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A test of two approximate two-state treatments for the dynamics of H-atom transfers between two heavy particles

Stephen J. Klippenstein, Vasil K. Babamov, and R. A. Marcus
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, [a] *Pasadena, California 91125*

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Reactive transition probabilities and Boltzmann-averaged reactive transition probabilities for a slightly off-resonant model H-atom transfer system with an appreciable energy barrier are calculated using the approximate methods of Babamov *et al.* and of Crothers–Stückelberg. Both are compared with the corresponding quantities obtained from a numerical two-state treatment of the same model system. The method of Babamov *et al.* is seen to give more accurate results for the transition probabilities at energies below and around the reaction threshold, and much more accurate results for the Boltzmann-averaged probabilities in a wide range of temperatures than the second method. The relative merits of the two formulas are discussed.

I. INTRODUCTION

There have been a number of recent theoretical studies of the dynamics of chemical reactions in which an H atom is exchanged between two different heavier atoms or molecular fragments.[1–14] A method for reducing the dynamics of the reactive collision to two coupled ordinary differential equations, in the case when the initial reactant state and the final product state are nearly degenerate, was proposed recently by Babamov *et al.*[5,7] and applied to a collinear collision using a model LEPS potential energy surface for such reaction. This two-state method, which is only applicable to reactions with a substantial potential energy barrier to the reaction, has been shown[9] to give results for the transition probabilities in good agreement with the corresponding accurate (many states) coupled-channel calculations.[9]

A simple analytical formula for the reactive transition probabilities within the two-state approximation has also been proposed by Babamov *et al.*[6] and shown to give results in good agreement in the threshold region with those obtained from a numerical solution of the two-state model, and thus with the results of the accurate coupled-channel calculations. The principal purpose of these treatments[5–8] has been to provide a practical simplified treatment of the dynamics of chemical reactions which correctly simulates the quantum mechanical tunneling of the light H atom and is also accurate in the range of energies which contribute significantly to the kinetics of the reaction under typical conditions.

More recently the use of the Crothers–Stückelberg (CS) perturbed symmetric resonance formula[15,16] has been suggested[11,12] as an alternative simplified analytical treatment of the two-state model. The two methods have been applied[12] to an approximate analytical fit of the two-state representation of Babamov *et al.* for comparison purposes. However, the use of an incorrect analytical fit to the two-state model[17] and the overlooking of the importance of the near-threshold region led to an incorrect conclusion[12] about the relative usefulness of the two methods.

In this paper reactive transition probabilities from the two approximate methods are compared with those obtained from the exact two-state (numerical) treatment, for the model system of Ref. 9, as a function of the total energy. The results are also given in terms of Boltzmann-averaged reaction rate probabilities $P_{02}(T)$. Limitations of the CS method, already specifically mentioned by Bárány and Crothers,[16] will be seen to appear here in the threshold region.

II. TWO-STATE APPROXIMATION AND REACTIVE TRANSITION PROBABILITY CALCULATIONS

Starting with the Schrödinger equation for the collision in mass-weighted polar (hyperspherical[18]) coordinates and expanding the solution in terms of the eigenfunctions for the "vibrational" motion[5,19] $\eta_i(\theta;\rho)$:

$$\psi(\theta,\rho)=\varphi_1(\rho)\eta_1(\theta;\rho)+\varphi_2(\rho)\eta_2(\theta;\rho), \tag{1}$$

one obtains, after some manipulation, a pair of coupled ordinary differential equations in the adiabatic representation[5,19,20]

$$\begin{aligned}&\left[-\frac{\hbar^2}{2m_H}\frac{d^2}{d\rho^2}+\epsilon_1(\rho)-E+\frac{Q_{11}}{2}\right]\varphi_1(\rho)\\&\quad=iP_{12}\frac{d\varphi_2(\rho)}{d\rho}-\frac{Q_{12}}{2}\varphi_2(\rho),\\&\left[-\frac{\hbar^2}{2m_H}\frac{d^2}{d\rho^2}+\epsilon_2(\rho)-E+\frac{Q_{22}}{2}\right]\varphi_2(\rho)\\&\quad=iP_{21}\frac{d\varphi_1(\rho)}{d\rho}-\frac{Q_{21}}{2}\varphi_1(\rho),\end{aligned} \tag{2}$$

where m_H is the mass of the H atom, E is the energy, the $\epsilon_i(\rho)$'s are the eigenvalues associated with the η_i, and the P_{ij}'s and Q_{ij}'s are matrix elements defined in Ref. 19. A closely related, but not entirely equivalent pair of coupled equations in the diabatic representation can also be defined[7,21]

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$$\begin{aligned}&\left\{-\frac{d^2}{d\rho^2}+\frac{2m_{\rm H}}{\hbar^2}[V_{11}(\rho)-E]\right\}\Psi_1(\rho)\\&\quad=\frac{-2m_{\rm H}}{\hbar^2}V_{12}(\rho)\Psi_2(\rho),\\&\left\{-\frac{d^2}{d\rho^2}+\frac{2m_{\rm H}}{\hbar^2}[V_{22}(\rho)-E]\right\}\Psi_2(\rho)\\&\quad=\frac{-2m_{\rm H}}{\hbar^2}V_{12}(\rho)\Psi_1(\rho).\end{aligned}\tag{3}$$

The Ψ_i in Eq. (3) are the coefficients in an expansion

$$\psi(\theta,\rho)=\Psi_1(\rho)\zeta_1(\theta;\rho)+\Psi_2(\rho)\zeta_2(\theta;\rho)\tag{4}$$

in which the ζ_i are localized vibrational wave functions obtained as linear combinations of the η_i. The matrix **V** in Eq. (3), with elements V_{ij}, can be obtained by applying to the diagonal matrix of the ϵ_i's the orthogonal transformation[21,22] that converts the adiabatic vibrational basis $\eta_i(\theta;\rho)$ into a diabatic one $\zeta_i(\theta;\rho)$. The ϵ_i's in Eq. (2) are then related to the V_{ij}'s by

$$\epsilon_{1,2}=\tfrac{1}{2}(V_{11}+V_{22})\mp\sqrt{\tfrac{1}{4}(V_{22}-V_{11})^2+V_{12}^2},\tag{5}$$

where the minus sign is for ϵ_1.

It has been shown[9] that the reactive transition probabilities $P_{02}(E)$ obtained from a numerical solution of Eq. (3) for the slightly off-resonant model system considered here are in good agreement with those of a 12-state accurate numerical quantum mechanical calculation[9] for the same system. Thus, the two-state treatment based on Eq. (3) provides an accurate simulation of the dynamics for the model system studied.

Babamov *et al.* gave[6] a simple analytical partially "exponentiated" distorted wave expression for the reactive transition probability from state n of the reactants to state m of the products, assuming approximately equal slopes[23] in plots of V_{11} and V_{22} vs ρ at the classical turning points:

$$\begin{aligned}&P^B_{nm}(E)\\&\quad=\exp\left(\frac{-\Delta^2}{\alpha F}\right)\sin^2\left\{\left[\left(\frac{2\pi}{\alpha \mathrm{F}}\right)\left[\frac{m_{\rm H}}{\hbar^2}V_{12}(\rho_0)\right]^2\exp\left(\frac{\alpha^3}{12F}\right)\right]^{1/2}\right\},\end{aligned}\tag{6}$$

where

$$\begin{aligned}\Delta&=(m_{\rm H}/\hbar^2)[V_{22}(\rho_0)-V_{11}(\rho_0)],\\\alpha&=\left[-\frac{d}{d\rho}\ln V_{12}(\rho)\right]_{\rho=\rho_0},\\F&=\left[-\frac{m_{\rm H}}{\hbar^2}\frac{d}{d\rho}V^0(\rho)\right]_{\rho=\rho_0}.\end{aligned}\tag{7}$$

Here, ρ_0 is the classical turning point for the ρ motion on a mean potential $V^0(\rho)=[V_{11}(\rho)+V_{22}(\rho)]/2$. The approximations contained in Eq. (6) are given in the Discussion. Another formula proposed by Babamov *et al.*[6] is treated in the Appendix. It should be stressed that the formula in the Appendix gives better results at higher energies than Eq. (6), and reduces to the exact two-state answer when Δ vanishes, but gives similar results in the threshold region. Equation (6) is easier to use than the equation in the Appendix.

The Crothers–Stückelberg expression $P^{\rm CS}_{nm}$ for the reactive transition probability, for a transition from state n to state m, in a perturbed symmetric resonance problem, is given by[15,16]

$$P^{\rm CS}_{nm}(E)=\operatorname{sech}^2\delta\,\sin^2(\sigma+\phi),\tag{8}$$

where

$$\sigma+i\delta=\int_{\rho_1}^{\rho_*}k_1(\rho)d\rho-\int_{\rho_2}^{\rho_*}k_2(\rho)d\rho;\tag{9}$$

$k_i(\rho)=\{2m_{\rm H}[E-\epsilon_i(\rho)]/\hbar^2\}^{1/2}$, ρ_i is the classical turning point for the ρ motion on the adiabatic potential $\epsilon_i(\rho)$, and ρ_* is the complex-valued ρ at which $\epsilon_1(\rho)=\epsilon_2(\rho)$. ϕ is a phase correction which to a good approximation[16] is zero for the perturbed symmetric resonance problem.

Nakamura *et al.*[12] recently suggested the application of Eq. (8) to the collinear H-transfer system studied in Ref. 9. As seen from Eqs. (8) and (9), the use of the formula does not explicitly require knowledge of the full coupled equations (2). It does, however, require knowledge of the two adiabatic potentials $\epsilon_i(\rho)$ in the complex plane, in order to determine the complex-valued crossing point ρ_* and to perform the integration in the complex plane. One procedure[11,12,14] for implementing the formula is to attempt to construct an analytic representation of the diabatic matrix elements V_{ij} in Eq. (3) by making simple approximate analytic fits to a known numerical description of the latter. The adiabatic potentials are then determined from Eq. (5), with analytic continuation serving to extend them into the complex plane. This continuation yields a value for ρ_*, namely the value of ρ where the square root in Eq. (5) vanishes. This procedure appears to be the one used by Nakamura and Ohsaki.[12]

The functional form assumed by the latter authors for the V_{ij}'s is[12]

$$\begin{aligned}V_{11}(\rho)&=A\exp\left[-\frac{G}{A}(\rho-\rho_c)\right],\\V_{22}(\rho)&=V_{11}(\rho)-\Delta_0,\\V_{12}(\rho)&=\{B+C\exp[B(\rho-\rho_c)]\}^{-1},\end{aligned}\tag{10}$$

where A, B, C, G, Δ_0, and β, are all constants obtained from a fitting procedure, and ρ_c is an arbitrarily chosen constant.

In our applications we adopt the functional form of Nakamura and Ohsaki given by Eq. (10) and determine the parameters by fitting the values of V_{11}, V_{22}, V_{12}, the first derivative of V^0, and the first and second derivatives of V_{12} to the corresponding quantities in the numerical two-state representation, all at a given ρ_c. The parameter ρ_c in Eq. (10) was chosen in Sec. III to be 31.75 bohr, which is approximately the value of ρ at the classical turning point at energies near the threshold energy. Other possible ways of applying the formula and of choosing ρ_c are explored in the Appendix.

III. RESULTS AND DISCUSSION

Since both the method of Babamov *et al.* and the CS method are based on the two-state approximation the results for these methods are compared with those from a numerical solution of the two-state model. The two-state representation was used for a model LEPS surface for H-atom transfer between two heavy atoms.[24] The transition probability

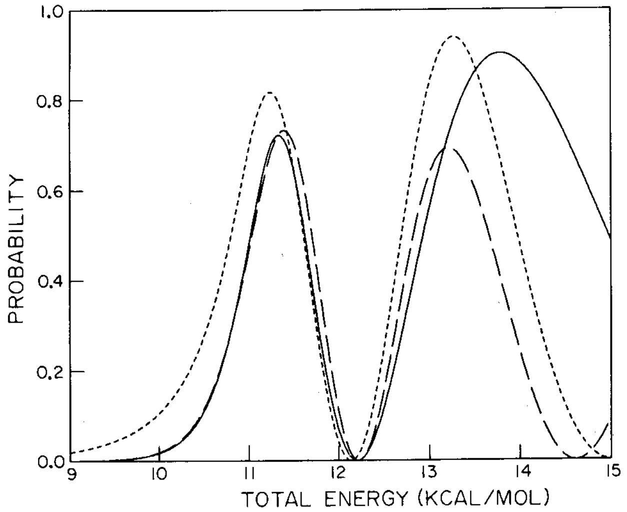

FIG. 1. The probabilities P_{02} as a function of the total energy E measured relative to the minimum of the HBr potential. The translational energy is 3.83 kcal/mol (i.e., the zero-point energy of the HBr well) less than E. $P_{02}(E)$ is the two-state numerical reactive transition probability and is denoted by —. $P_{02}^{B}(E)$ is the reactive transition probability of Babamov *et al.*, calculated from Eq. (6), and is denoted by - - -. $P_{02}^{CS}(E)$ is the reactive transition probability calculated from the CS expression, Eqs. (8) and (9), and is denoted by ---.

$P_{02}(E)$ obtained from the exact numerical solution of the two coupled equations as well as those from the two approximate formulas, $P_{02}^{B}(E)$ and $P_{02}^{CS}(E)$, were calculated for various energies. A plot of these quantities vs total energy is given in Fig. 1. One can see that at the lower energies the results of the formula of Babamov *et al.* $P_{02}^{B}(E)$ are in excellent agreement with those of the numerical solution of the two-state model $P_{02}(E)$. The agreement gradually becomes worse as the energy increases well above the threshold. The results of the Crothers–Stückelberg formula $P_{02}^{CS}(E)$ on the other hand are quite inaccurate at energies near and below the reaction threshold and become more accurate at higher energies. At a total collision energy of 10.0 kcal/mol $P_{02}^{CS}(E)$ is seen to be too large by a factor of about 6. At higher energies, $P_{02}^{CS}(E)$ is still not in good agreement with $P_{02}(E)$ although it does have the correct shape and is in better agreement than $P_{02}^{B}(E)$. Another formula of Babamov *et al.* which is more accurate than Eq. (6) at higher energies, albeit somewhat more laborious to evaluate, is discussed in the Appendix.

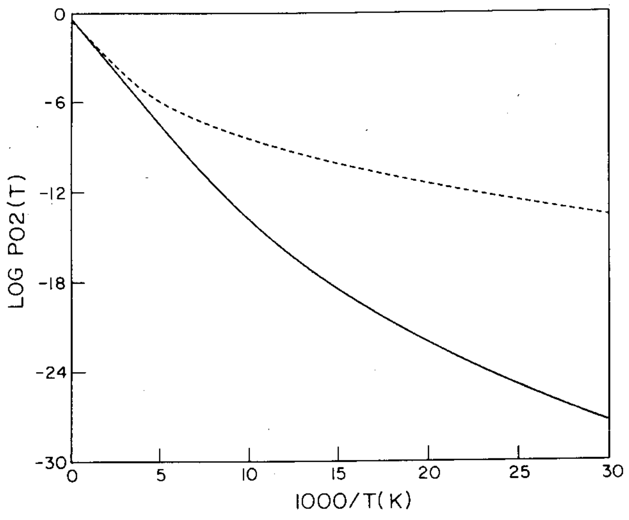

FIG. 2. Log_{10} of the probabilities P_{02} as a function of $1/T$ (K). $P_{02}(T)$ is the Boltzmann-averaged numerical transition probability and is denoted by —. $P_{02}^{B}(T)$, the Boltzmann-averaged transition probability from the method of Babamov *et al.*, is denoted by - - -. [This plot is not visible since it coincides with that of $P_{02}(T)$.] $P_{02}^{CS}(T)$, the Boltzmann averaged transition probability from the CS method, is denoted by ---.

In chemical reactions the quantity of primary interest is the reaction rate constant. For a collinear reaction a one-dimensional rate constant for the reaction from quantum state n of the reactants to form state m of the products can be defined as

$$k_{nm}(T) = \left(\frac{kT}{2\pi\mu}\right)^{1/2} P_{nm}(T), \tag{11}$$

where

$$P_{nm}(T) = \int_0^\infty P_{nm}(E) \exp\left(\frac{-E}{kT}\right) \frac{dE}{kT}; \tag{12}$$

μ is the Cl–HBr reduced mass and E is the translational energy of the reactants.

In Fig. 2 plots of $\log_{10} P_{02}(T)$, $\log_{10} P_{02}^{B}(T)$, and $\log_{10} P_{02}^{CS}(T)$ vs $1/T$ are given. At $T = 300$ K, the values of $P_{02}(T)$, $P_{02}^{B}(T)$, and $P_{02}^{CS}(T)$ are 6.2×10^{-6}, 6.3×10^{-6}, and 2.8×10^{-5}, respectively. At $T = 600$ K, they are 1.6×10^{-3}, 1.5×10^{-3}, and 2.7×10^{-3}, respectively. The corresponding one-dimensional rates $[k_{02}(T), k_{02}^{B}(T)$, and $k_{02}^{CS}(T)]$ given by Eq. (11) are 7.9×10^{-2}, 8.0×10^{-2}, and 3.6×10^{-1} cm molecule^{-1} s^{-1} at $T = 300$ K. At $T = 600$ K they are 29, 27, and 49 cm molecule^{-1} s^{-1}.

The rate constants $k_{02}(T)$ calculated using the $P_{02}(E)$ obtained from the exact numerical solution of the two-state problem are in good agreement with the rate constants calculated by Garrett *et al.*[13] using the $P_{02}(E)$ obtained from the accurate 12 channel[9] numerical solution. For example at $T = 300$ K the 12 channel rate constant[13] is 6.37×10^{-2} cm molecule^{-1} s^{-1} as compared with the above two channel rate constant of 7.9×10^{-2} cm molecule^{-1} s^{-1}. At $T = 600$ K the 12 channel result is 24.9 cm molecule^{-1} s^{-1} as compared with the above two channel result of 29 cm molecule^{-1} s^{-1}.

Approximate semiclassical calculations of one-dimensional rate constants summed over the final states have been reported by Garrett *et al.*[13] for the same model system using various versions of variational transition state theory.[25] Those rates, which are also in good agreement with the corresponding results obtained from the accurate twelve channel quantum mechanical calculations,[13] are not directly comparable to the 0→2 state to state rates presented here.

The effective reaction threshold occurs at a translational energy of ≈7 kcal/mol[26] which, when equated to kT, corresponds to a temperature T of 3500 K. Hence, for temperatures of practical interest the major contribution to $P_{nm}(T)$ arises from the reaction probabilities $P_{nm}(E)$ in the near-threshold region. Thus, although the application of the

CS expression is better at high energies than the method of Babamov *et al.*, one sees that as far as the important temperature region is concerned, the Boltzmann-averaged Babamov probabilities $P_{02}^{B}(T)$ are in better agreement with the exact two-state result $P_{02}(T)$ than are the Boltzmann-averaged CS probabilities $P_{02}^{CS}(T)$, for the model system studied (high energy barrier).

Some remarks about the "threshold region" are perhaps relevant here: At 125 K, 80% of the integral $P_{02}(T)$ in Eq. (12) is contributed by energies $\leqslant$ 11.0 kcal/mol. At 250 K and 500 K the corresponding energies are $\leqslant$11.3 and $\leqslant$ 11.8 kcal/mol, respectively. In these energy regions the $P_{02}^{B}(E)$ curve in Fig. 1 is seen to be accurate.

In order to study the possibility that the differences between the P_{02}^{CS}'s and the P_{02}'s are due to problems with the analytical fits, calculations were performed assuming that the dynamics occur on given analytical diabatic potentials of the form of Eq. (10). In Fig. 3 the quantities $P_{02}(E)$, $P_{02}^{B}(E)$, and $P_{02}^{CS}(E)$ are shown, as calculated using these analytic diabatic potentials, $P_{02}^{CS}(E)$ thus being the same as before. They are compared there as a function of total energy. Once again one sees that $P_{02}^{B}(E)$ is much better than $P_{02}^{CS}(E)$ at energies near and below the reaction threshold. Also, the superiority of the $P_{02}^{CS}(E)$ over the $P_{02}^{B}(E)$ at higher energies is again evident. Comparison of Figs. 1 and 3 also shows that at high energies there is a large discrepancy between $P_{02}(E)$ for the exact potentials and $P_{02}(E)$ calculated for the dynamics on the analytical fit in Eq. (10)

In Fig. 4 plots of $\log_{10} P_{02}(T)$, $\log_{10} P_{02}^{B}(T)$, and $\log_{10} P_{02}^{CS}(T)$ vs $1/T$ for the analytic diabatic potentials are given. The results observed in Fig. 4 reemphasize the fact that the transition probability vs energy dependence at high energies is not important for this model system, in determining the low to moderate temperature Boltzmann-averaged reactive transition probabilities. Thus, one can conclude that the discrepancies between $P_{02}^{CS}(T)$ and $P_{02}(T)$ found in Fig. 2 are not due to the analytical fit, but to the breakdown of the CS approximation in the threshold region.

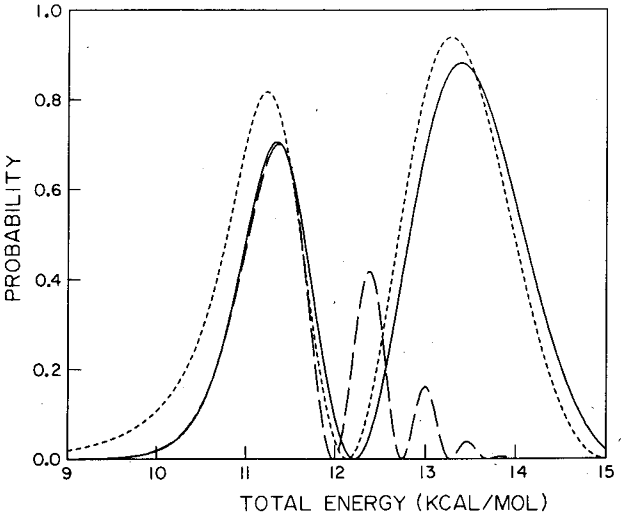

FIG. 3. The probabilities P_{02}, as a function of the total energy measured relative to the minimum of the HBr potential, obtained using model analytical diabatic potentials for all the calculations. The potential parameters used, as defined in Eq. (10), were $A = 6.880$ kcal/mol, $G = 1.062$ kcal/(mol bohr), $\rho_c = 31.75$ bohr, $\Delta_0 = 0.4162$ kcal/mol, $B = 0.9269$ mol/kcal, $C = 4.228$ mol/kcal, and $\beta = 2.052$ bohr^{-1}. $P_{02}(E)$ is denoted by —, $P_{02}^{B}(E)$ by – – –, and $P_{02}^{CS}(E)$ by ---. The discrepancy between the solid and long-dashed lines for $E > 12$ kcal/mol is discussed in the text.

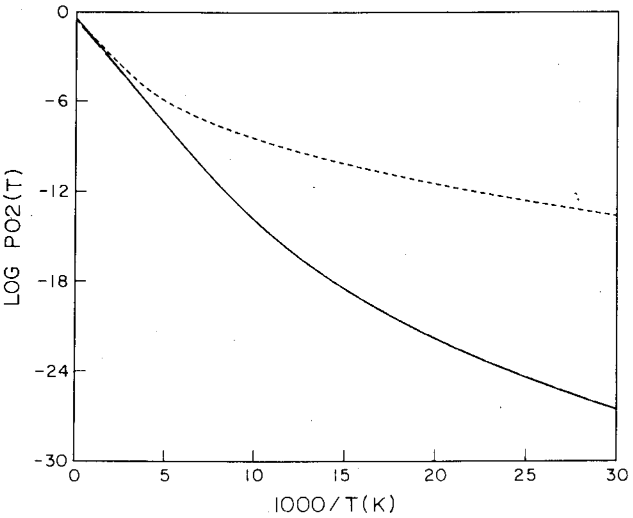

FIG. 4. $\log_{10}$ of the probabilities P_{02} as a function of $1/T$ (K) for which model analytical diabatic potentials are used for all the calculations. The potential parameters used were as in Fig. 4. $P_{02}(T)$ is denoted by —. $P_{02}^{B}(T)$ is denoted by – – –. [This plot is not visible since it coincides with that of $P_{02}(T)$]. $P_{02}^{CS}(T)$ is denoted by ----.

We turn next to a discussion of the error of the CS approximation in the threshold region. Bárány and Crothers pointed out[16] that as one condition of validity of Eq. (8) the real phase σ in Eq. (9) should not be small, more specifically not $\lesssim 1$. Values of σ are given in Table I. Comparison with Fig. 4 shows that Eq. (8) for $P_{02}^{CS}(E)$ indeed becomes invalid when $\sigma \lesssim 1$, confirming their prediction. At least in part, it is the smallness of the p momentum which makes σ small in the threshold region.

We mention here some pertinent approximations used in obtaining Eq. (6) for $P_{nm}^{B}(E)$, though they are evident in the derivation given in Refs. 5 and 6: (1) There are no potential wells in the V_{ii}'s as a function of ρ contributing importantly at the energy of interest. (This point, explicitly noted elsewhere,[5,27] follows from the derivation[5–7,28] which ex-

TABLE I. Crothers–Stückelberg σ as a function of energy.

E^{a} (kcal/mol)	σ	E^{a} (kcal/mol)	σ
7.0	0.22	10.5	0.72
7.5	0.24	11.0	1.25
8.0	0.26	11.5	2.10
8.5	0.29	12.0	2.95
9.0	0.33	12.5	3.70
9.5	0.39	13.0	4.39
10.0	0.50	13.5	4.99

[a] Total energy measured relative to the minimum of the HBr potential.

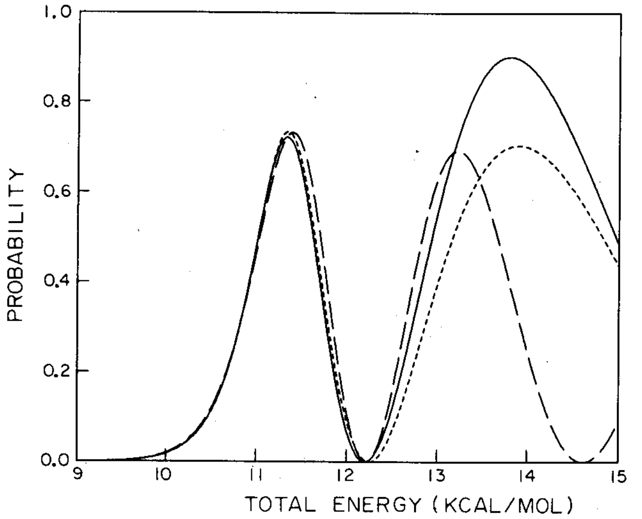

FIG. 5. The probabilities P_{02} as a function of the total energy measured relative to the minimum of the HBr potential. $P_{02}(E)$ is denoted by —, $P^{B}_{02}(E)$ by – – –, and $P^{B'}_{02}(E)$ by ---.

cludes[27] this possibility.) (2) The transition is largely localized in the vicinity of the classical turning-point ρ_0.[29,30] (3) The resonance defect Δ at ρ_0 is small relative to the vibrational spacing, at least if Eq. (6) is used in the higher energy region.

In virtue of (3) the accuracy of the formula at energies above the threshold region can be expected to gradually deteriorate with increasing resonance defect. However, it should be kept in mind that a good two-state approximation for the type of problem discussed above, valid in a wide energy region (as distinct from the threshold region), can only be made if the resonance defect Δ is small compared to the vibrational level spacing.

IV. CONCLUDING REMARKS

The formula of Babamov *et al.*, as shown in Figs. 1–4 above and Fig. 5 given in the Appendix, is an accurate approximation for energies near and below the reaction threshold, for this case of a high barrier slightly off-resonant reaction. At high energies the method is less accurate, but as seen in the previous section, these higher energies are not as important in determining the quantity of chemical interest $k_{nm}(T)$ for such reactions. In addition, the formula of Babamov *et al.*, given by Eq. (6), is a simple analytical formula and is expressed in terms of parameters that can be readily extracted from the numerical diabatic potentials.

The results obtained using the CS expression, on the other hand, are inaccurate at energies near and below the threshold for the present system, and begin to be accurate only at energies well above the threshold energy. Thus, the important quantity $k_{nm}(T)$ is not accurately given for this system at low and moderate temperatures by the CS expression. A second difficulty with the CS formula [Eqs. (8) and (9)], which may hinder its wide applicability at present, is that the adiabatic potentials must be known in the complex plane and the complex integrals must somehow be evaluated. Thus far, for that reason, the only applications of the CS formula to H-atom transfers have involved constructing a set of approximate diabatic potentials rather than using the adiabatic potentials directly.

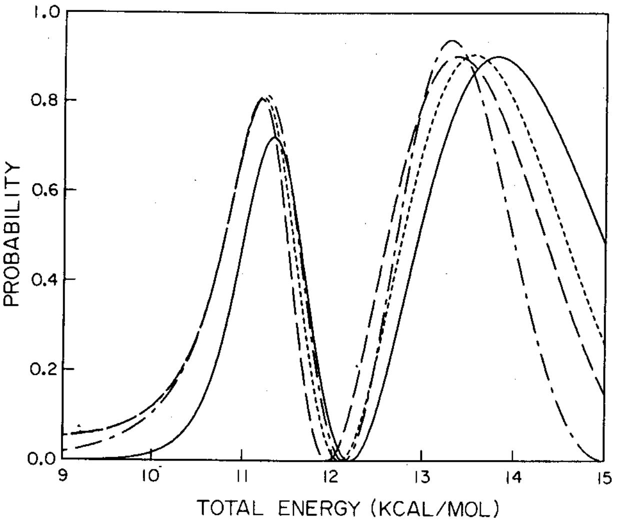

FIG. 6. The probabilities P_{02} as a function of the total energy measured relative to the minimum of the HBr potential. $P_{02}(E)$ is denoted by —, $P^{CS}_{02}(E)$ by —–—, $P^{CS'}_{02}(E)$ by – – – and $P^{CS''}_{02}(E)$ by ---.

It may be emphasized that the results presented here do not bear any relation to the applicability of the Crothers–Stückelberg formula to problems in which the energies of interest are well above the threshold. The CS formula, as well as other simpler semiclassical formulas, should be applicable to problems for which the transition probabilities at higher energies are the important ones. One example is the calculation of electron-transfer cross sections in medium energy (kev) atomic collisions for which such formulas are frequently used. The applicability of the CS formula to a low barrier reaction has been discussed elsewhere.[11,12,27]

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APPENDIX: ALTERNATIVE PROBABILITY CALCULATIONS

An alternative expression for the transition probability obtained by Babamov *et al.*[6,7] is

$$P^{B'}_{nm}(E) = \exp(-\Delta^2/\alpha F)\sin^2(\xi^s_0 - \xi^a_0), \qquad \text{(A1)}$$

where ξ^s_0 and ξ^a_0 are the elastic phase shifts for the ρ motion on the "symmetrized" potentials:

$$\begin{aligned} \epsilon^s(\rho) &= \tfrac{1}{2}[V_{11}(\rho) + V_{22}(\rho)] - V_{12}(\rho), \\ \epsilon^a(\rho) &= \tfrac{1}{2}[V_{11}(\rho) + V_{22}(\rho)] + V_{12}(\rho), \end{aligned} \qquad \text{(A2)}$$

In Fig. 5 plots of $P_{02}(E)$, $P^{B}_{02}(E)$, and $P^{B'}_{02}(E)$ vs energy are given. At energies near the reaction threshold and below they are all equivalent. However, at higher energies $P^{B'}_{02}(E)$ is seen to have the correct phase, whereas $P^{B}_{02}(E)$ does not. This difference in phase does not significantly affect the calculation of the Boltzmann-averaged transition probabilities for moderate and low temperatures. Two other expressions[31] given by Babamov *et al.* are not examined here. Our current calculations showed that they lead to reaction probabilities very similar to those of $P^{B}_{02}(E)$ and $P^{B'}_{02}(E)$. When Δ vanishes Eq. (A1) reduces to the exact two-state formula.[19]

We turn next to the choice of the value of ρ_c used in the functional forms for the V_{ij}'s [Eq. (10)] in the CS calculations. The choice of this ρ_c depends on the ρ region which needs to be the best represented. One can either use a single ρ_c, regardless of the collision energy, or let the choice of ρ_c depend on that energy.

In obtaining the real parts of the integrals in Eq. (9) one may use either the adiabatic potentials calculated from the analytic diabatic potentials of Eq. (10), or the adiabatic potentials calculated from the analytic diabatic potentials of Eq. (10), or the adiabatic potentials calculated from the real (numerical) diabatic potentials (i.e., not the fits to the diabatics). The adiabatic potentials calculated from the analytic diabatic potentials of Eq. (10) must be used in the determination of the imaginary parts of the integrals in Eq. (9).

For Fig. 6 we introduce the following notation: $P^{\mathrm{CS}}_{nm}(E)$ corresponds (as before) to calculations using the analytic fits of Eq. (10) at $\rho_c = 31.75$ bohr, independent of the energy, for both the real and imaginary parts of the integrals in Eq. (9). $P^{\mathrm{CS}'}_{nm}(E)$ corresponds to calculations using the fits of Eq. (10), with $\rho_c = \rho_0$ [the classical turning point for the mean potential $V^0(\rho)$ previously defined] at every collision energy, for both the real and imaginary parts of the integrals. Finally, $P^{\mathrm{CS}''}_{nm}(E)$ corresponds to using the actual diabatic potentials to calculate the adiabatic ones for the real parts of the integrals and using fits, with $\rho_c = \rho_0$ at every collision energy, for the imaginary parts of the integrals.

The $P^{\mathrm{CS}}_{02}(E)$'s are plotted along with $P_{02}(E)$ as a function of total energy in Fig. 6. $P^{\mathrm{CS}''}_{02}(E)$ shows the best agreement at higher energies and also involves the most complicated calculations. At energies well below the reaction threshold, not shown in Fig. 6, $P^{\mathrm{CS}'}_{02}(E)$ and $P^{\mathrm{CS}''}_{02}(E)$ are both less accurate than $P^{\mathrm{CS}}_{02}(E)$ and thus result in less accurate Boltzmann-averaged reactive transition probabilities.

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[17] The incorrectness of the fit as a whole is evident from the lack of resemblance between the circle results shown in Fig. 6 of Ref. 12 and the solid-line results shown in Fig. 3 of Ref. 7 (also shown in Fig. 1 here). An effective mass of 9000 a.u. was used in Ref. 12, whereas the correct mass to use should have been 1837.1 a.u. The value of the mass was not explicitly given [Ref. 20(a)] in Refs. 5–9. The use of an incorrect mass converted the original nearly degenerate problem into one where the off-resonance became equal to about one-quarter the spacing of the vibrational energy levels.

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[20] (a) The term $\hbar^2/m_{\mathrm{H}}$ in Eq. (2) [or the term $m_{\mathrm{H}}/\hbar^2$ in Eq. (3)] was intentionally omitted from the Schrödinger equation in Ref. 19 and Refs. 5–9. The term $m_{\mathrm{H}}/\hbar^2$, which in atomic units has a value of 1837.1 should be inserted into the Schrödinger equation and all the formulas derived from it if one wants to reproduce any of the final results using the values for the potential matrix elements given in the figures in Refs. 5, 7, and 19. The manner in which that term should be inserted into the formulas is as $m_{\mathrm{H}}/\hbar^2$ multiplying each variable which has a dimension of energy; (b) The units in Fig. 8 of Ref. 5 and Fig. 2 of Ref. 7 were not specified. These energies are in kcal/mol when they are multiplied by an appropriate conversion factor: $[627.503/(2\times 1837.1)]$. (This is $1/2m_{\mathrm{H}}$ in hartree converted to kcal/mol.)

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[22] The transformation in Ref. 21 that transforms the η_i into the ζ_i is defined as the one that maximizes the difference of the expectation values of θ in the two ζ_i. This approach allows one to calculate the potential matrix elements V_{ij} up to higher energies that the approach in Ref. 7. However, the final results for $P^{B}_{nm}(E)$ near and below the threshold region are negligibly different from those calculated by the procedure in Ref. 7.

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[24] The LEPS surface used has the asymptotic parameters of the ClHBr system. It is, however, not intended to accurately mimic the real ClHBr potential energy surface. [The barrier height of 11 kcal/mol (Ref. 13) for this LEPS surface is too high. In particular the collinear activation energy obtained from Fig. 2 is about 7 kal/mol whereas the experimental three-dimensional activation energy is about 1 kcal/mol.] [For example, see C.-C. Mei and C. B. Moore, J. Chem. Phys. **67**, 3936 (1977); R. Rubin and A. Persky, *ibid.* **79**, 4310 (1983).] The principal interest of this paper is in making comparisons for a given model surface with a substantial activation energy, and not in obtaining accurate reaction probabilities for the actual ClHBr system.

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[26] The zero-point vibrational energy of the HBr well is 3.83 kcal/mol and the classical barrier height is 11.0 kcal/mol (Ref. 13). Thus the energy above the zero-point energy at the effective reaction threshold is $\gtrsim 7$ kcal/mol, which is close to the activation energy of 7 kcal/mol for $P_{02}(T)$ in Fig. 2.

[27] V. K. Babamov and V. Lopez, J. Phys. Chem. **90**, 215 (1986). These authors point out that a recent treatment of a low barrier system (Ref. 11) inadvertently overlooked the stated limitation of no potential energy wells for the energies of interest.

[28] It was stated incorrectly in Ref. 7 that Eq. (3.6) there should apply even for reactions having a barrier of only a few kcal/mol for which "the latter plot [meaning $V_{ii}(\rho)$] may have a well as a function of ρ, which leads to quasibound states or resonances in the strong interaction region." In the above quote the "latter plot" should have read "the lower $\epsilon_i(\rho)$." As shown in Ref. 9 it is the well in the lower adiabatic potential $\epsilon_i(\rho)$ that is responsible for the resonances. Eq. (A1) applies when there are such wells but not Eq. (6).

[29] Thereby, in order that the V_{ii}'s be approximated legitimately by straight lines as in Ref. 5, the α in Eq. (7) should not be too small. In applications with realistic surfaces we expect that the slope $-dV_{12}/d\rho$ will be large enough for approximation (2) to be valid.

[30] The discrepancy in Fig. 3 between $P^{B}_{02}(E)$ and $P_{02}(E)$ for $E > 12$ kcal/

mol can be understood in terms of the breakdown of approximation (2) at those high energies when the "analytical fit" given by Eq. (10) is used there: The resulting α tends to zero in that case, causing the exponential in Eq. (6) to be abnormally small and the frequency of the oscillations in the sinusoidal term to be too large. In contrast, the original V_{12} (Fig. 8 of Ref. 5) is not a constant at ρ_0 (and hence $\alpha \neq 0$) when $E \sim 12$ kcal/mol.

[31] The two alternative expressions are obtained by an average over the exponential quantity in Eqs. (6) and (A1), respectively. This averaging procedure is defined in Eqs. (3.5)–(3.8) of Ref. 7.