ij} = V_{ji}$ since the vibrational basis set is real. The method used in the present study to obtain the matrix elements V_{ii}, V_{jj}, and V_{ij} was an improved version [13] of the methods in ref. [11]; however, use of the latter would have made little difference in the threshold region).

The coupled equations [eq. (2)] were solved in ref. [11] in the tunneling region by means of a perturbative (DWBA) treatment to give the following expression for the reactive transition probability (cf. eqs. (5.5) and (3.9) of ref. [11]):

$$P_{ij} = (2\pi T_{ij})^2 = [\exp(-\Delta^2/2aF)]^2\,P_{\mathrm{sym}}, \tag{3a}$$

where

$$P_{\mathrm{sym}} = [(2\pi/aF)^{1/2}\,\bar{V}_{ij}\,\exp(\alpha^3/24F)]^2. \tag{3b}$$

This P_{sym} is the DWBA approximation to the reactive transition probability for the corresponding symmetric problem defined by the V-matrix elements V^0_{ij}:

$$V^0_{ii} = V^0_{jj} = \tfrac{1}{2}(V_{ii} + V_{jj}), \qquad V^0_{ij} = V_{ij}\ (i \neq j), \tag{4}$$

in eq. (2), or alternatively in the adiabatic representation (eq. (1)) by

$$\epsilon^{\mathrm{a,s}} = V^0_{ii} \pm V^0_{ij}, \qquad A_{ij} = Q_{ij} = 0, \tag{5}$$

where the a refers to the plus sign and the s to the minus. $\bar{V}_{ij}$ in (3) is defined below. Eq. (3) was obtained by using the linear approximation for V^0_{ii} and for $\ln V_{ij}$ $(i \neq j)$ as a function of ρ near the turning point, i.e. by setting

$$\mathrm{d}V_{ii}/\mathrm{d}\rho = (\mathrm{d}V^0_{ii}/\mathrm{d}\rho)_{\rho_0} \equiv F,$$

$$\mathrm{d}\ln V_{ij}/\mathrm{d}\rho = (\mathrm{d}\ln V_{ij}/\mathrm{d}\rho)_{\rho_0} = -\alpha. \tag{6}$$

and by approximating the resonance defect $V_{ii}(\rho) - V_{jj}(\rho)$ by its value

$$\Delta = V_{ii}(\rho_0) - V_{jj}(\rho_0) \tag{7}$$

at the classical turning point ρ_0 for the ρ-motion on a potential $V^0_{ii}(\rho)$. $\bar{V}_{ij}$ is $V_{ij}(\rho_0)$.

Eq. (3) has the disadvantage typical of DWBA formulae of yielding probabilities higher than unity at high energies. To avoid this we can, in analogy to frequent practice in using DWBA results for calculating inelastic transition probabilities, limit the probability by setting

$$\max(P_{\mathrm{sym}}) = 1. \tag{8}$$

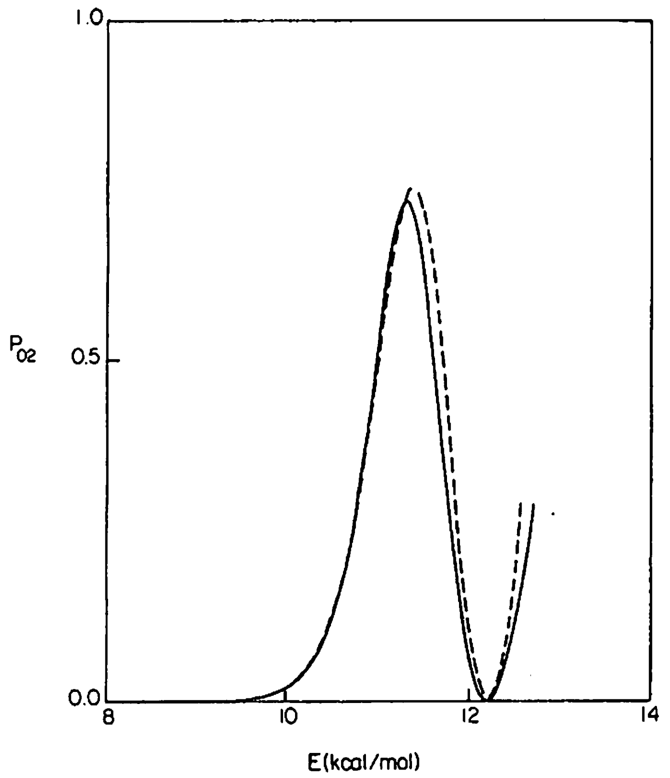

Fig. 1. Plot of P_{02} versus total energy of the reactants for the model system BrH + Cl → Br + HCl. The full line is the result of the numerical solution of eq. (2) and the dashed line is the approximation given by eq. (9).

A better approximation can be obtained by "exponentiating" [11,18] the symmetric part of the P_{ij}, namely by writing*

$$P_{ij}(E) = \exp(-\Delta^2/\alpha F)\,\sin^2 P_{\rm sym}^{1/2}\,, \tag{9}$$

where $P_{\rm sym}$ is defined by eq. (3). At low values of $P_{\rm sym}$ eq. (9) reduces to eq. (3a).

Eq. (9) gives excellent results around the reaction threshold, as seen in fig. 1, but not at energies much higher than the threshold due to the approximations of a linear $V_{ii}^0(\rho)$ and ln $V_{ij}(\rho)$ (eq. (6)). Fortunately, reaction rates for most reactions that have at least some activation energy are determined at low to moderate temperatures by the probabilities near the threshold. In order to examine the utility of eq. (9), and of eq. (3) plus (8), for calculating reaction rates for physical processes which involve H-atom or proton transfer at low and moderate temperatures it is convenient to test its accuracy by calculating a dimensionless Boltzmann-averaged reaction probability,

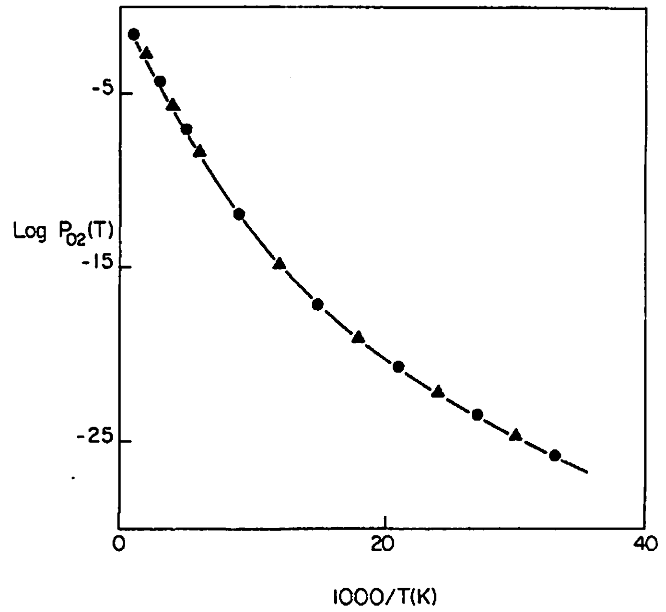

Fig. 2. Plot of the $\log_{10}$ of the Boltzmann averaged reaction probability $P_{02}(T)$ versus the inverse temperature. The full line is obtained from the accurate numerical solution of eq. (2), the circles are obtained using $P_{ij}(E)$ in eq. (9) and the triangles are obtained from eq. (8) plus eq. (3).

$$P_{ij}(T) = \int_0^\infty P_{ij}(E)\exp(-E/kT)\,\mathrm{d}E/kT. \tag{10}$$

The $P_{ij}(T)$ obtained using eq. (9) for $P_{ij}(E)$ and the one obtained using eq. (3) plus (8), are presented in fig. 2, together with the $P_{ij}(T)$ obtained from the numerical solution of the coupled equations (2). The results are in excellent agreement. $P_{ij}(T)$ above is related to a "one-dimensional rate constant" $k_{ij}^1(T)$ by $P_{ij}(T) = k_{ij}^1(T)\,hQ/kT$, where Q is the partition function of the reactants.

The linear restrictions (eq. (6)) which limit the validity of eq. (9) to the threshold region can be removed by using the exact two-state analog of $P_{\rm sym}$, given by eq. (4.10) of ref. [1]. We then have

$$P_{ij} = \exp(-\Delta^2/\alpha F)\,\sin^2(\xi_{\rm s} - \xi_{\rm a}), \tag{11}$$

where $\xi_{\rm s,a}$ are the elastic phase shifts of eq. (1) with the matrix elements defined by eq. (5). However, obtaining accurate transition probabilities at higher energies also requires extending the procedures for evaluating the matrix elements $V_{ij}(\rho)$ in ref. [11] to smaller ρ. Such extensions, as well as including the effect of variation of the resonance defect $V_{ii} - V_{jj}$ with ρ, are discussed in detail elsewhere [13].

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* Typically, the entire DWBA P_{ij} has been "exponentiated" rather than, as in the present case, only the symmetric part.

3. Extension to more complex systems

The question is frequently raised as to whether some of the "reorganization" of coordinates prior to an electron transfer in solution also occurs for H and for H^+ transfers. (An early review of electron transfer theory is given in ref. [19].) We consider this point in the following discussion.

We first note that the factor multiplying P_{sym} in eq. (3) can be shown [13] to have the form $\exp[-(\tau\Delta)^2]$, where τ is roughly the "duration" of the reactive collision. (The units are such that $\hbar = 1$.) This factor $\exp[-(\tau\Delta)^2]$ serves as a counterpart to the well-known Dirac delta function $\delta(\Delta)$ which appears in the Golden Rule formula for electronic transitions, e.g. ref. [20], including electron transfer reactions, e.g. refs. [19,21]. Because the ratio of the heavy to the light particles in H or H^+ transfers is much closer to unity than it is in electron transfers, this $\exp[-(\tau\Delta)^2]$ is a much less peaked function of the Δ than is $\delta(\Delta)$. Nevertheless, a suitable fluctuation of other coordinates q, prior to the H transfer, will reduce $\exp[-\Delta^2(q)/\alpha F]$. (The Δ in eq. (7) can now depend on q.) For example, the state-to-state contribution $k_{ij}(T)$ to the rate constant is given by eq. (12), using arguments analogous to those used in ref. [22],

$$k_{ij}(T) = \int \dots \int P_{ij}(E, q) \exp(-E/kT)\, \mathrm{d}E\, \mathrm{d}q Q_p / hQ, \tag{12}$$

when the q coordinates are treated classically. j is the quantum state of the H motion in the product that is closest in energy to the initial (ith) quantum state of the H motion in the reactants. In eq. (12) $P_{ij}(E, q)$ is given by eq. (9) and depends on q mainly via $\Delta(q)$. E includes not only the energy along the reaction coordinate but also $V_{ii}(\rho, q)$, which replaces the $V_{ii}(\rho)$ present previously and is the effective potential energy of the system when the reactants are in the ith quantum state for the H motion. Q is the partition function of the reactants, and Q_p is the momentum part of the classical partition function of the q degrees of freedom.

Fluctuations in the q coordinates which serve to reduce the value of $\Delta(q)$ will increase $P_{ij}(E)$ and hence be favored for enhancing the reaction rate provided they do not increase $V_{ii}(\rho, q)$ too much. Typically, one expects that eq. (12) for the reaction rate will be dominated by the P_{sym} factor in eq. (3), which is smaller for D than for H transfers. The expectation that the $\exp[-(\tau\Delta)^2]$ term is reduced in importance by a suitable and relatively minor fluctuation in coordinates q is indicated by the apparent absence of unusual isotope effects (D transfer faster than H transfer) in the literature. If this were not the case it might be possible to find a system in which the D-transfer rate exceeded the H-transfer rate because, accidentally, Δ was small for the deuterium case.

4. Discussion

The high degree of vibrational adiabaticity has been one of the most striking features in accurate calculations [6 7] of symmetric heavy-light-heavy (HLH) collinear reactive collisions. From an experimentalist's point of view vibrational adiabaticity may simply mean that the vibrational quantum number of the products equals that of the reactants. It is manifested in the results of the accurate numerical calculations by the absence of vibrational excitation when there are higher vibrational states open. When there are no excited vibrational states open vibrational adiabaticity is manifested by the close validity of the approximate formulae in ref. [1] derived on the basis of vibrational adiabaticity. The vibrational adiabaticity is also evident in the preservation of the vibrational action in classical trajectory calculations.

As noted in ref. [1], however, the dynamical nature of the vibrational adiabaticity in symmetric HLH reactions is radically different from that in the adiabatic model used by a number of investigators [23,24] and which was termed [24] vibrationally adiabatic. In that vibrationally adiabatic model [23,24] the system moves on a single effective potential energy surface. This motion was discussed in detail using natural collision coordinates [25]. In the new type of vibrational adiabaticity presented in ref. [1], the reaction is adiabatic in the sense that the quantum state of reactants is coupled only to a quantum state of the products with the same quantum number. However, two distinct quantum states and two effective adiabatic potentials are needed[*] to discuss the reaction.

Analogously, in the present case of a non-symmetric

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[*] In the case of ref. [1], symmetric and antisymmetric states were used for the reaction AH + A → A + HA and would also be necessary for an exact resonance AH + B → A + HB reaction.

reaction the vibrational state of the reactants is nearly degenerate with, and is coupled almost exclusively to, a vibrational state of the products which has a *different* quantum number. As a result the reaction is almost completely vibrationally nonadiabatic, i.e. it leads to a vibrational population inversion in the products. Both the dynamics of H-atom transfer and the present treatment are much more akin to those of the charge transfer processes in atomic collisions than to the vibrationally adiabatic treatment of chemical reactions in terms of natural collision coordinates.

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