COMPARISON OF MULTICHANNEL AND TWO-STATE CALCULATIONS FOR H-ATOM TRANSFER BETWEEN TWO NEARLY DEGENERATE STATES

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Multichannel and two-state calculations are made for a collinear H-atom transfer between two heavy masses. The particular reaction studied is on where the initial vibrational state of the reactants is nearly degenerate with a vibrational state of the products. The two sets of results for the reaction probability are in good agreement with each other.

1. Introduction

There have been numerous studies recently [1–14] on the dynamics of collinear light-atom exchange reaction between two heavy particles. Most of the studies have been concerned with the dynamics of *symmetric* exchange reactions [1–8]. Both the numerical treatment of the coupled equations in terms of polar coordinates and the approximate treatment of the dynamics are simpler for symmetric than for the asymmetric exchange reactions. Indeed there have been only a few studies on collinear asymmetric exchange reactions [9–14]: detailed accurate numerical calculations have been performed on the OHBr [9] and ClHBr [10,11] systems.

An interesting feature of the BrH + Cl → Br + HCl reaction is that the ground state of HBr is nearly degenerate with the $v = 2$ state of HCl. A similar but somewhat less well matched near-degeneracy exists between the $v = 1$ vibrational state of HBr and the $v = 3$ state of HCl, as well as between the higher corresponding pairs of states. In the case of symmetric transfer reactions the degeneracy between the corresponding vibrational states of the reactants and the products leads to nearly vibrationally adiabatic reactions [1]. Analogously, the vibrational distribution of the products in the BrH + Cl → Br + HCl reaction is dominated [11] by the transition to the nearly degenerate vibrational state.

The particular surface for the ClHBr reaction [10, 11] for which accurate numerical calculations were available prior to the present study, has a very small saddle point barrier and consequently no activation energy. The corresponding collinear reaction probability versus energy curve for the reaction is complicated by resonance peaks due to formation of long-lived quasi-bound states in the interaction region.

For H-atom transfer reactions on potential energy surfaces with appreciable barrier heights (such that the reaction has a non-zero activation energy) the reaction rate is, at low and moderate temperatures, determined mainly by the transition probabilities at energies near the classical reaction threshold. Simple analytical formu-

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lae for the reactive transition probability near and below the classical reaction threshold for such H-atom transfer reactions based on a two-state model for the reaction were devised recently [12]. They were used to calculated the transition probabilities for a model potential energy surface for the BrH + Cl reaction with a moderately high saddle-point barrier [12].

In this paper we present converged multichannel numerical calculations of the transition probabilities for the collinear BrHCl system with the moderately high barrier surface studied in ref. [12]. We also present results of an accurate numerical solution of the two-state model [12] for the same system and compare them to the accurate multichannel results. Comparison of the results of ref. [12] with the numerical solution of the two-state model is given elsewhere [13].

The potential surface and the accurate multichannel calculations are described and the results are presented in section 2. The probabilities for transitions between the two nearly degenerate states of the reactions and the products are calculated in section 3 by solving the equations for the two-state model. They are compared there with the results of the accurate multichannel calculations. The results are discussed in section 4.

2. Quantum mechanical treatment

It has been shown [15] that the Schrödinger equation, written in terms of mass-scaled coordinates, for a collinear atom–diatom reaction can be efficiently solved in terms of polar coordinates ρ, ϑ [16], by expanding the wavefunction in terms of wavefunctions for the ϑ motion at a fixed ρ, integrating over the ϑ motion and then integrating the resulting set of coupled equations for the ρ motion from some initial radius (ρ_0) to some final radius (ρ_{max}). The S matrix can be obtained by applying the appropriate scattering boundary conditions in the asymptotic region [15,17–19]. The details of the procedure used here are described elsewhere [19].

2.1. Reaction probabilities

The LEPS potential energy surface is that used by Babamov et al. [12]. Its parameters are listed in table 1. The integration parameters used are the initial radius (ρ_0 = 4.0 bohr), the final radius (ρ_{max} = 32.0 bohr),

Table 1
LEPS parameters for the potential surface

Quantity	HCl	HBr	ClBr
D_e(kcal/mol)	106.4	90.24	52.09
r_e (Å)	1.275	1.414	2.136
β_e (Å^{-1})	1.867	1.851	1.923
Sato parameters	0.02	0.02	0.0
zero point energy (kcal/mol)	4.23	3.83	–

the number of steps in ρ (N_ρ = 400), and the number of steps in ϑ (N_ϑ = 700). The ρ_{max} was chosen so that the initial and final states there were in the asymptotic region of the reactants' and products' space ‡. The masses used are: m_H = 1.0078 amu, m_{Cl} = 34.9688 amu, and m_{Br} = 78.9183 amu, which yield an acute angle ϑ_m of ≈11.58° for a plot of the skewed-axes [21] surface in mass-scaled coordinates.

Twelve vibrational basis functions, seven of which correspond asymptotically to the Br + HCl arrangement states and five to the Cl + HBr arrangement states, were used for generating the coupled equations for the ρ motion. The solution matrix only required stabilization [19] every ten steps. The number of open vibrational channels varied from 4 to 10 as E, the total energy measured relative to the bottom of the HBr diatomic well, was increased from 7.6 kcal/mol to 26.5 kcal/mol. The convergence, as size of the basis set was increased, was checked by comparing twelve-state calculations to sixteen-state calculations at selected energies. The resulting probabilities were virtually the same even at the highest energies. The convergence was also checked with respect to step size in ρ and step size in the vibrational coordinate ϑ. In all calculations, the dominant transition probabilities were converged to better than ±0.001%, flux was conserved to ±0.0008, and the devia-

‡ Let A be a point on the normal to x axis and having coordinates $(x,y) = (\rho_{max}, \frac{1}{2}\rho_{max} \tan \vartheta_m)$. ρ_{max} was chosen so that A is on the plateau region of the double well potential in the asymptotic region. The asymptotic vibrational states in the initial arrangement are determined along this vertical line and are effectively non-zero only in the region $(\rho_{max}, 0)$ to $(\rho_{max}, \frac{1}{2}\rho_{max} \tan \vartheta_m)$, where ϑ_m, the acute angle between the skewed axes, is given by $\tan \vartheta_m = [m_2(m_1 + m_2 + m_3)/m_1 m_3]^{1/2}$. Particle 2 is the middle atom, the hydrogen atom in this case. (The equation for ϑ_m is taken from a result in ref. [20].)

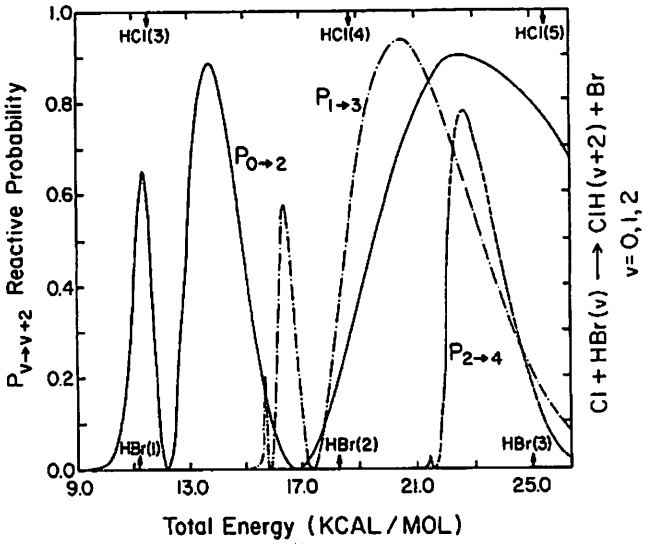

Fig. 1. Transition reactive probabilities for the reaction Cl + HBr(υ) → ClH(υ + 2) + Br with υ = 0,1,2, versus the total energy in kcal/mol relative to the bottom of the HBr diatomic well. The arrrows denote energetic thresholds.

tion of the dominant S matrix elements from symmetry was negligible even at the highest energy considered, where 10 out of 12 channels were energetically accessible.

As mentioned earlier an important feature of the ClHBr system is the near-degeneracy of the vibrational levels υ of the HBr molecule with the vibrational levels υ + 2 of the HCl molecule. Analogous to symmetric heavy–light–heavy (H–L–H) systems such as IHI, the

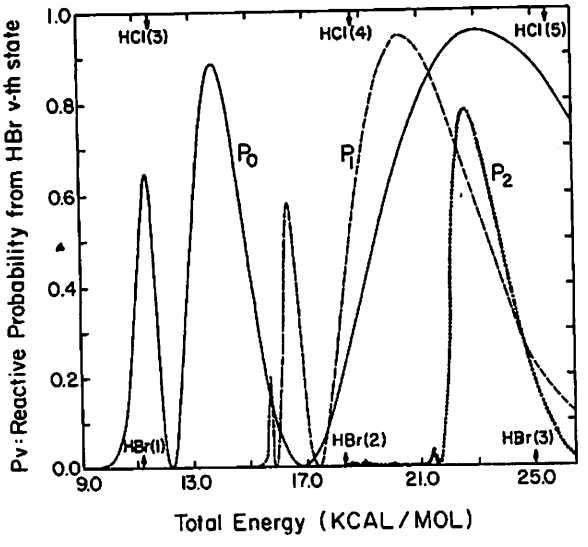

Fig. 2. Total reaction probabilities P_υ from the first three vibrational levels of HBr versus the total energy in kcal/mol relative to the bottom of the HBr diatomic well.

dominant reactive transitions occur between nearly degenerate levels. In fig. 1, the reactive probabilities P^R_{02}, P^R_{13}, and P^R_{24} for the reaction BrH + Cl → Br + HCl are plotted versus the total energy. One sees that at ≈12 kcal/mole there is a resonance spike in the threshold region of the HBr(υ = 1) to HCl(υ = 3) transition. The total reaction probabilities from the υ = 0,1, 2 levels of HBr in the same energy range are plotted in fig. 2. Comparison of figs. 1 and 2 shows clearly that there is very little HCl formed in any state other than the one nearly degenerate with the initial vibrational state of HBr.

2.2. Resonances

The spikes featured in fig. 1 in the reactive probabilities just below the thresholds of the reactions BrH(υ = 1) + Cl → Br + HCl(υ = 3) and BrH(υ = 2) + Cl → Br + HCl(υ = 4), are due to formation of quasibound states. In order to estimate a delay time, as in ref. [21], we have calculated the lifetime matrix [22] for the multichannel problem,

$$Q_{ij}(E) = i\hbar \sum_k S_{ik}\, \mathrm{d}S^*_{jk}/\mathrm{d}E. \qquad (1)$$

A 6 × 6 complex lifetime matrix (corresponding to the six open channels υ = 0 to 1 for HBr and 0 to 3 for HCl) was calculated in the energy region 15.5 to 16.0 kcal/mol, measured relative to the bottom of the HBr well. The derivatives of the S^*_{jk} were numerically evaluated with a five-point formula [23] with a fixed step size of 0.01 kcal/mol. The lifetime matrix was then diagonalized to yield the proper time delays.

3. Comparison of the two-state results to the multichannel ones

As discussed elsewhere [12–14] the main features of the dynamics of the BrH + Cl → Br + HCl reaction can be represented by a pair of coupled equations

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

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

where i denotes the initial vibrational state of HBr and j denotes the i + 2 vibrational state of the HCl which

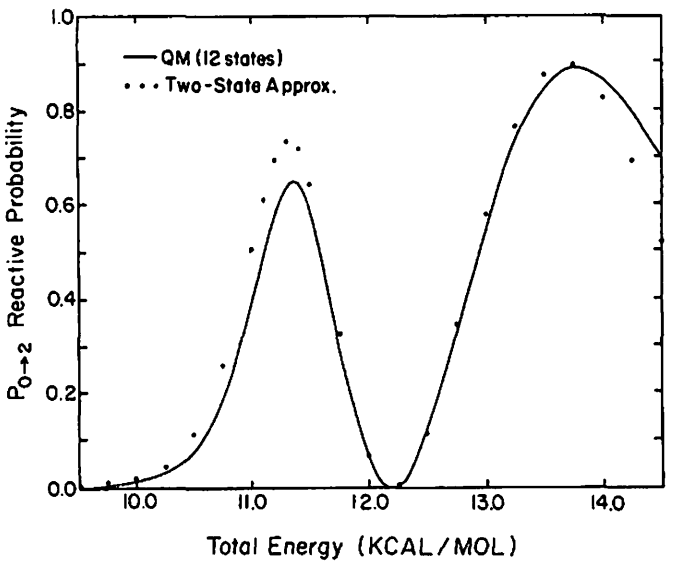

Fig. 3. Reactive transition probability P^{R}_{02} for the BrH(v = 0) + Cl → Br + HCl (v = 2) reaction. The solid line is obtained from a converged (twelve-state) calculation in section 2 and the points are obtained from solving the two-state model [eq. (2)]. The energy is measured from the bottom of the HBr well.

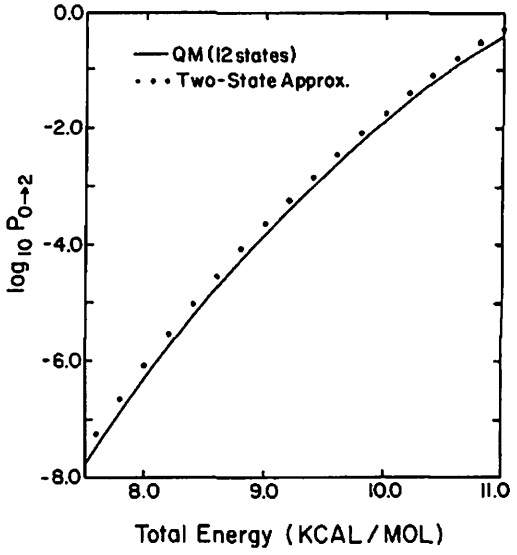

Fig. 5. The $\log_{10}$ of the reaction transition probability P^{R}_{02} for the BrH(v = 0) + Cl → Br + HCl(v = 2) reaction at energies below the classical threshold (the tunneling region). The solid line represents the accurate twelve-state calculations (section 2) and the points are obtained from the two-state model [eq. (2)].

is nearly degenerate with the initial HBr one. The procedure of obtaining eq. (2) is discussed elsewhere [12], as are approximate methods of solving it [12–14].

Eq. (2) was solved numerically to obtain the reactive transition probabilities P^{R}_{02} and P^{R}_{13}. The resulting reactive transition probabilities P^{R}_{02} and P^{R}_{13} are shown in figs. 3 and 4, respectively, together with the results of the multichannel calculations from section 2. The logarithm of the transition probabilities P^{R}_{02} and P^{R}_{13} at energies below the classical threshold are shown in figs. 5 and 6, respectively.

The quasibound state of the uncoupled adiabatic equation,

$$[-\tfrac{1}{2}\mathrm{d}^2/\mathrm{d}\rho^2 + \epsilon_i(\rho)]\,\varphi_i(\rho) = E\varphi_i(\rho), \qquad (3)$$

which correlates asymptotically to the v = 1 state of HBr, is mostly responsible for the resonance peak on the P^{R}_{13} probability versus energy curve (fig. 4).

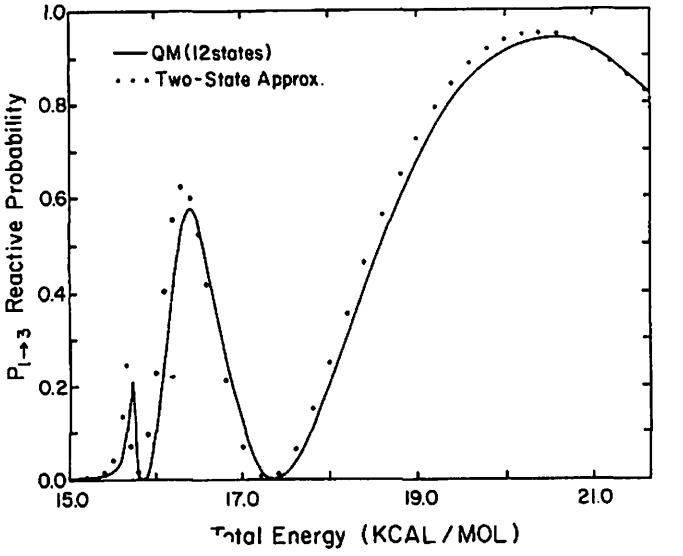

Fig. 4. Same as fig. 3 for the v = 1 state of HBr and the v = 3 state of HCl.

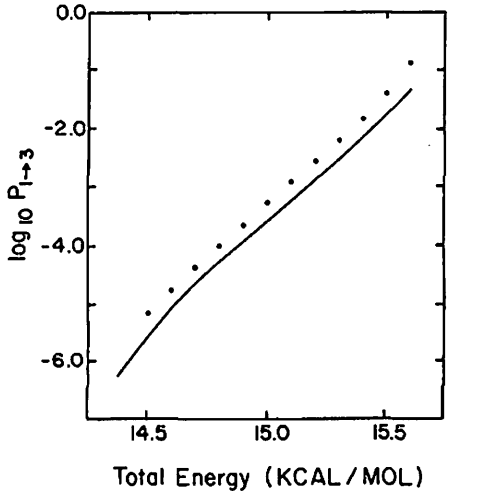

Fig. 6. Same as fig. 5 for the v = 1 state of HBr and the v = 3 state of HCl.

4. Discussion

A comparison of the results presented in figs. 3–6 shows that the two-state model, given by eq. (2) for H-atom transfer between two nearly degenerate states, simulates well the main features of the dynamics. The deviations of the two-state results from the converged multichannel ones are similar to the differences between the two-state [1] results and the multichannel ones [6,24] for the higher vibrationally excited states in the symmetric reaction.

The results for the reactive transition probabilities between the two nearly degenerate states show oscillations somewhat similar to those between the exactly degenerate states with same quantum number in a symmetric exchange reaction [1–8]. The main difference from the symmetric case is that the oscillations do not approach the maximum probability of 1 as closely as they do in the symmetric case. This difference is due to the lack of exact resonance between the reactant and product vibrational levels. Approximate analytical formulae for the model based on eq. (2) [13] show that in addition to the sine square term responsible for the oscillations in the symmetric case [1] the transition probability is reduced by an additional factor which depends exponentially on the resonance energy defect for the reaction. In the present formalism this factor is responsible for the maxima of the P_v values in fig. 2 and for the P_{ij} values in figs. 3 and 4 being smaller than unity.

As in ref. [21], the resonance is localized in a single eigendelay which corresponds to an eigenstate dominated by the $v = 1$ HBr vibrational state. The peak in the resonant ClHBr delay time is $\approx 6.6 \times 10^{-13}$ s.

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