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Comparison of 3D Classical Trajectory and  
Transition-State Theory Reaction Cross Sections

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In a companion paper,<sup>1</sup> a comparison is made of the energy dependent reaction probability<sup>2</sup> calculated for a variety of collinear systems from classical trajectories and from transition-state theory. Although there is excellent agreement for a system such as  $\text{H}^+\text{H}_2 \rightarrow \text{H}_2+\text{H}$ , in which both the potential and the particle masses are symmetric, significant deviations occur for more asymmetric reactions (e.g.,  $\text{Br}+\text{H}_2 \rightleftharpoons \text{HBr}+\text{H}$ ). A detailed analysis shows that the calculated differences arise from the violation of two assumptions of transition-state theory; that is, the transition-state distribution does not have the equilibrium form and/or the transmission coefficient is not equal to unity. Since there are significant constraints on the dynamics of a reacting system that is restricted to collinear collisions (1D), it is essential to perform corresponding comparisons for the three-dimensional problem (3D). For the symmetric  $\text{H}_3$  system, excellent agreement with transition-state theory is obtained for both 3D and 1D trajectories.<sup>3</sup> This note reports the results obtained on an extended LEPS surface for a thermo-neutral reaction with a well-defined asymmetric barrier.<sup>1,4</sup> The surface parameters, which correspond to an artificially modified  $\text{H}_3$  system,<sup>4</sup> are chosen so that the barrier is in the entrance valley for the forward reaction ( $\text{A}+\text{BC} \rightarrow \text{AB}+\text{C}$ ) and, therefore, in the exit valley for the backward reaction ( $\text{C}+\text{BA} \rightarrow \text{CB}+\text{A}$ ); the reactions  $\text{A}+\text{BC} \rightleftharpoons \text{AC}+\text{B}$  are excluded by the choice of parameters. As masses for the atoms, the values  $m_{\text{A}}=m_{\text{C}}=1$ ,  $m_{\text{B}}=2$  were chosen because this combination leads to a simply defined transition state.

To compare the trajectory and transition-state theory results, the average reaction cross section  $\bar{S}(E)$  introduced in I was used. For the case of an atom and a diatomic molecule with a linear transition state,

the functional form obtained from classical transition-state theory is<sup>2</sup>

$$\bar{S}_{\text{Art}}(E) = \frac{\kappa}{32\pi\mu_{A,BC}} \frac{\nu_v}{\nu_s \nu_b^2} \frac{I_{\ddagger}}{I_I} \frac{(E-E_c)^4}{E^3} \quad (\kappa=1) \quad (1)$$

where  $E$  is the total system energy (relative to the separated atom and diatomic molecule),  $E_c$  is the barrier height (relative to the same energy zero);  $I_{\ddagger}$  and  $I_I$  are the moments of inertia of the transition state and the reactant molecule, respectively;  $\nu_v$ ,  $\nu_s$ , and  $\nu_b$  are the molecular stretching frequency and the transition-state symmetric stretching and bending frequencies, respectively;  $\mu_{A,BC}$  is the reduced mass of A and BC, and  $\kappa$  is the transmission coefficient. The calculated values of  $\bar{S}_{\text{Art}}(E)$  for a series of total energies  $E$  are listed in the last column of Table I. They are of course identical for the forward and reverse reactions since the reactant and saddle point properties of the surface are the same. In column 4 of Table I are listed the average cross sections  $\bar{S}_r(E)$  determined by using the usual Monte Carlo variables<sup>5</sup> to specify the initial translational, rotational, and vibrational energy of the collision trajectories subject to the restriction that they sum to the total energy  $E$ .

It is clear from the table that the cross sections for the forward and reverse reactions disagree with those from transition-state theory and that the deviations for both are of corresponding magnitudes, the ratio of  $\bar{S}_{\text{Art}}$  to  $\bar{S}_r$  being a factor of 2 to 3 for the energies studied. However, in agreement with transition-state theory, the forward and backward reactions do have very similar rates; the reason for their somewhat greater divergence at  $E = 1.0\text{eV}$  is not clear.

As a first step in determining the source of the transition-state theory error for these reactions, we list in column 3 as  $\bar{S}_{tr}(E)$  the values of the cross section that would be obtained if all trajectories reaching the transition state went on to give products. As in the 1D results, the ratio of  $\bar{S}_r/\bar{S}_{tr}$  is a measure of the transmission coefficient, while the difference between  $\bar{S}_{tr}$  and  $\bar{S}_{Art}$  is a consequence of nonequilibrium distributions in the transition state. From the results in Table I at the lower energies ( $E \leq 1.5\text{eV}$ ), the value of  $\kappa$  is in the range  $0.83 < \kappa < 1.0$ ; at  $E=2$  for the backward reaction  $\kappa$  is significantly smaller for a somewhat artificial reason.<sup>6</sup> Of particular interest is the fact that the values of  $\kappa$  for the two reactions are not greatly different even though the barrier is in the entrance valley for the forward reaction and in the exit valley for the backward reaction. Thus, the 3D calculations here contrast sharply with the 1D treatment, in which deviations in the forward direction arose primarily from  $\kappa < 1$  and in the reverse reaction from a nonequilibrium transition-state distribution. Clearly in the 3D trajectories, the additional degrees of freedom of system make reflection a less likely occurrence.

It is now well known that a sufficient condition for the validity of transition-state theory, modified to take account of inaccessible regions of phase spaces,<sup>1,7</sup> is that the motion along the reaction coordinate can be separated from the other degrees of freedom, which behave adiabatically.<sup>8</sup> On this basis, Polanyi and Wong<sup>3,9</sup> suggested that the forward reaction should obey transition-state theory while the backward reaction should not, since in the former the barrier is encountered before the system

rounds the "bend" in the energy surface (i.e., before vibrational and translational energy are transposed) while in the latter, the barrier is encountered after rounding the bend. The trajectory analysis of the transition-state distribution does show that, as far as the symmetric stretching mode is concerned, the backward reaction deviates more from adiabaticity than the forward reaction which is nearly adiabatic. However, it is clear from Table I that the  $\bar{S}(E)$  values do not reflect this difference; i.e., the two reactions show corresponding deviations from the transition-state theory. Further analysis is in progress, particularly of the importance of the transition-state bending modes, to complete our understanding of the origins of deviations from transition-state theory in three-dimensional collisions.

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9. PW refer to the forward and reverse reaction as being on surfaces I and II, respectively.

Table I. Average Reaction Cross Sections

Forward Reaction (A+BC → AB+C)				
$E(\text{eV})$	$E-E_c(\text{eV})$	$\bar{S}_{\text{tr}}(E)^{a,b}$	$\bar{S}_r(E)^{a,b}$	$\bar{S}_{\text{Art}}(E)$
0.5	.194	0.041	$0.38 \pm 0.008$	0.122
0.75	.444	0.605	$0.594 \pm 0.063$	0.992
1.0	.694	1.56	$1.44 \pm 0.12$	2.50
1.5	1.194	3.70	$3.39 \pm 0.22$	6.49
2.0	1.694	6.45	$5.82 \pm 0.35$	11.10
Reverse Reaction (AB+C → A+BC)				
0.5	.194	0.046	$0.046 \pm 0.013$	0.122
0.75	.444	0.515	$0.509 \pm 0.083$	0.992
1.0	.694	2.26	$2.22 \pm 0.26$	2.50
1.5	1.194	4.42	$3.87 \pm 0.44$	6.49
2.0	1.694	9.71	$5.91 \pm 0.64$	11.10

<sup>a</sup> Values in a.u.; the error limits correspond to the standard deviation of the mean.

<sup>b</sup> Average collisional cross section weighted by the relative translational energy (J. Chem. Phys. 51, 5193 (1970), Eq. 21).