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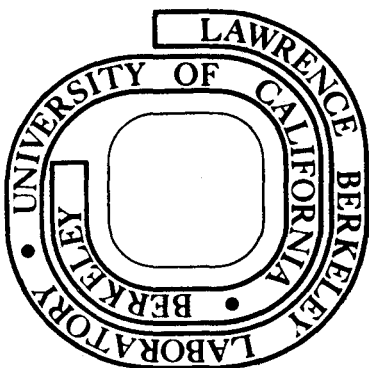
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ACCURACY OF TRANSITION STATE THEORY
FOR THE THRESHOLD OF CHEMICAL REACTIONS WITH ACTIVATION ENERGY :
COLLINEAR AND THREE DIMENSIONAL H + H₂

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Abstract

Microcanonical classical transition state theory is compared to the appropriate classical trajectory calculations (not the usual "quasi-classical" type) for the collinear and the three dimensional H + H₂ reaction. The results show that transition state theory is essentially exact up to several tenths of an eV above the barrier height; at higher energies it begins to fail, but much less so for the three-dimensional case. These results show that the fundamental assumption of transition state theory is excellent for the threshold region. If transition state theory can be implemented quantum mechanically, therefore, it should provide a quantitative description of rate constants for such reactions.

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One of the major failures of the classical trajectory description of chemical reactions is the inability to deal correctly with the threshold region of a reaction with an activation barrier, for here quantum effects (i.e., tunneling) become important. This is a serious shortcoming, too, since it is primarily this threshold region which determines the thermally averaged rate constant.¹

For low energies, however, the fundamental assumption² of transition state theory--namely, that flux through a particular surface in configuration space which divides reactants from products can be identified as the reactive flux--becomes valid. As has been recently emphasized,^{3,4} though, the additional assumption of separability of motion along a reaction coordinate, which is invoked in traditional transition state theory, is a poor approximation in the threshold region.

The suggestion has been made,³ therefore, that transition state theory should provide an accurate description of the threshold region provided it can be applied quantum mechanically and without invoking additional approximations such as separability.

To gain a more quantitative feeling about the validity of transition state theory for the threshold region, we have carried out, and report here, classical calculations for the collinear and for the three dimensional $H + H_2 \rightarrow H_2 + H$ reaction on the Porter-Karplus⁵ potential surface. The classical trajectory calculations were not with the usual "quasi-classical" initial conditions,⁶ which are designed to approximate the quantized aspect of the vibrational degree of freedom, but rather involved a classical microcanonical average over all initial conditions, including vibration; it is this latter type of classical trajectory calculation to which classical microcanonical transition state theory corresponds. The relevant expressions⁷ were evaluated without any subsidiary approximations, such as harmonic expansions of the potential energy about the saddle point, etc.

Although these classical calculations are not of direct physical significance--because they ignore quantum effects which are important in the threshold region of this

reaction--they do provide a rigorous and meaningful⁸ test of the fundamental assumption of transition state theory, i.e., that all the flux through the specially chosen dividing surface is reactive flux. To the extent that this assumption is valid classically, one expects it also to be valid quantum mechanically.

Figure 1 shows the reaction probability of the collinear $H + H_2$ reaction as a function of total energy above the barrier height, for the microcanonical classical trajectory calculation (CL DYN = classical dynamics) and for microcanonical transition state theory (CL TST). Pechukas and McLafferty⁹ devised an ingenious geometrical criterion which showed that classical transition state theory is formally exact in this case for energies up to about 0.1 eV above the barrier height. The present numerical results show it to be essentially exact to over 0.2 eV above the barrier height, and then it begins to fail substantially, being over a factor of 2 too large at 1 eV.

The three dimensional trajectory and transition state results for the microcanonical reactive cross section of $H + H_2$ are shown in Figure 2. The transition state approximation is seen to be essentially exact up to a few tenths of an eV, and even as it begins to fail, the failure is much less drastic than in the collinear version; at 1 eV above the barrier height the transition state theory cross section is only about 10% too large.

These classical results provide extremely encouraging support for the accuracy of transition state theory for the threshold region of chemical reactions with activation energy, and the outlook is substantially better in three dimensions than for the collinear model. Should this accuracy be maintained for the quantum mechanical version of transition state theory,³ then one will have a quantitative description of rate constants for such reactions. Work in progress seems to indicate this to be the case.

Acknowledgment

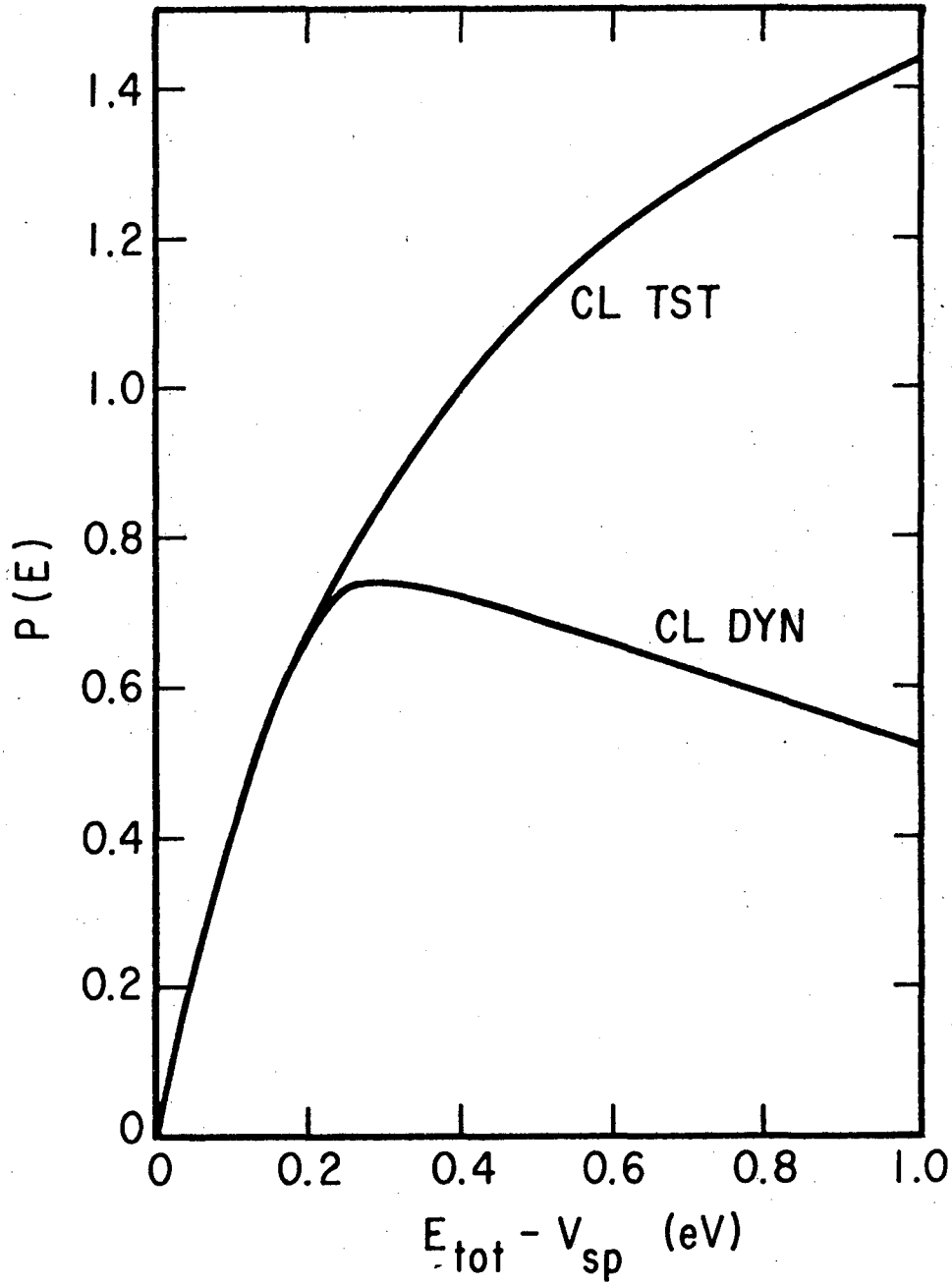
Support by the U. S. Atomic Energy Commission, the National Science Foundation (GP-41509X), and a Teacher-Scholar grant to WHM from the Camille and Henry Dreyfus Foundation are gratefully acknowledged. The computations reported herein were performed on a Datacraft 6024/4 mini-computer funded by NSF grant GP-39317.

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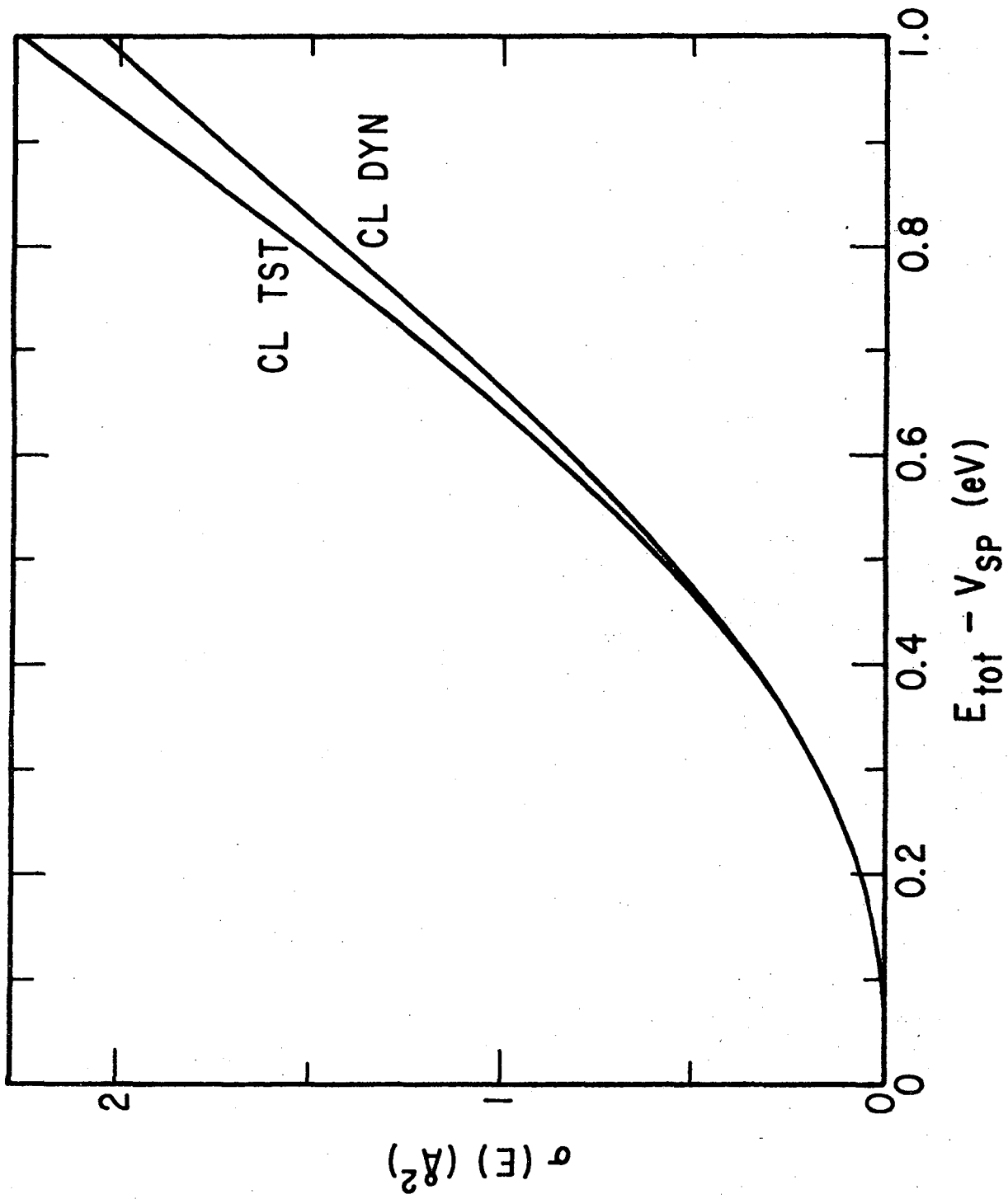
FIGURE CAPTIONS

1. Reaction probability for the collinear $H + H_2$ reaction on the Porter-Karplus potential surface from a microcanonical classical trajectory calculation (CL DYN) and microcanonical classical transition state theory (CL TST), as a function of total energy above the barrier height. (lev = 23.06 Kcal/mole)
2. Same as Figure 1, except that $\sigma(E)$ is the reactive cross section for the three dimensional $H + H_2$ reaction.



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Fig. 1



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Fig. 2

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