Submitted to Journal of Chemical Physics

LBL-3791
Preprint c

SEMICLASSICAL TRANSITION STATE THEORY FOR NON-SEPARABLE SYSTEMS: APPLICATION TO THE COLLINEAR H + H_2 REACTION

Sally Chapman, Bruce C. Garrett, and William H. Miller

April 1975

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

SEMICLASSICAL TRANSITION STATE THEORY FOR NON-SEPARABLE SYSTEMS: APPLICATION TO THE COLLINEAR H + H_2 REACTION*

Sally Chapman, Bruce C. Garrett and William H. Miller

Department of Chemistry, and Inorganic Materials Research Division
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

0 0 1 0 4 3 0 2 5 9 8

ABSTRACT

Two different kinds of semiclassical approximations are used to evaluate a previously obtained quantum mechanical transition state theory rate expression. No assumptions, however, such as separability of the Hamiltonian, vibrationally adiabatic motion along a reaction coordinate, etc., are incorporated. Application is made to the collinear $H + H_2$ reaction, and agreement with accurate quantum scattering calculations is found to be reasonably good. The results indicate that transition state theory--provided no assumptions of separability are included--is probably as accurate quantum mechanically as it has been found to be classically for describing the threshold of chemical reactions with an activation barrier.

I. INTRODUCTION.

The accurate description of the threshold region of a chemical reaction with an activation barrier is one of the few important features of chemical reaction dynamics that can not be adequately described by the usual classical trajectory methods. Because of the importance of this region for determining the thermal rate constant, however, this is a serious shortcoming of a completely classical description. The complex-valued classical trajectory approach of classical S-matrix theory[1] has shown that it can describe this tunneling region well, but it is often a difficult calculation to carry out and one desires simpler models which are accurate.

There have been several recent studies which indicate that the "fundamental assumption"[2] of transition state theory--i.e., the identification of all flux through a specially chosen surface in coordinate space as reactive flux--is quite accurate for energies in the threshold region. Pechukas and McLafferty,[3] for example, have shown that within the realm of classical mechanics transition state theory is exact for sufficiently low energy; for collinear system they have also found a simple geometrical criterion to determine a lower limit to this energy below which transition state theory is exact. Also, Chapman, Garrett, and Miller[4] have compared the microcanonical version of classical transition state theory with a microcanonical classical trajectory calculation for the collinear and for the three-dimensional $H + H_2$ reaction. In the three-dimensional case, for example, they find that transition state theory is in essentially exact agreement with the trajectory results for energies up to about 0.3 eV above the height of the activation barrier, and even at the relatively high energy of 1 eV above the barrier height it is only 10% larger than the exact trajectory result. This means that in a strictly classical world transition state theory would give the rate constant for this reaction essentially exactly for temperatures up to thousands of degrees. Work by Marcus[5] and by Morokuma and Karplus[6] has also indicated that classical transition state theory is a good approximation to classical dynamics for collision energies not too far above the barrier height.

As noted above, however, quantum effects are important in the threshold region, so that a quantum mechanical version of transition state theory is required. Previous quantum mechanical versions of transition state theory,[7,8] however, incorporate other approximations--e.g., separability of the Hamiltonian about the saddle point of the potential surface, vibrationally adiabatic motion along a reaction coordinate, etc.,--in addition to the "fundamental assumption" itself. It is our hypothesis that these additional dynamical approximations are the reason that transition state theory has given poor agreement with accurate quantum scattering calculations;[9] i.e., we believe that the fundamental assumption of transition state theory is itself accurate--as in the classical examples described above--but that it must be implemented quantum mechanically and without introducing any dynamical approximations, such as separability.

Such a theory has recently been formulated,[10] i.e., a fully quantum mechanical theory which invokes the fundamental assumption of transition state theory but makes no other dynamical approximations. By introducing a semiclassical approximation for the Boltzmann operator,[11] the semiclassical limit of this quantum mechanical transition state theory has also been derived.[12] This "semiclassical transition state theory"[12] leads to a very interesting and physically intuitive picture of the tunneling dynamics which characterizes the threshold region: The tunneling takes place along a periodic classical trajectory on the upside-down potential surface, and the stability parameters[13] which characterize the periodic orbit appear in the theory as the generalization of the normal mode frequencies of the "activated complex". It is important that although this model invokes a semiclassical approximation to the quantum transition state rate expression obtained in reference 10 , no approximations such as separability, or vibrational adiabaticity, are introduced.

This paper presents the first numerical results of this semiclassical limit of quantum transition state theory, here for the simplest possible example, the collinear $H + H_2$ reaction. The agreement with quantum scattering calculations is reasonably good, and one sees, for example, how the tunneling "cuts the corner" increasingly as the energy is decreased. Section II summarizes the semiclassical limit of quantum transition state theory, and the results of the calculations are presented in Section IV.

Section III describes another kind of semiclassical approach to evaluating the quantum rate expression, this based on a semiclassical approximation for the quantum mechanical phase space distribution function. The results of calculations based on this model are also presented in Section IV, and they too are in good agreement with accurate scattering calculations. It is important that this approach is relatively simple to implement, so that it may be a practical procedure for treating reactive systems in three-dimensions.

II. SUMMARY OF PERIODIC ORBIT THEORY.

The rate constant for a collinear A + BC reaction given by

$$k_{b\leftarrow a}(T) = Q_a(T)^{-1} (2\pi\hbar)^{-1} \int^{\infty} dE\ N(E) \quad , \tag{2.1}$$

where E is a total energy and $Q_a(T)$ is the partition function per unit volume (actually per unit length for a collinear system) for noninteracting reactants. N(E) is the "cummulative reaction probability" that was designated P(E) in reference 12; we have made this change in notation in order to conform more closely with previous work of other researchers. Eq. (2.1) is no approximation in itself, and to see how the semiclassical "periodic orbit" result of reference 12 relates to other theories, it is illustrative to review the form taken by N(E) in various quantum mechanical and classical approximations.

The dynamically exact quantum mechanical rate constant, for example, corresponds to Eq. (2.1) with N(E) given in terms of reactive S-matrix elements which come from a quantum scattering calculation:

$$N_{QM}(E) = \sum_{n_b, n_a} |S_{n_b, n_a}(E)|^2 \quad , \tag{2.2}$$

where n_a and n_b denote the quantum state of the reactant and product molecules, BC and AB, respectively. Dynamically exact classical mechanics corresponds to Eq. (2.1) with N(E) given by

$$N_{CL}(E) = 2\pi\hbar\ h^{-F} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\ \ \delta(E-H)\ \delta[f(\underset{\sim}{q})]$$

$$\times\ \frac{1}{2}\left|\frac{\partial f}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{p}/m\right| \frac{1 + (-1)^M}{2(M + 1)} \quad ,$$

$$(\underset{\sim}{q},\underset{\sim}{p}) = (q_i,p_i),\ i = 1,2,\ldots,\ F \tag{2.3}$$

where F is the number of degrees of freedom (F = 2 in the collinear case), $f(\underset{\sim}{q})$ is the function of coordinates which defines the surface in configuration space, $f(\underset{\sim}{q}) = 0$, which divides reactants and products, and M is the number of time a trajectory which begins with initial conditions $(\underset{\sim}{p},\underset{\sim}{q})$ on the dividing surface recrosses this surface as time is run forward to $+\infty$ and backward to $-\infty$. $N_{CL}(E)$ is independent of the particular choice of the dividing surface.

Classical transition state theory corresponds to Eq. (2.1) with N(E) given by Eq. (2.3) with the assumption M = 0, i.e., the assumption that there are no trajectories which recross the dividing surface;[2,3] this result, of course, is not invariant to the choice of the dividing surface. Thus,

$$N_{CL\ TST}(E) = 2\pi\hbar\ h^{-F} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\ \ \delta(E-H)\ \delta[f(\underset{\sim}{q})]\ \frac{1}{2}\left|\frac{\partial f}{\partial \underset{\sim}{q}}\cdot\frac{\underset{\sim}{p}}{m}\right| \quad . \tag{2.4}$$

If the coordinate q_F measures distance normal to the dividing surface, then

$$f(\underset{\sim}{q}) = q_F \quad ,$$

and it is not hard to show that Eq. (2.4) then becomes

$$N_{CL\ TST}(E) = h^{-(F-1)} \int d\underset{\sim}{p}_{F-1} \int d\underset{\sim}{q}_{F-1}\, h(E - H_{F-1}) \quad , \qquad (2.5)$$

where h(x) is the step-function

$$h(x) = 1,\ x > 0$$
$$\qquad 0,\ x < 0 \quad ,$$

and the F-1 dimensional phase space average is over all degrees of freedom other than q_F; H_{F-1} is the Hamiltonian for the remaining F-1 degrees of freedom with the potential energy surface evaluated at $q_F = 0$. For the collinear case, Eq. (2.5) reads

$$N_{CL\ TST}(E) = h^{-1} \int dp_u \int du\, h[E - \frac{p_u^2}{2m} - V(u,0)] \quad , \qquad (2.6)$$

where u is the coordinate along the dividing surface (actually a dividing line in the collinear case) and V(u,s) is the total potential energy function; s is the coordinate perpendicular to the dividing surface. (See Figure 1 of reference 10.) It is clear from Eqs. (2.5) and (2.6) that $N_{CL\ TST}(E)$ is the classical approximation to the number of quantum states for the system with F-1 degrees of freedom which have energy less than or equal to E.

The conventional quantum mechanical version of transition state theory[7] is meaningful only if the potential is assumed to be separable;

$$V(u,s) = V_1(u) + V_2(s) \quad ; \qquad (2.7)$$

$V_1(u)$ is a potential well, and $V_2(s)$ a potential barrier. If $P_{tun}(E_t)$ is the one dimensional tunneling probability for the s degree of freedom with translational energy E_t and if $\{\varepsilon_n\}$, $n = 0,\ldots$ are the vibrational eigenvalues for the potential well V_1, then N(E) is given in the separable limit of quantum mechanical transition state theory by

$$N_{Sep\ QM\ TST}(E) = \sum_{n=0} P_{tun}(E - \varepsilon_n) \quad . \tag{2.8}$$

Although the vibrationally adiabatic model[8] does not assume separability in precisely the same form as Eq. (2.7), it leads to a function N(E) of the same form as Eq. (2.8).

The more general quantum mechanical transition state theory derived in reference 10 corresponds to Eq. (2.1) with N(E) given by

$$N_{QM\ TST}(E) = 2\pi\hbar\ \mathrm{tr}[\delta(E - H)\ \delta(s)\ \tfrac{1}{2}|P_s/m|] \quad , \tag{2.9}$$

which one recognizes as the obvious quantum mechanical version of Eq. (2.4). The semiclassical limit[12] of this expression involves a periodic trajectory on the <u>upside-down</u> potential surface. If $\theta(E)$ is the classical action integral (in units of $\hbar$) along this periodic trajectory with energy E and u(E) the stability parameter which characterizes it (it is an <u>unstable</u> periodic trajectory), then the semiclassical limit of Eq. (2.9) is

$$N_{SC\ TST}(E) = \sum_{n=0} \frac{1}{1 + \exp[2\theta(E) + (n + \frac{1}{2})\ u(E)]} \quad . \tag{2.10}$$

The period of the periodic trajectory is related to the action integral by

$$\tau_f(E) = -2\hbar\theta'(E) \quad ,$$

and it is useful to define the frequency $\omega(E)$ by

$$\omega(E) = u(E)/\tau_f(E) \quad ;$$

Eq. (2.10) then reads

$$N_{SC\ TST}(E) = \sum_{n=0} \frac{1}{1 + \exp[2\theta(E) - 2\theta'(E)\ \hbar\omega(E)(n + \frac{1}{2})]} \quad . (2.11)$$

If the potential function is separable, as in Eq. (2.7), then the action integral $\theta(E)$ is the ordinary one dimensional barrier penetration integral for the potential barrier $V_2(s)$, and ω--which is not a function of energy in this case--is the harmonic frequency for the potential well $V_1(u)$.

Eq. (2.11), however, actually gives poor agreement with the exact quantum mechanical $N_{QM}(E)$ of Eq. (2.2), and this can be understood in the following way. For a separable potential function [Eq. (2.7)] Eq. (2.8) is the correct result for quantum mechanical transition state theory. The one dimensional WKB approximation for the tunneling probability is[14]

$$P_{tun}(E_t) = \frac{1}{1 + \exp[2\theta(E_t)]} \quad , \qquad (2.12)$$

where $\theta(E_t)$ is the barrier penetration integral for the potential barrier $V_2(s)$ with translational energy E_t. With this semiclassical approximation for the one dimensional tunneling probability and with a harmonic approximation to the energy levels of the potential well $V_1(u)$,

$$\varepsilon_n = (n + \frac{1}{2})\hbar\omega \quad , \tag{2.13}$$

Eq. (2.8) becomes

$$N_{Sep\ QM\ TST}(E) \simeq \sum_{n=0} \frac{1}{1 + \exp[2\theta(E - (n + \frac{1}{2})\hbar\omega]} \quad . \tag{2.14}$$

This is seen to be identical to Eq. (2.11) <u>if</u> one makes the approximation

$$\theta(E - (n + \frac{1}{2})\hbar\omega) \simeq \theta(E) - \theta'(E)\hbar\omega\ (n + \frac{1}{2}) \quad , \tag{2.15}$$

i.e., if one keeps only the lowest order term in an expansion in powers of $\hbar$. The approximation in Eq. (2.15) is certainly consistent with the semiclassical nature of the theory, but for very quantum-like systems, such as $H + H_2$, the frequency ω is large enough to make Eq. (2.15) a poor approximation.

The idea for correcting Eq. (2.11), therefore, is to identify the exponent as the first two terms of a Taylor series expansion in powers of $\hbar$ and then to "unexpand" it. One thus defines the energy E_n so that

$$\theta(E_n) = \theta(E) - \theta'(E)\, \hbar\omega(E)\, (n + \tfrac{1}{2}) \quad ,$$

to lowest order in $\hbar$, and this leads to the choice

$$E_n = E - \hbar\omega(E_n)\, (n + \tfrac{1}{2}) \quad ; \tag{2.16}$$

i.e., E_n is the root of this equation (which is easily solved by successive substitution). The interpretation is that E_n is the translational energy for motion along the "reaction coordinate"--i.e., the periodic path--if the transverse degree of freedom is in vibrational quantum state n. The modified expression for semiclassical transition state theory becomes

$$N_{SC\ TST}(E) = \sum_{n=0} \frac{1}{1 + \exp[2\theta(E_n)]} \quad , \tag{2.17}$$

with E_n determined for a given value of E by Eq. (2.16).

In the separable limit the frequency $\omega(E)$ becomes energy independent, and Eqs. (2.16) and (2.17) give Eq. (2.14); the only approximation in this case is the WKB approximation for one dimensional tunneling, and one knows this to be quite adequate. The interest in the semiclassical version of transition state theory, however, is for the nonseparable case, and Section IV gives numerical results for the comparison of Eqs. (2.16) and (2.17) with the exact quantum result for N(E), Eq. (2.2).

III. A SEMICLASSICAL PHASE SPACE DISTRIBUTION.

The quantum mechanical rate expression of transition state theory obtained in reference 10 was shown to be equivalent to the completely classical expression if the classical distribution function, $h^{-F}\, e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})}$, is replaced by the Wigner distribution function, $W(\underset{\sim}{p},\underset{\sim}{q})$:

$$W(\underset{\sim}{p},\underset{\sim}{q}) = h^{-F} \int d\underset{\sim}{q}' \; e^{-i\underset{\sim}{p}\cdot\underset{\sim}{q}'/\hbar} \langle \underset{\sim}{q} + \tfrac{1}{2}\underset{\sim}{q}' | e^{-\beta H} | \underset{\sim}{q} - \tfrac{1}{2}\underset{\sim}{q}' \rangle \quad . \tag{3.1}$$

That is, the rate constant of quantum transition state theory[10] is

$$k_{b\leftarrow a}(T) = Q_a(T)^{-1} \int d\underset{\sim}{p} \int d\underset{\sim}{q} \; W(\underset{\sim}{p},\underset{\sim}{q}) \; \delta[f(\underset{\sim}{q})] \, \tfrac{1}{2} \left| \frac{\partial f}{\partial \underset{\sim}{q}} \cdot \frac{\underset{\sim}{p}}{m} \right| \quad , \tag{3.2}$$

$f(\underset{\sim}{q}) = 0$ defining the "dividing surface" in the usual way.

This Section describes another kind of semiclassical approximation for the rate constant which is obtained by introducing a semiclassical approximation for the quantum mechanical phase space distribution function. The distribution function we use is suggested by expressions which arose in considering the classical path approximation for the Boltzmann operator.[11] Thus the quantum partition function, which is given in terms of the distribution function by

$$Q = \int d\underset{\sim}{p}_0 \int d\underset{\sim}{q}_0 \; W(\underset{\sim}{p}_0,\underset{\sim}{q}_0) \quad , \tag{3.3}$$

is also given by

$$Q = \int d\underset{\sim}{q}_0 \langle \underset{\sim}{q}_0 | e^{-\beta H} | \underset{\sim}{q}_0 \rangle$$

$$= \int d\underset{\sim}{q}_1 \int d\underset{\sim}{q}_0 \; |\langle \underset{\sim}{q}_1 | e^{\frac{-\beta H}{2}} | \underset{\sim}{q}_0 \rangle|^2 \quad . \tag{3.4}$$

Using the classical path approximation for the matrix elements in Eq. (3.4) and changing variables of integration (see ref. 11 for more details) gives the following semiclassical approximation for the partition function:

$$Q = h^{-F} \int d\underset{\sim}{p}_0 \int d\underset{\sim}{q}_0 \; \exp[-\frac{2}{\hbar} \int_0^{\frac{\hbar\beta}{2}} d\tau \; H(\tau)] \quad , \tag{3.5}$$

where $H(\tau) \equiv H(\underset{\sim}{p}(\tau), \underset{\sim}{q}(\tau))$ is the value of the Hamiltonian at "time" τ, with $\underset{\sim}{q}(\tau)$ and $\underset{\sim}{p}(\tau)$ determined by the equations of motion

$$\underset{\sim}{q}'(\tau) = \frac{\partial H}{\partial \underset{\sim}{p}} = \underset{\sim}{p}/m \tag{3.6a}$$

$$\underset{\sim}{p}'(\tau) = \frac{\partial H}{\partial \underset{\sim}{q}} = + \frac{\partial V}{\partial \underset{\sim}{q}} \tag{3.6b}$$

(note the + sign in Eq. (3.6b)) with initial conditions

$$\underset{\sim}{q}(0) = \underset{\sim}{q}_0 \tag{3.7a}$$

$$\underset{\sim}{p}(0) = \underset{\sim}{p}_0 \quad . \tag{3.7b}$$

Eq. (3.6) describes a classical trajectory in the time variable τ on the upside-down potential surface $-V(\underset{\sim}{q})$.

Comparing Eqs. (3.3) and (3.5), the temptation is to identify the integrand of Eq. (3.5) as an approximation to the Wigner distribution function. Liouville's theorem, however, implies that

$$d\underset{\sim}{p}_0 \, d\underset{\sim}{q}_0 = d\underset{\sim}{p}(\tau) \, d\underset{\sim}{q}(\tau) \quad ,$$

for any τ, so it follows simply that

$$Q = h^{-F} \int d\underset{\sim}{p}_0 \int d\underset{\sim}{q}_0 \ \exp\left[-\frac{2}{\hbar} \int_{-\tau_0}^{\frac{\hbar\beta}{2}-\tau_0} d\tau \ H(\tau)\right] \quad , \tag{3.8}$$

for <u>any</u> value of τ_0, with $(\underset{\sim}{q}(\tau), \underset{\sim}{p}(\tau))$ still determined by Eq. (3.6) with the initial conditions in Eq. (3.7). Although Q is independent of the choice for τ_0 in Eq. (3.8), the integrand--the function of $\underset{\sim}{p}_0$ and $\underset{\sim}{q}_0$ which one wishes to identify as the distribution function--is not.

The choice for τ_0 which seems most justified is the one which is most symmetrical,

$$\tau_0 = \frac{\hbar\beta}{4} \quad ; \tag{3.9}$$

one then identifies the integrand of Eq. (3.8) as the semiclassical distribution function:

$$W(\underset{\sim}{p}_0, \underset{\sim}{q}_0) = h^{-F} \ \exp\left[-\frac{2}{\hbar} \int_{-\frac{\hbar\beta}{4}}^{\frac{\hbar\beta}{4}} d\tau \ H(\tau)\right] \quad , \tag{3.10}$$

where the trajectory $(\underset{\sim}{p}(\tau), \underset{\sim}{q}(\tau))$ is determined by Eqs. (3.6)-(3.7). This choice for τ_0 is reinforced by the fact that for a one-dimensional parabolic barrier,

$$V(x) = -\frac{1}{2} m\omega^2 x^2 \quad , \tag{3.11}$$

the one-dimensional tunneling coefficient Γ,

$$\Gamma \equiv 2\pi\hbar\beta \quad e^{\beta V(0)} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \quad W(p,x)\ \delta(x)\ \frac{1}{2}\ |p| \quad , \tag{3.12}$$

which one obtains with the distribution function in Eq. (3.10) is found to be

$$\Gamma = \frac{1}{2}\hbar\omega\beta/\sin(\frac{1}{2}\hbar\omega\beta) \quad , \tag{3.13}$$

which is the exact result for this case. The choice $\tau_0 = \frac{\hbar\beta}{4}$ is the only one which gives the correct tunneling coefficient, Eq. (3.13), for the parabolic barrier. One can also show that Eq. (3.10) gives the exact partition function for a harmonic oscillator, but any value of τ_0 in Eq. (3.8) will do this.

One already knows that the distribution function of Eq. (3.10) gives partition functions quite well,[11] and the only other feature that it must describe for the present application is tunneling. It was noted above that it gives the exact result for a one-dimensional parabolic barrier, but to get a more revealing measure of its accuracy in this regard we have considered tunneling through the one-dimensional Eckart barrier,

$$V(x) = V_0 \operatorname{sech}^2(x/a) \quad . \tag{3.14}$$

This is a convenient test case since Johnston[16] has tabulated the exact value of Γ for the potential for a wide range of the two dimensionless parameters

$$u = \frac{\hbar\beta}{a} \left(\frac{2V_0}{m}\right)^{1/2} \tag{3.15a}$$

$$\alpha = \frac{\pi a}{\hbar} (2m\,V_0)^{1/2} \quad ; \tag{3.15b}$$

u is proportional to 1/T, T the temperature, and α is a measure of how quantum-like the system is (the smaller α, the more quantum-like).

Figure 1 shows the comparison between the exact[16] tunneling factor Γ (solid line) and the result given by Eqs. (3.10) and (3.12) (broken line) as a function of u for two values of α. [$\lim_{u\to 0} \Gamma = 1$ in all cases.] The one-dimensional barrier for the $H + H_2$ reaction, for example, corresponds to $\alpha \simeq 10$–12, so that $\alpha = 4$ is considerably more quantum-like than the $H + H_2$ system, and $\alpha = 20$ is more classical-like. These one-dimensional results are therefore quite encouraging and suggest that the distribution function in Eq. (3.10) is sufficiently accurate so far as the one-dimensional aspect of tunneling is concerned.

For the collinear $H + H_2$ reaction Eq. (3.2), with Eq. (3.10) for the distribution function, gives the rate constant as

$$k_{b\leftarrow a} = Q_a^{-1} (2\pi\hbar)^{-2} \int_{-\infty}^{\infty} dp_s \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dp_u \; \frac{1}{2} \left|\frac{p_s}{m}\right| \exp\left[-\frac{2}{\hbar} \int_{-\frac{\hbar\beta}{4}}^{\frac{\hbar\beta}{4}} d\tau \; H(\tau)\right], \tag{3.16}$$

where $H(\tau)$ is evaluated along the classical trajectory that evolves on the upside-down potential surface with initial conditions

$$\begin{aligned} s(0) &= 0 \\ u(0) &= u \\ p_s(0) &= p_s \\ p_u(0) &= p_u \end{aligned} \quad ; \qquad (3.17)$$

one integrates the equations of motion forward from $\tau = 0$ to $\tau = \frac{\hbar\beta}{4}$, and backward from $\tau = 0$ to $\tau = -\frac{\hbar\beta}{4}$, in order to compute the exponent in the integrand of Eq. (3.16). The three dimensional integral is evaluated numerically, and in higher dimensional systems one would probably resort to Monte Carlo integration methods.

Finally, it should be noted that within this model it is a trivial matter to include the full classical dynamics of the reaction in real time, eliminating the need to make the "fundamental assumption" itself; this follows from the discussion in Section V of ref. 10. For the collinear $H + H_2$ reaction, for example, the necessary modification to Eq. (3.16) is simply to insert in the integrand the factor

$$\frac{1 + (-1)^M}{2(M + 1)} \quad , \qquad (3.18)$$

where M is the number of times that the trajectory, with the initial conditions of Eq. (3.17), crosses the line $s = 0$ as <u>real</u>

time is run forward to + ∞ and backward to − ∞. (Note that this trajectory is on the ordinary, right-side up potential surface.) This procedure essentially amounts to a Keck-type[17] classical trajectory calculation with the modification that the classical distribution function is replaced by the above semiclassical one. One thus carried out a classical trajectory calculation in real time to determine the "transmission coefficient", Eq. (3.18), and then with the same initial conditions carries out another trajectory calculation on the upside-down potential surface to determine the value of the semiclassical distribution function for the given initial point in phase space. The reader should recognize that a calculation such as this should be quite practical even for three-dimensional A + BC collision systems.

IV. RESULTS.

Consider first the results of the periodic orbit model described in Section II. Calculations were carried out for the collinear reaction,

$$H + H_2 \rightarrow H_2 + H \quad , \tag{4.1}$$

using the Truhlar-Kuppermann[18] potential surface for H_3 (a Wall-Porter[19] fit to the scaled Shavitt-Stevens-Minn-Karplus[20] potential surface) and also for the Porter-Karplus[21] potential surface.

Figure 2 shows the periodic trajectory for two different energies E, one just below the barrier and one far below it. So long as $E < V_{sp}$ (the only region considered in this paper) the trajectories are all real valued and relatively easy to find because of their high symmetry. There is only one such trajectory for a given energy. As $E \rightarrow V_{sp}$ the trajectory becomes infinitesimally short in length and moves to the saddle point of the potential surface; for lower energies the periodic trajectory "cuts the corner" of the potential surface, the more so the lower the energy.

Figures 3 and 4 show the action integral $\theta(E)$ and the stability parameter $\omega(E)$ as a function of the total energy for the Truhlar-Kuppermann potential surface. One notes that

$$\lim_{E \rightarrow V_{sp}} \theta(E) = 0 \tag{4.2a}$$

$$\lim_{E \rightarrow V_{sp}} \omega(E) = \omega^{\dagger} \quad , \tag{4.2b}$$

where $\omega^{\dagger}$ is the symmetric stretch frequency at the saddle point, the quantity which appears in conventional transition state theory. It is tempting to suspect that the zero energy limit of $\omega(E)$ might be ω_{H_2}, the vibrational frequency of the isolated H_2 molecule:

$$\lim_{E\to 0} \omega(E) = \omega_{H_2} \quad . \tag{4.3}$$

Although this is clearly the trend seen in Figure 4, it does not appear to be quantitatively true.

The cummulative reaction probability for the two potential surfaces is shown in Figures 5 and 6. The solid lines are the exact quantum mechanical values,[22] Eq. (2.2), and the dashed lines are the semiclassical transition state theory approximation given by Eq. (2.17). The agreement between the two is seen to be reasonably good. The accuracy of this semiclassical transition state theory is, in fact, almost as good as the results of classical S-matrix theory.[1]

The results based on the semiclassical phase space distribution of Section III are shown in Figures 7 and 8; the quantity shown is the rate constant for reaction (4.1) as a function of temperature on the Truhlar-Kuppermann[18] and Porter-Karplus[21] potential surfaces, respectively. For comparison the rate constant of conventional transition state theory,

$$k_{b\leftarrow a} = Q_a^{-1} \frac{kT}{h} \left[2 \sinh\left(\frac{\hbar\omega^{\dagger}\beta}{2}\right)\right]^{-1} \quad , \tag{4.4}$$

where $\omega^{\dagger}$ is the symmetric stretch frequency at the saddle point, is also shown (the lower solid line). No tunneling factor is included in Eq. (4.4) since Truhlar and Kuppermann[9] find that the use of any of the variety of one-dimensional tunneling corrections tends to do more harm than good. One sees that this semiclassical approximation to quantum transition state theory has gone a long way toward correcting the deficiencies of conventional transition state theory. At 200°K, for example, conventional transition state theory is about a factor of 30 and 70 too small, respectively, for the Truhlar-Kuppermann and Porter-Karplus potential surfaces, while this semiclassical approximation to quantum transition state theory is correspondingly a factor of 1.6 and 2.3 too small.

V. CONCLUDING REMARKS.

The results of both of the semiclassical approximations to the quantum transition state theory rate constant are in reasonably good agreement with the corresponding quantum scattering calculations. The indication is, therefore, that the "fundamental assumption" of transition state theory is valid in the threshold region of this reaction quantum mechanically, just as it has been seen to be classically.[4] It is not possible to say whether the remaining discrepancy is due to transition state theory itself or to the approximations used to evaluate the quantum expression. Other ways of evaluating the quantum rate expression are being explored, and it may be that they can help answer this question.

The semiclassical limit,[12] summarized in Section II is the theoretically more appealing of the two approaches described in this paper. It is obtained from a well established prescription--the stationary phase approximation--and the resulting periodic trajectory and its stability parameters have interesting physical interpretations. The approach based on the semiclassical distribution function of Section III, however, is clearly the more practical of the two, and it seems to be no less accurate. It would certainly seem that calculations of this type are feasible for three-dimensional A + BC reactive systems, and applications such as these are planned.

ACKNOWLEDGMENTS

The calculations reported in this paper were performed on a Datacraft 6024/4 minicomputer funded by NSF grant GP-39317. One of us (WHM) also acknowledges support of a Camille and Henry Dreyfus Teacher-Scholar grant.

REFERENCES

* Supported in part by the U. S. Energy Research and Development Administration, and by the National Science Foundation under grant GP-41509X.

1. T. F. George and W. H. Miller, J. Chem. Phys. **56**, 5722 (1972); **57**, 2458 (1972). See also S. M. Hornstein and W. H. Miller, J. Chem. Phys. **61**, 745 (1974).
2. E. Wigner, Trans. Faraday Soc. **34**, 29 (1938). Wigner refers to what we call the "fundamental assumption" as the third assumption; in the classical version of the theory it is the assumption that no trajectories cross the dividing surface more than once.
3. P. Pechukas and F. J. McLafferty, J. Chem. Phys. **58**, 1622 (1973).
4. S. Chapman, S. M. Hornstein, and W. H. Miller, J. Am. Chem. Soc. **97**, 892 (1975).
5. R. A. Marcus, J. Chem. Phys. **45**, 2138 (1966).
6. K. Morokuma and M. Karplus, J. Chem. Phys. **55**, 63 (1971).
7. See, for example, H. Eyring, Trans. Faraday Soc. **34**, 41 (1938), or any textbook on chemical kinetics.
8. R. A. Marcus, J. Chem. Phys. **45**, 2630 (1966); see also reference 5.
9. See, for example, D. G. Truhlar and A. Kuppermann, Chem. Phys. Lett. **9**, 269 (1971).
10. W. H. Miller, J. Chem. Phys. **61**, 1823 (1974).

11. W. H. Miller, J. Chem. Phys. **55**, 3146 (1971); **58**, 1664 (1973); S. M. Hornstein and W. H. Miller, Chem. Phys. Lett. **13**, 298 (1972).

12. W. H. Miller, J. Chem. Phys. **62**, 1899 (1975).

13. E. T. Whittaker, A Treatise on the Analytical Dynamics of Particles and Rigid Bodies, Cambridge U. P., 1965, pp. 395-406.

14. J. Heading, An Introduction to Phase-Integral Methods, Wiley, 1962, pp. 94-101.

15. E. Wigner, Phys. Rev. **40**, 749 (1932).

16. H. S. Johnston, Gas Phase Reaction Rate Theory, Ronald Press, New York, 1966, p. 44.

17. J. C. Keck, Adv. Chem. Phys. **13**, 85 (1967); Adv. At. Mol. Phys. **8**, 39 (1972).

18. D. G. Truhlar and A. Kuppermann, J. Chem. Phys. **52**, 3841 (1970); **56**, 2232 (1972).

19. F. Wall and R. N. Porter, J. Chem. Phys. **36**, 3256 (1962).

20. I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, J. Chem. Phys. **48**, 2700 (1968).

21. R. N. Porter and M. Karplus, J. Chem. Phys. **40**, 1105 (1964).

22. (a) D. G. Truhlar, A. Kuppermann, and J. T. Adams, J. Chem. Phys. **59**, 395 (1973) , for the Truhlar-Kuppermann potential surface, and (b) J. M. Bowman and A. Kuppermann, J. Chem. Phys. **59**, 6524 (1973), for the Porter-Karplus potential surface.

FIGURE CAPTIONS

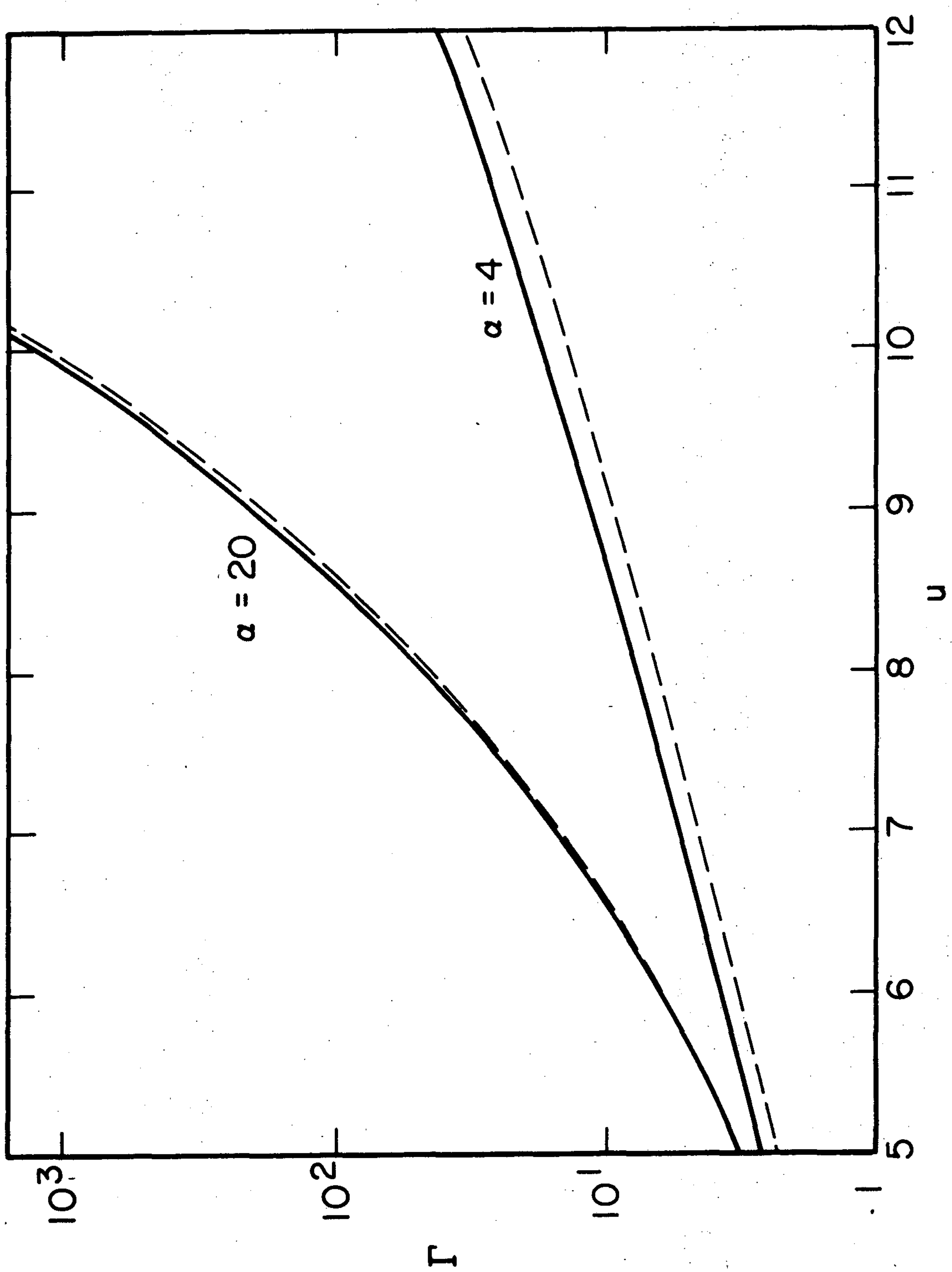
1. One dimensional tunneling coefficient for the Eckart barrier [Eq. (3.14)]; the dimensionless parameters α and u are defined by Eq. (3.15). The solid line is the exact quantum mechanical values given in reference 16, and the broken line the result given by Eq. (3.12) with the semiclassical phase space disbribution function of Eq. (3.10).
2. A perspective view of the upside-down H_3 potential surface with the periodic trajectories corresponding to two different energies. The circle shows the position of the saddle point.
3. The classical action integral (a generalized barrier penetration integral) along the periodic trajectory on the upside-down H_3 potential surface, as a function of total energy E. V_{sp} is the height of the saddle point.
4. The stability frequency (defined following Eq. (2.10)) for the (unstable) periodic trajectory on the upside-down H_3 potential surface, as a function of total energy E. The quantity plotted is the ratio of the stability frequency to the vibrational frequency of the free H_2 molecule, ω_{H_2}.
5. The cummulative reaction probability N(E) as a function of total energy $E \equiv E_0 + \frac{1}{2}\hbar\omega_{H_2}$, here for the collinear $H + H_2$ reaction on the Truhlar-Kuppermann (reference 18) potential surface. The solid line is the exact quantum mechanical result, Eq. (2.2), of reference 22, and the points connected

by the broken line are the values given by the semiclassical limit of quantum transition state theory, Eq. (2.17).

6. Same as Figure 5 except with the Porter-Karplus (ref. 21) potential surface.

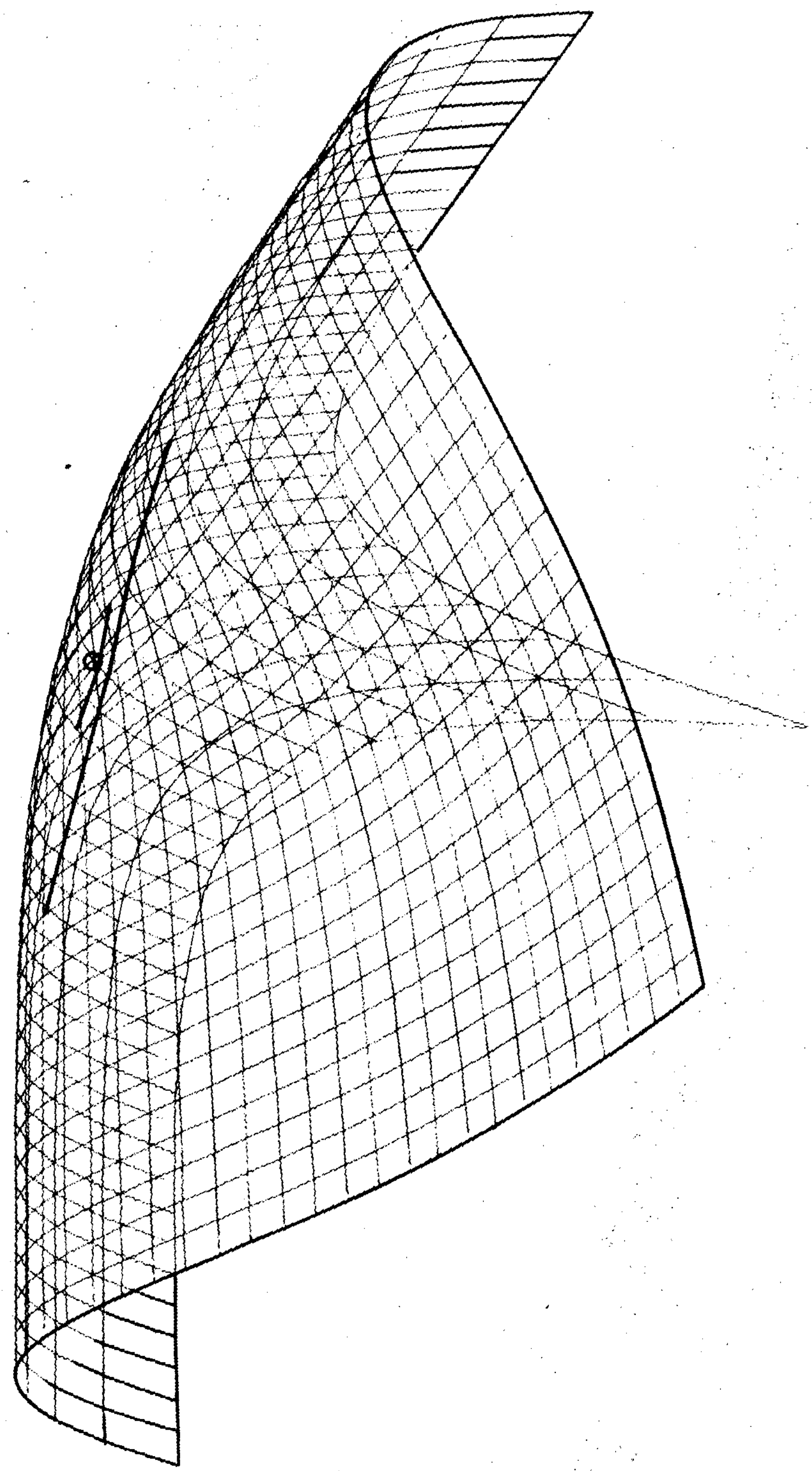
7. Rate constant as a function of temperature for the collinear $H + H_2$ reaction, here with the Truhlar-Kuppermann (ref. 18) potential surface. The upper line is the exact quantum result (ref. 9), the lower line the result of conventional transition state theory, Eq. (4.4), and the points the results given by the Eq. (3.16) which is based on use of the semiclassical phase space distribution function.

8. Same as Figure 7 except with the Porter-Karplus (ref. 21) potential surface.



XBL 753-5899

Fig. 1.



XBL 753-693

Fig. 2.

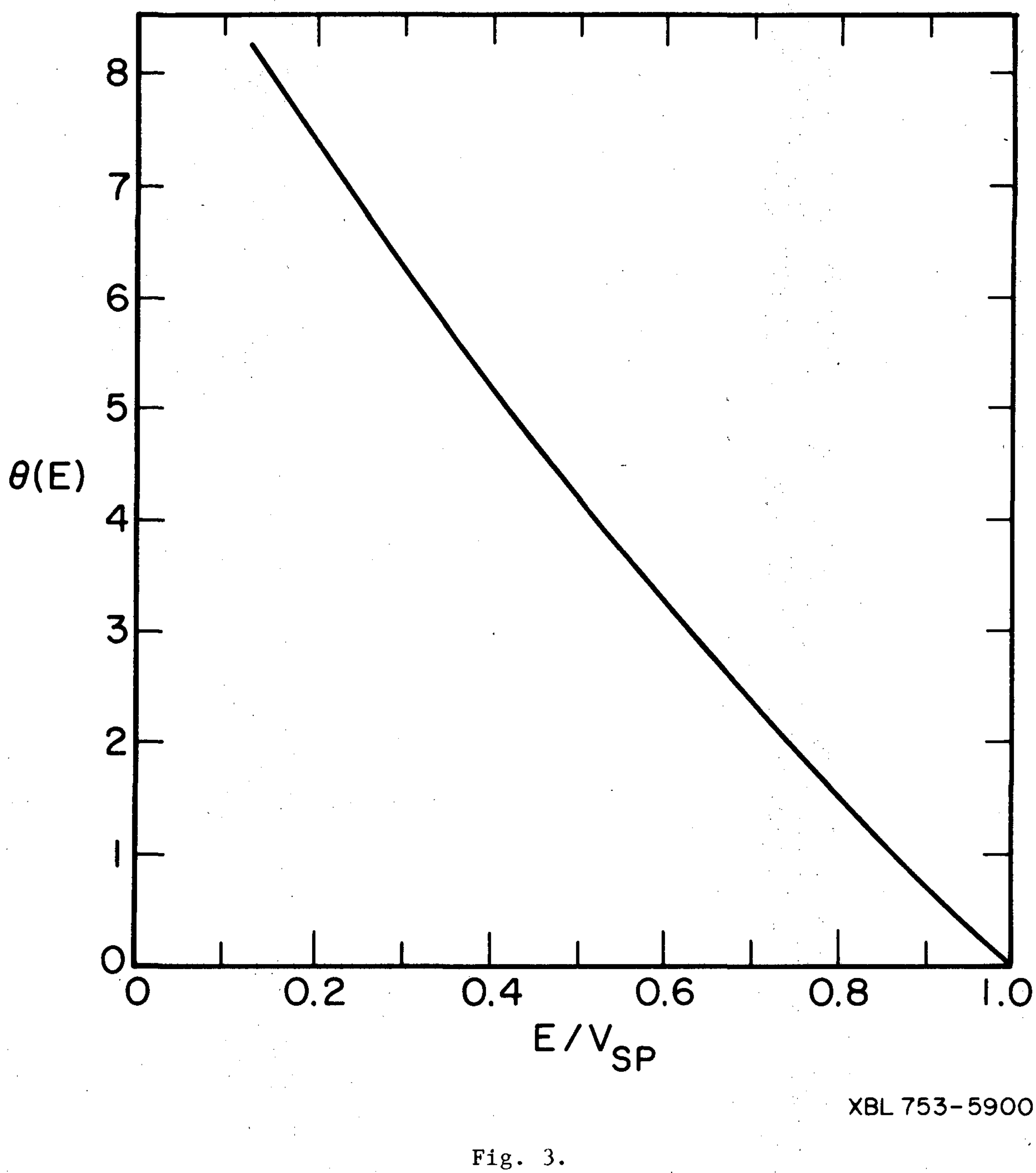


Fig. 3.

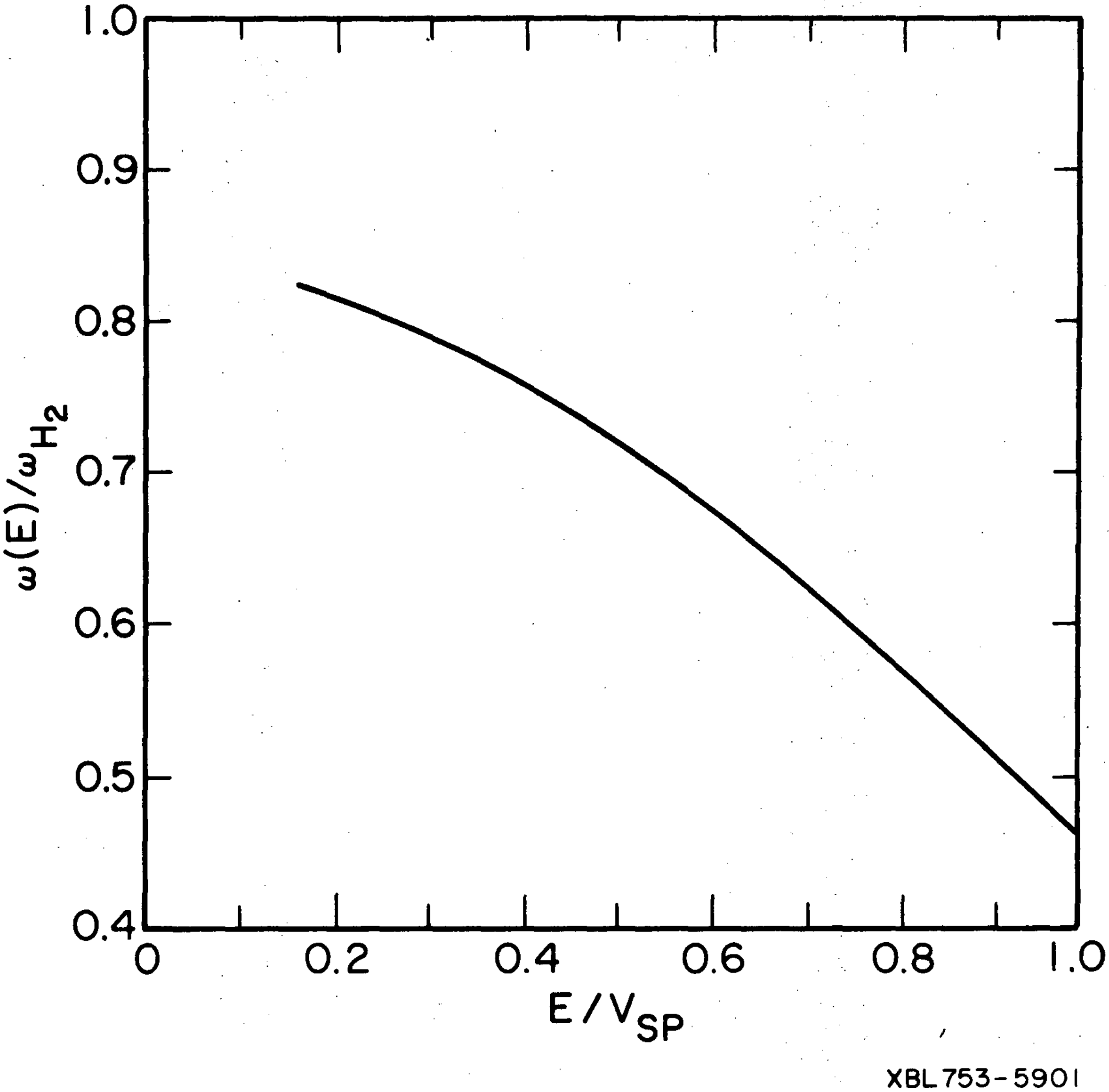
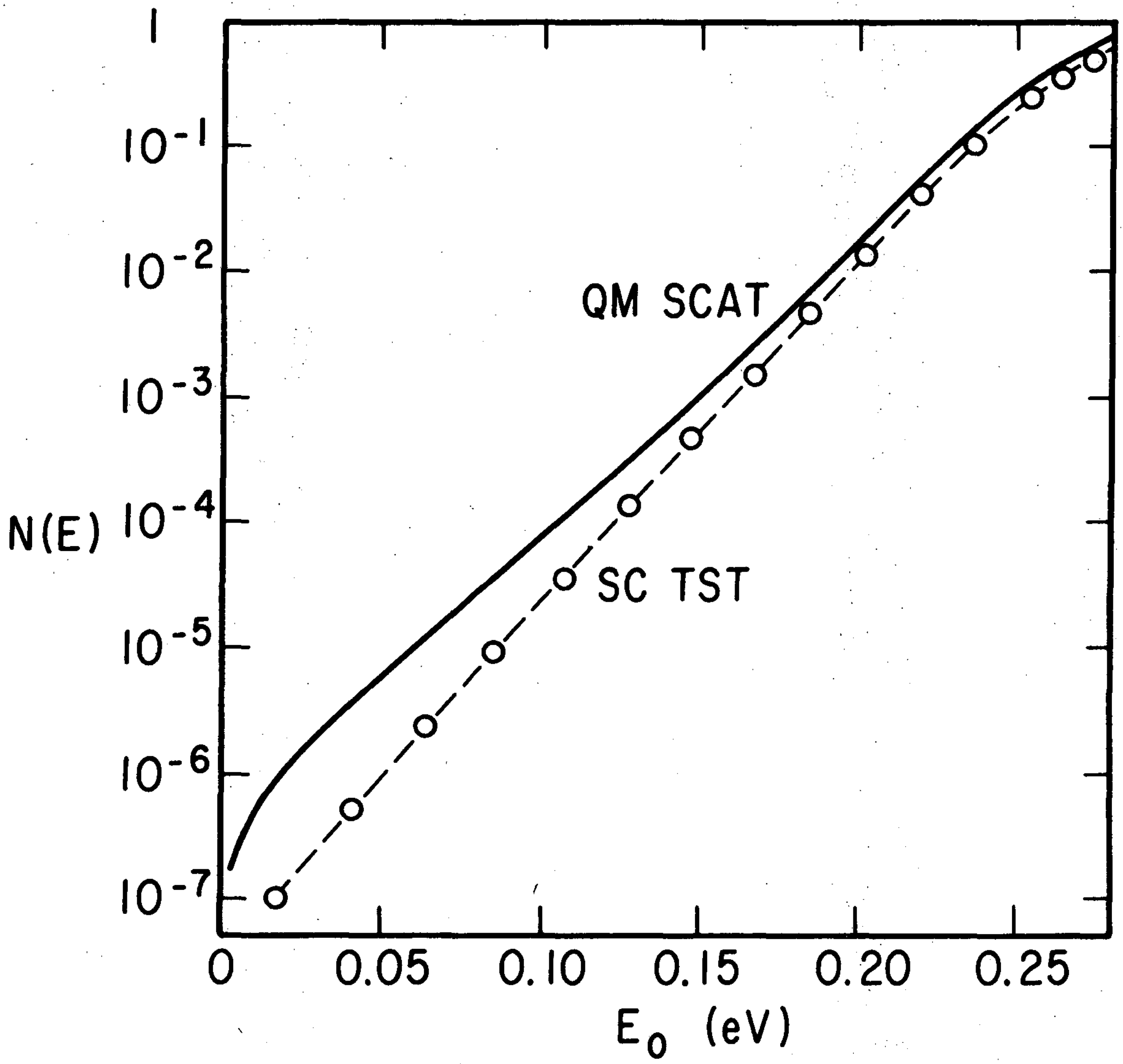

1.0
0.9
0.8
0.7
0.6
0.5
0.4
$\omega(E)/\omega_{H_2}$
0
0.2
0.4
0.6
0.8
1.0
E/V_{SP}
XBL 753-5901

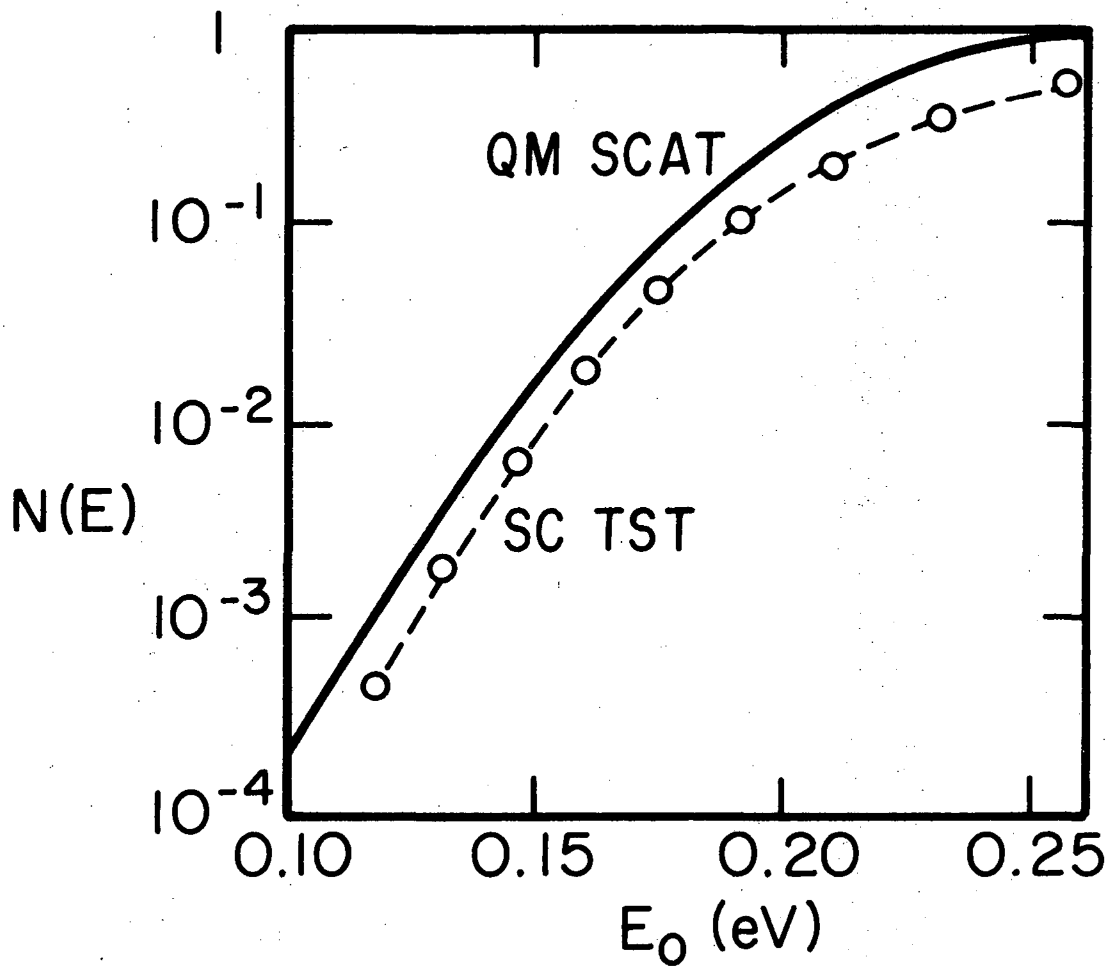
Fig. 4.



XBL 751-5660

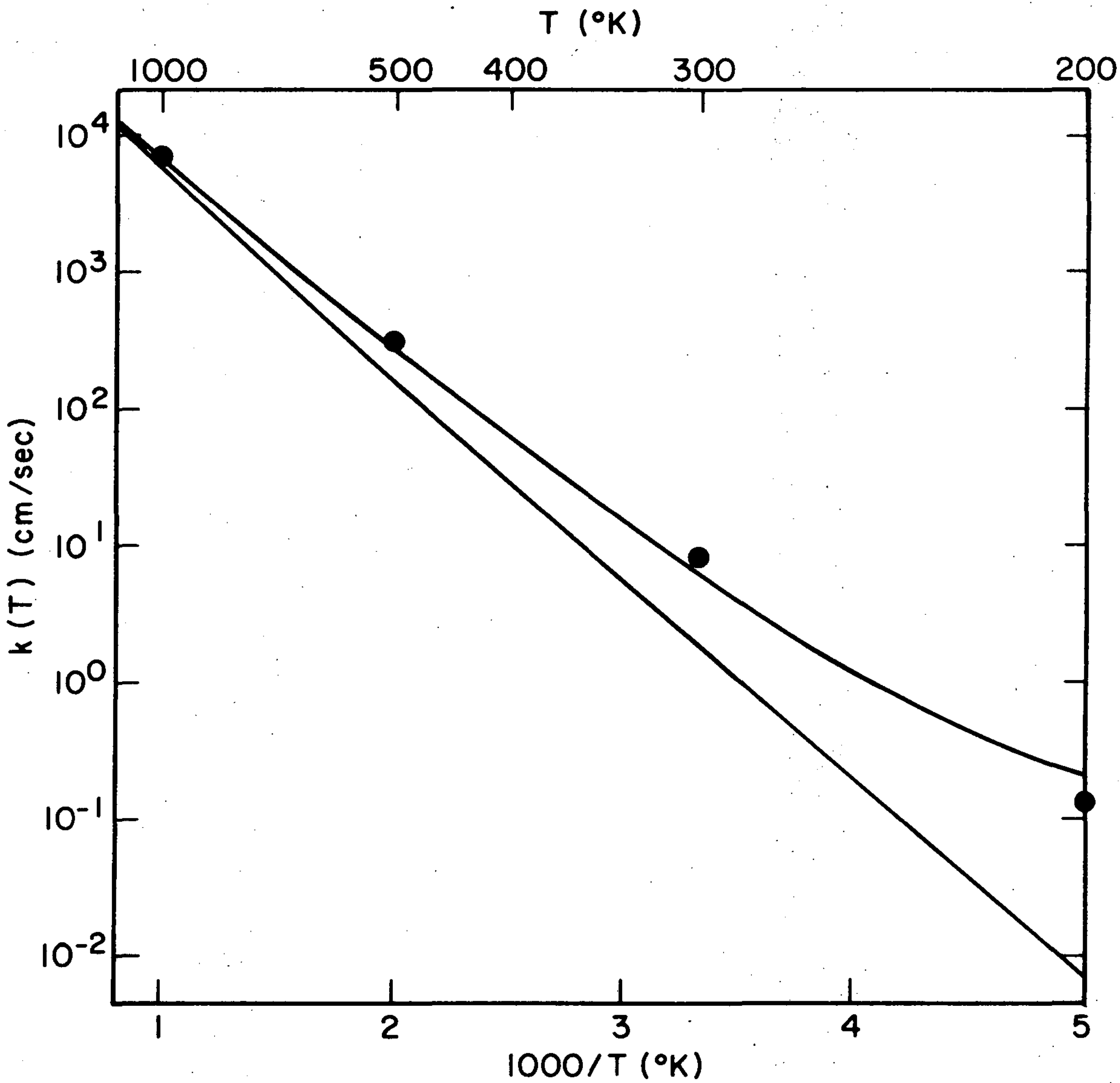
Fig. 5.

0 0 0 0 4 3 0 3 2 8 0



XBL 751-5661

Fig. 6.



XBL-7411-7555

Fig. 7.

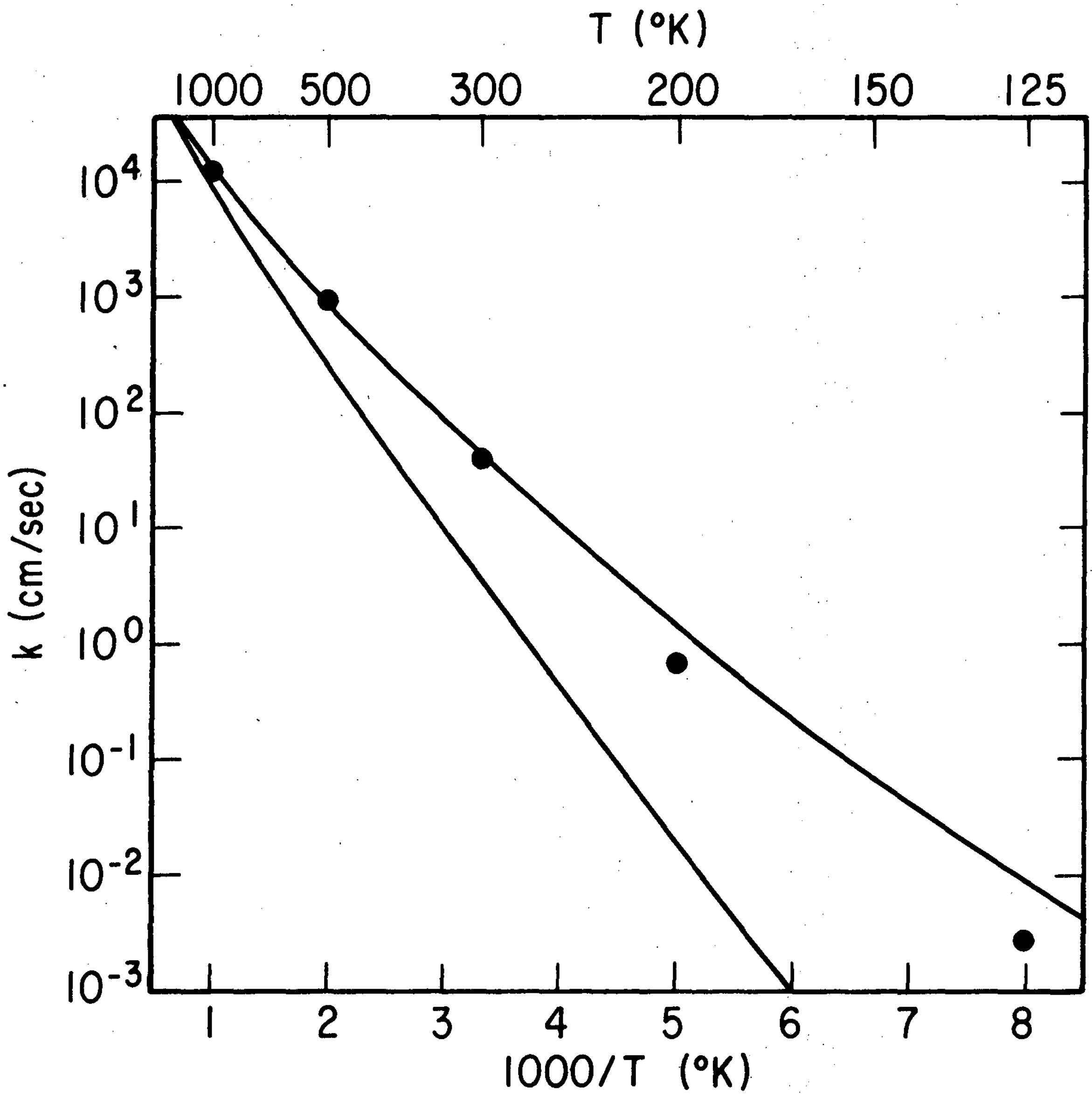

T (°K)
1000
500
300
200
150
125
k (cm/sec)
10⁴
10³
10²
10¹
10⁰
10⁻¹
10⁻²
10⁻³
1
2
3
4
5
6
7
8
1000/T (°K)
XBL 754-6046

Fig. 8.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720