

# On the theory of translational energy distributions of product molecules of molecular beam reactions involving transient complexes. II

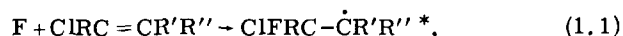
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(Received 8 March 1977)

A statistically adiabatic model for chemical reactions involving a tight or loose transition state in the exit channel was used in Part I to obtain an integral equation for the individual reaction probabilities, i.e., for the magnitude of the  $S$  matrix elements. In the present paper this integral equation is explicitly solved for the general case of product orbital ( $l$ ) and rotational ( $j$ ) angular momenta constrained only by energy and angular momentum conservation. The reaction probabilities are shown to be related to a contour integral of a product of canonical partition functions. The theory includes an effect of the evolution of the bending vibrations of the transition state into free rotations of the product molecules. The distribution of final translational energy for the general ( $l, j$ ) case is then obtained by averaging the reaction probabilities over various quantum states of the product molecules. The results are compared with the special cases in the literature for which (i) the transition state in the exit channel is loose ("phase space theory"), (ii) this case but with  $l \gg j$ , and (iii) tight transition state theory with  $l \gg j$  (Part I). The results are also compared with experimental data obtained from the molecular beam reaction  $F + (CH_3)_2C = CH_2 \rightarrow F(CH_3)_2\dot{C}CH_2^* \rightarrow CH_3 + FCH_2C = CH_2$ . The data and the theoretical results are now in better agreement. In the treatment described here and in Part I a loose transition state in the entrance channel was assumed. Expressions for the energy distribution are also given for the case when the entrance channel transition state is tight. Finally, a statistically adiabatic  $S$  matrix, which is useful for reactions proceeding through long-lived collision complexes having tight transition states, is described, and its possible application to angular distributions and angular momentum polarization experiments is discussed.

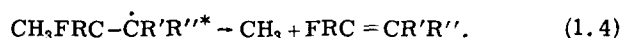
## I. INTRODUCTION

Various theoretical methods have been devised to calculate the distribution of internal energy states of the product molecules of molecular beam experiments. One such method was that recently described by Safron *et al.*<sup>1</sup> In this treatment an angular momentum distribution of the transient energetic molecules appropriate to the beam conditions plus RRKM theory<sup>2</sup> were used to calculate the distribution of internal energy states of the transition state. For the case of a loose transition state in the exit channel no coupling of the radial and internal coordinates exists, and therefore the final state distribution of the transition state automatically provided the distribution of internal states of the products. The method has been applied to various reactions,<sup>1,3</sup> including the following system<sup>3</sup>:



where  $R$ ,  $R'$ , and  $R''$  are alkyl groups. There is negligible activation energy for the reverse step in Eq. (1.2) and so the activated complex is expected to be loose. Exit channel effects are then absent, and the data agreed well with the theoretical distributions.

In another interesting series of experiments the distribution of final translational energy of the products of a similar reaction but involving methyl instead of Cl elimination was measured<sup>3</sup>



Here, however, the experimental distribution was shifted to higher values of translational energy than the

calculated one. (A figure describing the disagreement is given later.) The results suggested, thereby, either that exit channel effects distort the products' translational energy distribution, or that the assumption of a statistical distribution is inapplicable, or both. For example, when the exit channel transition state is tight, some coupling of radial and internal coordinates must occur, and this coupling distorts the final energy distribution.<sup>4</sup>

One of the possible exit channel effects which *can* occur is the following<sup>4</sup>: When the exit channel transition state is tight, it has bending vibrations which become free rotations when the product molecules are formed. Since bending vibrational energy levels are more widely spaced than rotational levels, any "statistical adiabaticity" (i.e., any tendency to distribute quantum numbers about the adiabatically determined values for these bending vibrational-rotational degrees of freedom) would tend to shift the translational energy distribution to higher energies and hence yield better agreement with the experimental distribution. This effect is more fully illustrated in Fig. 1. In addition to this statistical adiabaticity the theory presented in Part I and here is a statistical theory, i.e., energy randomization is assumed in the collision complex.

It should be *stressed* that energy randomization in the collision complex plus statistical adiabaticity in the exit channel region constitute merely one set of assumptions which can be made. Other assumptions involving exit channel interactions might also give agreement with experiment. However, the main purpose of the present paper is to explore the consequences of the first assumption, without using adjustable parameters.

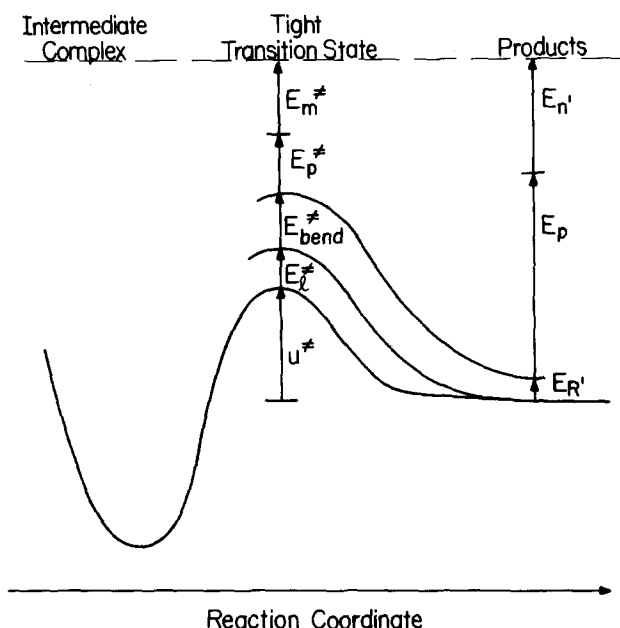


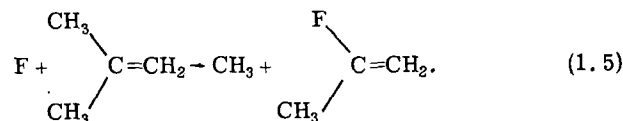
FIG. 1. A plot of the potential energy hypersurface as a function of the reaction coordinate for the exit channel is shown.  $E_t^\ddagger = l^2/2I^\ddagger$ ;  $E_p^\ddagger$  and  $E_p$  denote the values of the translational energy along the reaction coordinate at the transition state and in the asymptotic product region, respectively;  $E_{\text{bend}}^\ddagger$  is the energy associated with the bending vibrations;  $E_m$  is the energy associated with all other active degrees of freedom of the transition state;  $E_R$  denotes the energy associated with the rotational degrees of freedom of the product molecules that are bending vibrations in the transition state; and  $E_{R'}$  denotes the vibrational energy plus the extra rotational energy not included in  $E_R'$ . When the transition state is tight,  $E_{R'} < E_{\text{bend}}^\ddagger$ . When the transition state is loose,  $E_t^\ddagger + E_p^\ddagger + u^\ddagger = E_p$ . By conservation of total energy one has  $E_t^\ddagger + E_m^\ddagger + E_{\text{bend}}^\ddagger + E_p^\ddagger + u^\ddagger = E_p + E_{n'} + E_{R'} = E$ .

The present statistical theory differs from the usual statistical theories for the case of a tight exit channel transition state in including a coupling along the reaction coordinate from the exit channel transition state to the separated product species. Since the transition state in the exit channel of Eq. (1.4) is tight, any theory capable of predicting the energy distribution for Eq. (1.4) should include some dynamical coupling in the exit channel, as does the theory presented in Part I and here.

When the present exit channel effect problem was treated in Part I, an integral equation for the various transition probabilities was obtained, Eq. (3.3) of the present paper. It was solved for the special cases of  $l \gg j$  and  $j \gg l$ . In the present paper we solve it without imposing these angular momentum restrictions. At first solution of Eq. (3.3) by standard numerical methods based on quadratures was attempted.<sup>5</sup> Since the known function in the integrand increases rapidly with increasing energy, namely, the density of states increases rapidly with energy, unreliable (oscillating and even negative) values for the relatively slowly varying reaction probabilities were obtained. It was then realized, at first numerically, that apart from a relatively minor factor the integral was a product of two convolutions, a fact obscured by the complicated angular momentum and energy constraints on the domain of

integration. A suitable change of variables then demonstrated this property analytically, and yielded a form convenient for a straightforward solution by a combination of Laplace transform and numerical methods. The correction for the neglected factor is found (Appendix C) to be about only 0.02% in the present system.

The numerical results of this theory are compared with those for (1) loose transition state theory with full angular momentum restrictions ("phase space theory"),<sup>6</sup> (2) loose transition state theory with  $l \gg j$ , (3) tight transition state theory with  $l \gg j$ ,<sup>4</sup> and (4) experiment<sup>3</sup> for the following system:



The organization of the paper is as follows: In Sec. II a glossary of notation is given. In Sec. III the general theoretical energy distributions are developed. Section IV deals with a statistically adiabatic S matrix and its application to angular distributions and rotational polarization experiments. The paper concludes in Sec. V with a discussion of a numerical example and the results. Appendix A deals with energy distributions for the special case of  $l \gg j$ . In Appendix B energy distributions are derived when the entrance channel transition state is tight.

## II. GLOSSARY OF NOTATION

$J, M$	Total rotational angular momentum quantum number and its projection along a spaced fixed axis
$l, l_0$	Orbital angular momentum quantum number of products and reactants, respectively
$j, j_0$	Total rotational angular momentum quantum number of products and reactants, respectively
$E$	Total energy
$\sigma_0$	Total reaction cross section
$j_1, j_{10}(j_2, j_{20})$	Rotational angular momentum quantum number of product and reactant molecule one (two)
$k_1, k_{10}(k_2, k_{20})$	Second angular momentum quantum number of product and reactant molecule one (two) needed to specify energy eigenvalues in case the molecules are nonlinear
$v, v_0$	Denotes the totality of vibrational quantum numbers of the product and reactant molecules, respectively
$n, n_0$	Denotes $\{j_1, j_2, k_1, k_2, v\}$ and $\{j_{10}, j_{20}, k_{10}, k_{20}, v_0\}$ , respectively.
$l_m, l_{0m}$	Maximum of $l$ and $l_0$ , respectively $\{l_m = [2I^\ddagger(E_p - u^\ddagger)]^{1/2}\}$
$I_{a1}, I_{a2}$	Smallest (largest) moment of inertia for oblate (prolate) top product molecule one and two
$I_{c1}, I_{c2}$	Largest (smallest) moment of inertia for oblate (prolate) top product molecule

	one and two		
$u^\ddagger, u^{0\dagger}$	Activation barrier with respect to product and reactant state, respectively	$d\sigma_{E_p, j_0 n_0 E} / dE_p$	Translational energy distribution per unit energy
$E_p, E_{p_0}$	Final and initial translational energy in the center of mass system of coordinates	$S_{jnl\alpha - j_0 n_0 l_0 \alpha_0}^{JE}$	The S matrix for a transition from $j_0 n_0 l_0 \alpha_0 JE$ to $jnl\alpha JE$
$E_v, E_{v_0}$	Vibrational energy of product or reactant molecules in a state with vibrational quantum number $v$ or $v_0$ , respectively	$\rho_1, \rho_2$	Total partition function for product molecule 1 and 2, respectively
$I^\ddagger, I_0^\ddagger$	$I^\ddagger = \mu r^{\ddagger 2}$ , $I_0^\ddagger = \mu_0 r_0^{\ddagger 2}$ , where $\mu$ ( $\mu_0$ ) is the reduced mass of products (reactants) and where $r^\ddagger$ ( $r_0^\ddagger$ ) is the approximate classical turning point for the formation of a complex in the exit (entrance) channel	$J_\zeta$	Minimum of $l_{0m}$ and $l_m + j$
$B_i^\ddagger, B_{i_0}^{0\dagger}$	Effective barrier in exit and entrance channel, respectively. $B_i = u^\ddagger + l^2/2I^\ddagger$ and $B_{i_0}^{0\dagger} = u^{0\dagger} + l_0^2/2I_0^\ddagger$	$E_j^\ddagger$	$J^2/2I^\ddagger$
$E_R$	The rotational energy of the product molecules associated with the quantum state $j_1 k_1 j_2 k_2$	$B_j^\ddagger$	$u^\ddagger + E_j^\ddagger$
$I_1^\ddagger$	Moment of inertia associated with $J$ in the exit channel activated state	$Q_1, Q_2, Q$	$\int_0^\infty \rho_1(x) \exp(-\beta x) dx$ , $\int_0^\infty \rho_2(x) \exp(-\beta x) dx$ , and $Q_1 Q_2$ , respectively
$E_{1J}^\ddagger$	$J^2/2I_1^\ddagger$	$N_{J\alpha}^\ddagger$	Total number of quantum states in exit channel transition state for a given value of $J$ , $E$ , and $\alpha$
$E_n$	The internal energy associated with quantum state $n$	$N_{J\alpha_0}^{0\dagger}$	Total number of quantum states in the entrance channel transition state for a given $J$ , $E$ , and $\alpha_0$
$\beta$	$1/k_B T$ , where $k_B$ is Boltzmann's constant and $T$ is the temperature ( $^\circ K$ )	$Q_{J\alpha_0}^{0\dagger}$	Partition function of all active degrees of freedom of the entrance channel transition state
$B_{1J}^\ddagger$	$u^\ddagger + E_{1J}^\ddagger$	$\rho_0(x)[\rho(x)]$	Vibrational-rotational density of states of the reactant (product) molecules at energy $x$
$\sigma_{j_0 n_0}$	Total cross section when the initial state is $j_0 n_0$ and the entrance channel activated complex is tight	$Q_0$	Vibrational-rotational partition function of the reactant molecules, i. e., $\int_0^\infty \rho_0(x) \exp(-\beta x) dx$
$k_0$	Wavenumber in the entrance channel	$\mathfrak{F}$	An operator denoting $\int_0^\infty dj_1 \int_{-j_1}^{j_1} dk_1 \int_0^\infty dj_2 \times \int_{-j_2}^{j_2} dk_2 H(k_1) H(k_2)$
$\sigma_{jn, j_0 n_0 E}$	The internal state to state cross section from $j_0 n_0 \alpha_0$ to $jn\alpha$ at energy $E$	$P(E_p)$	The normalized translational energy distribution function
$w_{jnlE}^J$	Reaction probability to form complex from products in state $JnlE\alpha$	$P_0(J)$	$[(2J+1)/l_{0m}^2] h(l_{0m} - J)$
$w_{j_0 n_0 l_0}^J$	Reaction probability to form complex from reactants in state $Jj_0 n_0 l_0 E \alpha_0$	$m_{j_1}, m_{j_2}, m_l$	Projection of $j_1, j_2$ , and $l$ along, say, the initial relative velocity vector
$l_\zeta$	Minimum of $J+j$ and $l_m$	$\delta(x)$	Dirac delta function
$\alpha_0, \alpha$	Reactant or product channel, respectively		
$j_\zeta$	Minimum of $l+J$ and $j_1+j_2$		
$j_\zeta$	Maximum of $ J-l $ and $ j_1-j_2 $		
$h(x)$	Heaviside step function		
$\rho_v(x)$	Vibrational-internal rotational density of states of products at energy $x$		
$B(j_1 j_2 l J)$	$h(j_\zeta - j_\zeta) (j_\zeta - j_\zeta)$		
$H(k_1), H(k_2)$	Functions depending on the symmetry of product molecules one and two. If molecule one is a symmetric top or spherical top then $H(k_1) = 1$ , whereas if it is a linear molecule $H(k_1)$ equals the Dirac delta function $\delta(k_1)$		
$Q_{J\alpha}^\ddagger$	Partition function of all active degrees of freedom of the exit channel transition state		
$Q_v$	Partition function of all vibrational-internal rotational degrees of freedom of the product molecules		
$\bar{G}^J$	Nonseparable "partition function" of the external rotations of the product molecules		

### III. GENERAL THEORY

In this section general expressions are given for the reaction probabilities and energy distributions when the entrance channel transition state is loose and the exit channel transition state is tight. In Sec. IIIA the general expression for the internal state to state cross section is given. Section IIIB is concerned with the derivation and solution of an integral equation for the reaction probabilities. Finally, in Sec. IIIC a general expression for the products' energy distribution is derived. In all formulas of this paper  $\hbar = 1$ .

#### A. An expression for the internal state cross section

When the energetic molecules need to be distinguished only by their total angular momentum  $J$  and their total energy  $E$  in the center-of-mass system, the internal state to state cross section for the  $\alpha$ th channel of products using microscopic reversibility and the statistical approximation can be written as<sup>4,6</sup>

$$\sigma_{jn, j_0 n_0 E} = \sigma_0 \sum_{J=0}^{l_{0m}} P_0(J) h(l_\zeta - |J-j|) \times \left( \sum_{\alpha} N_{J\alpha}^\ddagger \right)^{-1} \int_{l=|J-j|}^{l_\zeta} dl \omega_{jnlE}^J, \quad (3.1)$$

where  $w_{jnlE}^J$  is the probability of forming an energized

molecule from the collision of the  $\alpha$ th set of products having a given  $j$ ,  $n$ ,  $l$ ,  $J$ , and  $E$ ;  $l_c$  is the maximum allowed value of  $l$ , namely, the minimum of  $J+j$  and  $l_m$ , where  $l_m$  is  $[2I^\ddagger(E_p - u^\ddagger)]^{1/2}$  for a tight transition state.  $N_{J\alpha}^\ddagger$  in Eq. (3.1) is the number of quantum states in the activated complex for a given value of  $E$ ,  $J$ ,  $M$ , and  $\alpha$ .  $\alpha$  is deleted from all symbols in Eq. (3.1), except for  $N_{J\alpha}^\ddagger$ , for notational brevity. [Eq. (3.1) can also be derived from the results of Sec. IV and standard quantum mechanical expressions for the cross section.] When the transition state in the entrance channel in Eq. (3.1) is assumed to be loose and when  $l_0 \gg j_0$ , the distribution function  $P_0(J)$  of the total angular momentum of the transition state is given by<sup>4</sup>

$$P_0(J) = (2J+1)/l_{0m}^2, \quad J < l_{0m}, \\ = 0, \quad J > l_{0m}. \quad (3.2)$$

### B. An integral equation for the reaction probabilities

Once the  $w_{jnlE}^\ddagger$ 's in Eq. (3.1) are evaluated the internal state cross sections can be calculated. In order to perform this task we assume microcanonical transition state theory<sup>7</sup> [Eq. (3.3)] and statistical adiabaticity [Eq. (3.7)] hold. By assuming statistical adiabaticity the translational energy of the products is utilized to overcome statistically any barrier arising in the reverse reaction (1.4) from the fact that the energy level spacing of the bending vibrations of the transition state exceeds that of the free rotations of the products.

From microcanonical transition state theory, treating the product rotations and reaction coordinate classically, one obtains Eq. (3.3). This equation states that the microcanonical-ensemble weighted integral of reaction probabilities from the products of a given  $E$ ,  $J$ , and  $\alpha$  is equal to the total number of energy levels of the transition state for a given  $E$ ,  $J$ , and  $\alpha$ . A  $2J+1$  degeneracy is absent from both sides of Eq. (3.3).

Equation (3.3) below can be derived without assuming an equilibrium or quasiequilibrium between products and transition states. In fact, Eq. (3.3) is just the microcanonical analog of Wigner's formulation<sup>8</sup> of transition state theory, but for the present system rather than for bimolecular reactions

$$N_{J\alpha}^\ddagger = N_{J\alpha}^\ddagger(E - u^\ddagger - E_{1J}^\ddagger) \\ = \int_{E_p=0}^{\infty} dE_p \int_{l=0}^{\infty} dl \mathcal{F} \left[ \rho_v(E - E_p - E_R) h(j_c - j_s) \right. \\ \left. \times \int_{j=j_s}^{j_c} w_{jnlE}^\ddagger dj \right], \quad (3.3)$$

where one has the angular momentum restrictions given by

$$j_c = \min\{l+j, j_1+j_2\}, \\ j_s = \max\{|J-l|, |j_1-j_2|\}. \quad (3.4)$$

and where for notational simplicity the integral operator  $\mathcal{F}$  is introduced and defined to be

$$\mathcal{F} = \int_{j_1=0}^{\infty} dj_1 \int_{k_1=j_1}^{j_1} dk_1 \int_{j_2=0}^{\infty} dj_2 \int_{k_2=j_2}^{j_2} dk_2 H(k_1) H(k_2). \quad (3.5)$$

$H(k_1)$  and  $H(k_2)$  are functions dependent on the symmetry of the product molecules. For the cases of symmetric top and spherical top molecules  $H(k_1) = H(k_2) = 1$ , whereas for a linear molecule  $H(k_1) = \delta(k_1)$  and  $H(k_2) = \delta(k_2)$ , where  $\delta(k_1)$  is the Dirac delta function. Here  $j_1$  and  $j_2$  are coupled to yield  $j$ , which is coupled to  $l$  to yield  $J$ ,<sup>9</sup> i. e., a total angular momentum basis set is considered, where the rotational-orbital quantum numbers are  $j_1$ ,  $k_1$ ,  $j_2$ ,  $k_2$ ,  $j$ ,  $l$ ,  $J$ , and  $M$ . On the other hand, in the uncoupled representation the rotational-orbital quantum numbers are  $j_1$ ,  $m_{j_1}$ ,  $j_2$ ,  $m_{j_2}$ ,  $l$ ,  $m_l$ ,  $k_1$ , and  $k_2$ , where  $m_{j_1}$ ,  $m_{j_2}$ , and  $m_l$  are projections of  $j_1$ ,  $j_2$ , and  $l$ , respectively, along, say, the initial relative velocity vector.  $\rho_v(E - E_p - E_R)$  in Eq. (3.3) is the vibrational-internal rotational density of states and is defined to be zero when  $E - E_p - E_R$  is negative.  $E_R$  denotes rotational energy levels of the rigid product molecules. For example, for oblate symmetric tops the rotational energy levels are given by the following expression<sup>10</sup>:

$$E_R = \frac{j_1^2}{2I_{a1}} + \frac{j_2^2}{2I_{a2}} + \frac{k^2}{2} \left( \frac{1}{I_{c1}} - \frac{1}{I_{a1}} \right) + \frac{k^2}{2} \left( \frac{1}{I_{c2}} - \frac{1}{I_{a2}} \right), \quad (3.6)$$

where  $I_{a1} < I_{c1}$  and  $I_{a2} < I_{c2}$ .

The assumption of statistical adiabaticity<sup>4</sup> described earlier is introduced into Eq. (3.3) by making  $w_{jnlE}^\ddagger$  a function of the translational energy in excess of the effective barrier  $B_1^\ddagger$ ,  $E_p - B_1^\ddagger$ . To ensure, also, that  $E$  exceeds  $u^\ddagger + E_{1J}^\ddagger$  [as on the left hand side of Eq. (3.3)] we introduce a step function  $h(E_p + E_n - u^\ddagger - E_{1J}^\ddagger)$ . Thereby,

$$w_{jnlE}^\ddagger \cong w^J(E_p - B_1^\ddagger) h(E_p + E_n - u^\ddagger - E_{1J}^\ddagger). \quad (3.7)$$

One can then immediately integrate over  $j$  in Eq. (3.3), and then interchange the order of the operator  $\mathcal{F}$  with the  $E_p$  and  $l$  integrals

$$N_{J\alpha}^\ddagger(E - u^\ddagger - E_{1J}^\ddagger) = \mathcal{F} \left[ \int_{E_p=u}^{E-E_R} dE_p \rho_v(E - E_p - E_R) \right. \\ \left. \times h(E_p + E_n - u^\ddagger - E_{1J}^\ddagger) \int_{l=0}^{l_m} dl w^J(E_p - B_1^\ddagger) B(j_1 j_2 l J) \right], \quad (3.8)$$

where

$$B(j_1 j_2 l J) = h(j_c - j_s)(j_c - j_s) \quad (3.9)$$

and  $\mathcal{F}$  is given by Eq. (3.5). The practical limits of integration over  $E_p$  and  $l$  in Eq. (3.8) are determined from the condition that  $\rho_v$  and  $w^J$  vanish when their arguments are negative, i. e.,

$$E_p \leq E - E_R, \quad (l^2/2I^\ddagger) + u^\ddagger \leq E_p, \quad (3.10)$$

for the case of a tight transition state. This integration domain over  $E_p$  and  $l$  is given in Fig. 2. [For the case of a loose transition state the separation distance  $r^\ddagger$  in the transition state, as well as  $I^\ddagger$  and  $u^\ddagger$ , would vary with  $l$ , yielding thereby a more complicated (but definite) maximum value of  $l$  for each  $E_p$ .]

To show that the right hand side of Eq. (3.8) is approximately a product of two convolutions it is conve-

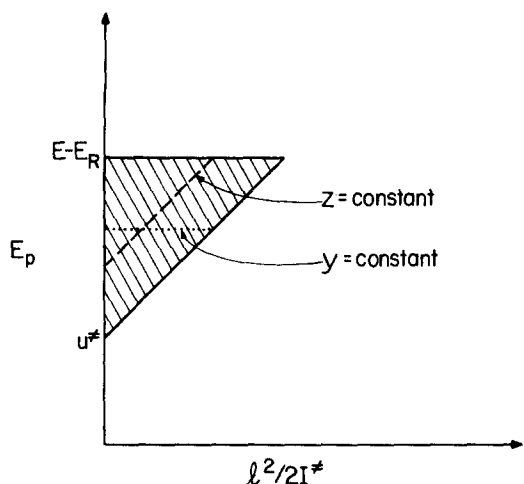


FIG. 2. The shaded region is the integration domain. For a given value of  $E_p$ ,  $l$  is integrated from 0 to  $[2I^\ddagger(E_p - u^\ddagger)]^{1/2}$ , and then  $E_p$  is integrated from  $u^\ddagger$  to  $E - E_R$ . Dashed line: line of constant  $z$ ,  $z = E - E_R - u^\ddagger - y - l^2/2I^\ddagger$ . Dotted line: line of constant  $y$ ,  $y = E - E_p - E_R$ . Change of variables: in the integration domain, for a given value of  $y$ ,  $z$  varies from  $z = 0$  to  $E - E_R - y - u^\ddagger$ , and then  $y$  varies from  $y = 0$  to  $E - E_R - u^\ddagger$ .

nient to transform the variables so as to exhibit explicitly the vanishing of  $\rho_v(x)$  and  $w^J(x)$  when  $x < 0$ , namely, variables  $y$  and  $z$  are introduced:

$$y = E - E_p - E_R, \quad (3.11)$$

$$z = E_p - B_1^\ddagger = E_p - u^\ddagger - (l^2/2I^\ddagger).$$

The absolute value of the Jacobian of the transformation<sup>11</sup> from  $(E_p, l)$  to  $(y, z)$ , i. e.,  $|\partial(E_p, l)/\partial(y, z)|$ , is  $I^\ddagger/l$ . Since  $E - E_p - E_R \geq 0$  and  $E_p \geq B_1^\ddagger$ , the domains integrated over  $(E_p, l)$  and  $(y, z)$  are as in Fig. 2:

$$N_{J\alpha}^\ddagger(E - u^\ddagger - E_{1J}^\ddagger) = I^\ddagger \int_{y=0}^{E-u^\ddagger-E_R} dy \rho_v(y) h(E - u^\ddagger - E_{1J}^\ddagger) \times \int_{z=0}^{E-u^\ddagger-E_R-y} dz w^J(z) l^{-1} B(j_1 j_2 l J), \quad (3.12)$$

where, from Eq. (3.11),

$$l = [2I^\ddagger(E - E_R - u^\ddagger - y - z)]^{1/2}. \quad (3.13)$$

The limits on  $y$  and  $z$  ensure that  $l^2$  will never be negative. One can now readily interchange the  $\mathcal{F}$  operator and the  $(y, z)$  integrals, by first introducing the Heaviside step function  $h(l^2)$  into Eq. (3.12) to ensure  $l^2 > 0$ . One can then replace the limits as indicated below:

$$N_{J\alpha}^\ddagger(E - u^\ddagger - E_{1J}^\ddagger) = \int_{y=0}^{E-u^\ddagger-E_R} dy \rho_v(y) h(E - u^\ddagger - E_{1J}^\ddagger) \times \int_{z=0}^{E-u^\ddagger-y} dz w^J(z) G^J(E - y - u^\ddagger - z), \quad (3.14)$$

with

$$G^J(E - u^\ddagger - y - z) = I^\ddagger \mathcal{F}[l^{-1} h(l^2) B(j_1 j_2 l J)]. \quad (3.15)$$

$G^J$  in Eq. (3.15) is a function of  $E - u^\ddagger - y - z$ :  $h(l^2)$  ensures that  $E - u^\ddagger - y - z - E_R \geq 0$  and one integrates in Eq. (3.15) over the variables in  $E_R$ , i. e., over  $j_1 j_2 k_1 k_2$ .

Approximately, as shown in Appendix C, Eq. (3.14) can be rewritten as

$$N_{J\alpha}^\ddagger(E - u^\ddagger - E_{1J}^\ddagger) \cong \rho_v^* w^J * G^J, \quad (3.16)$$

where the symbol  $*$  denotes a convolution. This convolution integral equation (3.16) can be easily solved by Laplace transformation. By multiplying both sides of Eq. (3.16) by  $\exp[-\beta(E - u^\ddagger)]$ , integrating  $E - u^\ddagger$  from 0 to  $\infty$ , and applying the convolution theorem twice Eq. (3.16) is converted into (3.17):

$$\bar{w}^J(\beta) = Q_{J\alpha}^\ddagger(\beta)/\beta Q_v(\beta) \bar{G}^J(\beta), \quad (3.17)$$

where

$$Q_{J\alpha}^\ddagger(\beta) = \int_0^\infty \exp(-\beta x) [dN_{J\alpha}^\ddagger(x - E_{1J}^\ddagger)/dx] dx, \quad (3.18)$$

$$Q_v(\beta) = \int_0^\infty \exp(-\beta x) \rho_v(x) dx,$$

$$\bar{w}^J(\beta) = \int_0^\infty \exp(-\beta x) w^J(x) dx,$$

$$\bar{G}^J(\beta) = \int_0^\infty \exp(-\beta x) G^J(x) dx.$$

Inversion of Eq. (3.17) yields an expression for  $w^J(x)$ . By replacing  $x$  by  $E_p - B_1^\ddagger$  one obtains

$$w^J(E_p - B_1^\ddagger) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} [Q_{J\alpha}^\ddagger(\beta)/\beta Q_v(\beta) \bar{G}^J(\beta)] \exp[\beta(E_p - B_1^\ddagger)] d\beta, \quad (3.19)$$

where  $Q_{J\alpha}^\ddagger(\beta)$  is the vibrational-internal rotational partition function of the active modes of the transition state (at a temperature  $T = 1/k_B\beta$  and at a total angular momentum  $J$ ),  $Q_v$  is the vibrational-internal rotational partition function of all active modes of the product molecules, and  $\bar{G}^J(\beta)$  defined by Eqs. (3.15) and (3.18) is a nonseparable rotational partition function. Equation (3.19) applies to symmetric tops, as well as to spherical tops and linear molecules. The integral in Eq. (3.19) denotes an integration along the line  $(c - i\infty, c + i\infty)$  in the complex plane, where  $c$  is a positive constant. The contour is closed in the left half or right half part of the complex  $\beta$  plane depending on whether  $E_p - B_1^\ddagger$  is positive or negative. Methods to evaluate Eq. (3.19) are given in Sec. V.

### C. An expression for the energy distribution function

$$d\sigma_{E_p, j_1, j_2, E} / dE_p$$

The distribution of the final translational energy of the products per unit energy in the range  $E_p$  to  $E_p + dE_p$  is defined by<sup>12</sup>

$$d\sigma_{E_p, j_1, j_2, E} / dE_p = \sum_{j_n} \sigma_{j_n, j_1, j_2, E} \delta(E - E_p - E_n), \quad (3.20)$$

where the sum over  $j$  is from  $|j_1 - j_2|$  to  $j_1 + j_2$ . By assuming classical rotations and quantum mechanical vibrations one readily sees that Eq. (3.20) is equivalent to (3.21):

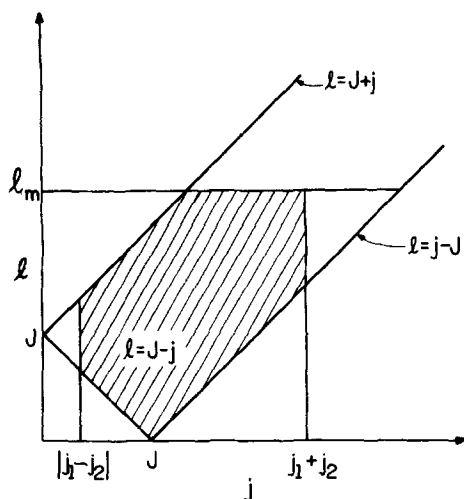


FIG. 3. In the domain of integration (shaded) for a given value of  $j$ ,  $l$  varies from  $|j - j|$  to  $l_{\zeta} = \min\{l_m, J + j\}$ , then  $j$  varies from  $|j_1 - j_2|$  to  $j_1 + j_2$ .  $l_{\zeta}$  is always greater than  $|J - j|$  to ensure angular momentum conservation. If one interchanges the order of integration, for a given value of  $l$ ,  $j$  varies from  $j_>$  to  $j_{\zeta}$ , then  $l$  varies from 0 to  $l_m$ .  $j_{\zeta}$  is always greater than  $j_>$  to ensure angular momentum conservation.

$$d\sigma_{E_p, j_0 n_0 E} / dE_p = \mathcal{F} \left[ \int_{E_v=0}^{\infty} \rho_v(E_v) \times \delta(E - E_p - E_R - E_v) \int_{j=|j_1-j_2|}^{j_1+j_2} dj \sigma_{j n, j_0 n_0 E} \right], \quad (3.21)$$

where  $E_v$  is the energy in the vibrational degrees of freedom and  $E_n$  was written as  $E_R + E_v$ . From Eqs. (3.1), (3.2), and (3.7), the properties of delta functions, and by interchanging the order of integration over  $l$  and  $j$  (as described in Fig. 3) the final expression for the energy distribution becomes

$$d\sigma_{E_p, j_0 n_0 E} / dE_p = \sigma_0 \sum_{j=0}^{l_0 m} \left[ (2J+1) / \left( l_{0m}^2 \sum_{\alpha} N_{J\alpha}^{\dagger} \right) \right] \times \mathcal{F} \left[ \rho_v(E - E_p - E_R) \int_{l=0}^{l_0 m} dl h(E - u^{\dagger} - E_{1J}^{\dagger}) w^J(E_p - B_1^{\dagger}) B(j_1 j_2 l J) \right], \quad (3.22)$$

where the various symbols were defined in Sec. III B.

Calculations can be performed to determine the energy distribution from the formulas in this section for either a loose or a tight transition state in the exit channel. For the case of a tight exit channel transition state  $N_{J\alpha}^{\dagger}$  is calculated from the geometry of the transition state and  $w^J(E_p - B_1^{\dagger})$  is determined from Eq. (3.19). By combining  $N_{J\alpha}^{\dagger}$  and  $w^J(E_p - B_1^{\dagger})$  with Eq. (3.22) the energy distribution  $d\sigma_{E_p, j_0 n_0 E} / dE_p$  can be determined. On the other hand, if the transition state is loose, the  $w^J(E_p - B_1^{\dagger})$  is a unit step function  $h(E_p - B_1^{\dagger})$  instead of Eq. (3.19), and  $N_{J\alpha}^{\dagger}$  is evaluated by replacing  $w_{j n l E}^{\dagger}$  with  $h(E_p - B_1^{\dagger})$  in Eq. (3.3). The distribution of the final translational energy per unit energy can then be calculated from Eqs. (3.1), (3.2), and (3.21).

#### IV. STATISTICALLY ADIABATIC S MATRIX, ANGULAR DISTRIBUTIONS, AND ROTATIONAL POLARIZATION EXPERIMENTS

Since any physical observable can be calculated once the S matrix elements are determined (i. e., once the collision problem is solved), a parametrization of this matrix within the framework of a statistically adiabatic theory is desirable and is given in the present section in terms of the reaction probabilities of Sec. III and Appendix B.

By applying Feshbach's theory of resonance scattering and examining in detail the structure of the S matrix it has been shown that<sup>13</sup>

$$\left| S_{j n l \alpha - j_0 n_0 l_0 \alpha_0}^{J E} \right|^2 = (1 - w_{j n l E}^{\alpha J} \delta_{j j_0} \delta_{n n_0} \delta_{l l_0} \delta_{\alpha \alpha_0} + w_{j n l E}^{\alpha J} w_{j_0 n_0 l_0 E}^{\alpha_0 J} \sum_{\alpha} N_{J\alpha}^{\dagger}), \quad (4.1)$$

where now  $\alpha j n l J E$  or  $\alpha_0 j_0 n_0 l_0 J E$  refers to a state of the products or the reactants. When it refers to the reactants, then  $w_{j_0 n_0 l_0 E}^{\alpha_0 J}$  is the probability of forming the complex from the reactants.

In Eq. (4.1) the last term is the probability of forming a complex initially  $w_{j_0 n_0 l_0 E}^{\alpha_0 J}$  multiplied by  $w_{j n l E}^{\alpha J} / \sum_{\alpha} N_{J\alpha}^{\dagger}$ , the probability of its dissociation to form a state  $\alpha j n l J E$ . Equation (4.1) neglects the formation of any state  $\alpha j n l J E$  by a direct process, other than the initial state  $\alpha_0 j_0 n_0 l_0 J E$ . [Such events could be included by suitably generalizing Eq. (4.1), introducing thereby probabilities for the direct process.] The first term on the right side of Eq. (4.1) is zero unless  $\alpha j n l J E$  is the initial state, i. e.,  $\alpha_0 j_0 n_0 l_0 J E$ , and then equals the probability of not forming a complex. The S matrix elements in Eq. (4.1) satisfy the principle of microscopic reversibility. The S matrix is also diagonal in  $J$ ,  $E$ , and  $M$  and, in the present case of absence of external fields, independent of  $M$  since different values of  $M$  can be obtained by rotating the coordinate system, an operation which does not affect the collision dynamics. It is readily verified that the sum of the squares of the S matrix elements given by Eq. (4.1) satisfy (4.2):

$$\sum_{j n l \alpha} \left| S_{j n l \alpha - j_0 n_0 l_0 \alpha_0}^{J E} \right|^2 = 1. \quad (4.2)$$

The phase of the S matrix is treated by imposing the random phase approximation,<sup>14</sup> i. e., by assuming the interference among different partial waves for a given  $J$  randomly cancel and by neglecting cross terms in double sums over  $J$ 's (e. g., Ref. 15). Therefore, with this choice of phase the S matrix is completely determined since the magnitudes are given in Eq. (4.1).

With the S matrix parametrized as above it is now possible to calculate other properties besides the energy distribution of the product molecules for reactions proceeding through tight transition states. For example, the angular distribution or its moments can be determined in the center-of-mass system of coordinates (or in the laboratory system of coordinates if the proper Jacobian of the transformation<sup>16</sup> is considered) by combining standard quantum mechanical expressions for the differential cross section in terms of S matrix ele-

ments<sup>15</sup> with Eq. (4.1) and the random phase approximation. Also, the rotational polarization cross section of the product molecules,<sup>17</sup> e.g., the cross section for a given product angular momentum  $j_1$  and its projection on any quantization axis, or its specific moments (as studied by Herschbach and co-workers<sup>17</sup>) can be determined again by applying standard quantum mechanical expressions for these cross sections in terms of the  $S$  matrix elements (4.1). (The classical limit of the squares of the Clebsch–Gordan coefficients and Wigner rotation matrices that occur in the angular distributions can be determined from Ref. 18.) It should be remarked that Eq. (4.1) applies to either loose or tight transition states and the form of the transition state determines the form of the reaction probabilities.

## V. DISCUSSION AND NUMERICAL EXAMPLE

In the preceding sections the transition state in the entrance channel was treated as loose. These results can be extended to include the case of an entrance channel tight transition state and the resulting equations are given in Appendix B. In the present section, instead, the results of the previous sections and Appendix A are applied to a numerical example. An experimental example, where the entrance channel transition state is loose and the exit channel transition state is tight, is now available.<sup>3</sup> The data comes directly from the beautiful molecular beam experiments of Y. T. Lee and co-workers. The reaction considered is Eq. (1.5).

### A. Numerical parameters

The vibrational frequencies of the products of Eq. (1.5) can be found in Refs. 19 and 20. Most of the frequencies of the activated complex were chosen to be identical to the product molecules for the purpose of this calculation. The four bending vibrations were chosen to be approximately 250  $\text{cm}^{-1}$  in order that the zero point energy of the exit channel transition state was similar to that of Ref. 3. The low frequency bending vibrations were treated as classical for simplicity. The most probable collision energy in the center of mass system is 2.15 kcal/mole and the total energy for redistribution among the active degrees of freedom of the product molecules is 25.0 kcal/mole.<sup>3</sup> The value of  $u^\ddagger$ , which includes effects of differences of zero point energies of product molecules and the exit channel transition state, was taken to be 5.5 kcal/mole.<sup>3</sup> The value of  $I^\ddagger$  was determined from  $I^\ddagger = \mu r^{\ddagger 2}$ , where  $\mu$  is the reduced mass of the final products and  $r^\ddagger$ , the classical turning point for complex formation, was taken to be 2 Å.<sup>3</sup> The density of states and sum of states were calculated using the semiempirical quantum mechanical expressions of Whitten and Rabinovitch.<sup>21</sup> The value of  $l_{0m}$  was approximated using a value of 7.3 Å<sup>2</sup> for  $\sigma_0$ .<sup>3</sup> The moments of inertia were taken to be<sup>3</sup>  $I_{a_1} = 53.9$  and  $I_{c_1} = 105.3 \text{ amu Å}^2$  for the 2-fluoropropene product of Eq. (1.5) and  $I_{a_2} = 1.82$  and  $I_{c_2} = 3.63 \text{ amu Å}^2$  for the methyl radical.

Under the given experimental conditions it sufficed to consider only a single reaction channel, i.e., to replace  $\sum_\alpha N_{J\alpha}^\ddagger$  by  $N_{J\alpha}^\ddagger$ . All the  $d\sigma_{E_p, j_0^\alpha E} / dE_p$  vs  $E_p$  plots

were normalized in  $E_p$  space. The units on  $d\sigma_{E_p, j_0^\alpha E} / dE_p$  are  $(\text{kcal/mole})^{-1}$  and the units for  $E_p$  are kcal/mole.

Since  $N_{J\alpha}^\ddagger$  is only weakly dependent on  $J$ , the sums over  $J$  in Eq. (3.22) were made at only three values, namely,  $J=5, 20,$  and  $38$ .<sup>3</sup> To check this last approximation the normalized  $d\sigma_{E_p, j_0^\alpha E} / dE_p$  was evaluated as a function of  $E_p$  taking  $J=5$ , then taking  $J=5$  and  $20$ , and finally taking  $J=5, 20,$  and  $38$ . The peak height of the normalized curves differed by less than 0.5%, and the full width at 1/4, 1/2, and 3/4 height was the same within 1.0% for the three different cases considered. Therefore, it is reasonable to conclude that in the interval  $(0, l_{0m})$  the  $J$  summand in Eq. (3.22) is relatively independent of  $J$  for this example, and so the sum over  $J$  becomes the summand at an average  $J$  multiplied by  $(l_{0m} + 1)^2$ . The  $l_{0m} + 1$  is independent of  $E_p$  and so does not affect a calculated normalized  $E_p$  distribution.

Now, to further show that the approximation made in Eq. (3.17) is valid, we choose  $J$  relatively small, e.g.,  $J=5$ , and then Eq. (3.16) is an exact convolution integral equation. The  $w$ 's are now solved by the Laplace transform method and the energy distribution is calculated from Eq. (3.22) for this small  $J$  [i.e., the sum in Eq. (3.22) is evaluated over one  $J$  since the  $J$  summand is insensitive to  $J$ ]. When this calculation was performed [i.e., when  $E_{1J}^\ddagger$  was neglected in Eq. (3.16)] we found the peak height and width for this energy distribution differed by less than 1.0% of that computed by the other more rigorous method.

### B. Numerical methods

The single integrals were calculated by Simpson's rule. The multiple integrals were evaluated by using a tenth degree Gauss–Legendre quadrature formula.<sup>22, 23</sup> Since the integrands were smoothly varying and not oscillatory, the accuracy of all numerically evaluated integrals were three decimal places, judging from convergence on adding extra points.  $Q_{J\alpha}^\ddagger$ ,  $Q_v$ , and  $\bar{G}^J(\beta)$

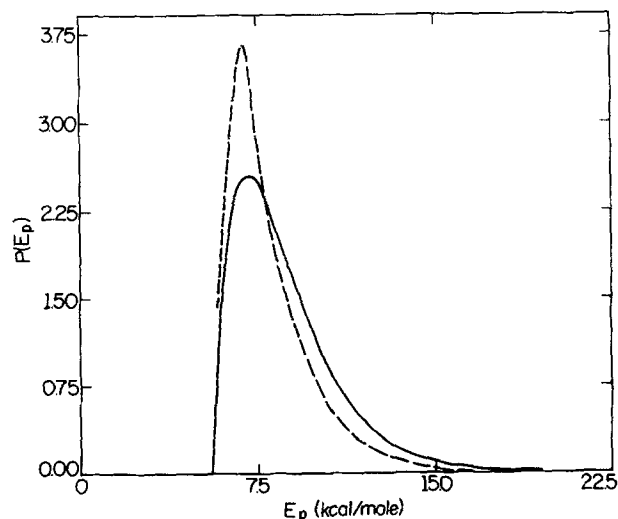


FIG. 4. A plot of the normalized energy distribution vs  $E_p$ . The solid line is phase space theory, and the dashed line is loose transition state theory when  $l \gg j$ .

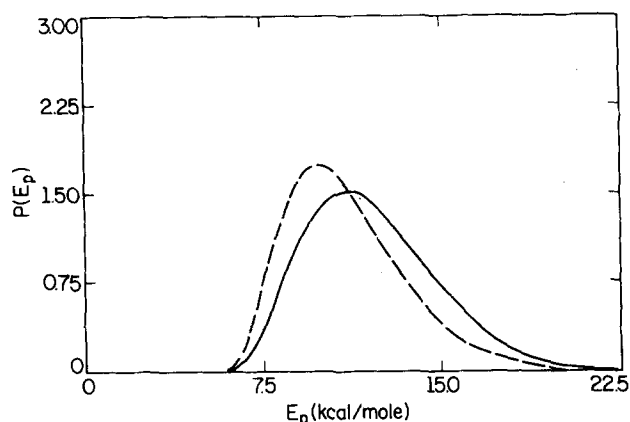


FIG. 5. A plot of the normalized energy distribution vs  $E_p$ . The solid line is general tight transition state theory, and the dashed line is tight transition state theory when  $l \gg j$ .

in Eq. (3.18) were evaluated by numerically Laplace transforming the Whitten-Rabinovitch sum of states for  $Q_{j,\alpha}^\ddagger$ , the Whitten-Rabinovitch density of states for  $Q_v$ ,<sup>21</sup> and  $G^J(x)$  [defined in Eq. (3.15)], respectively, using a Gauss-Laguerre quadrature formula.<sup>22,23</sup> The numerical function  $Q_{j,\alpha}^\ddagger/\beta Q_v \bar{G}^J(\beta)$  was tabulated for various values of  $\beta$  and fit to a polynomial series  $\sum_i C_i/\beta^i$  using a least squares criterion. Typically, eight or nine terms in the series were used to obtain an accurate fit over the range of interest for  $\beta$ .  $w^J$  was then obtained by inverse Laplace transforming the series fit  $\sum_i C_i/\beta^i$  term by term, analytically. To check the accuracy of the solution 20 different values of  $E - u^\ddagger$  were chosen for every integral equation solved and the left hand side of Eq. (3.16) (calculated by the Whitten-Rabinovitch approximation) was compared to the right hand side of Eq. (3.16) (calculated by a numerical quadrature) for each of the 20  $E - u^\ddagger$ 's. The average error from all checks was found to be less than 2.0%.

TABLE I. General tight transition state energy distributions.

$E_p$ (kcal/mole)	$P(E_p)$ (kcal/mole) <sup>-1</sup>
5.52	0.0
6.20	0.0005
6.82	0.0090
7.44	0.0316
8.06	0.0645
8.67	0.0974
9.30	0.1227
9.92	0.1403
10.5	0.1500
11.2	0.1508
11.8	0.1450
12.4	0.1333
13.6	0.1012
14.9	0.0675
16.1	0.0400
17.4	0.0206
18.6	0.0097
19.8	0.0038
21.1	0.0013
22.3	0.0003

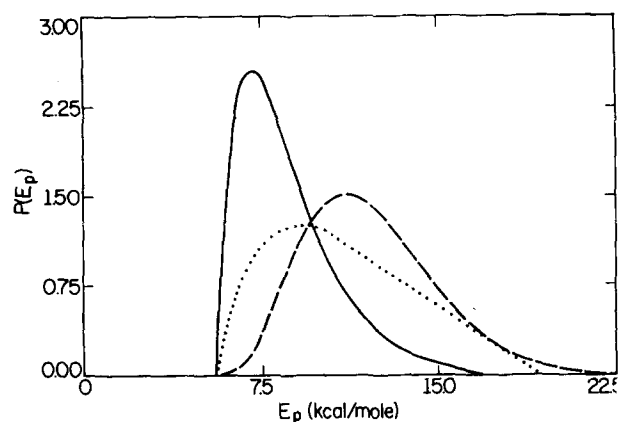


FIG. 6. A plot of the normalized energy distribution vs  $E_p$ . The solid line is phase space theory, the dashed line is general tight transition state theory, and the dotted line is the experimental result of Ref. 3.

### C. The results

In Fig. 4 the results from phase space theory [i. e., Eqs. (3.1)–(3.3) and (3.21) with  $w_{inE}^J = h(E_p - B^\ddagger)$ ] are compared to the results of loose transition state theory when  $l \gg j$  [i. e., Eq. (A1)]. The analogous results for the tight transition state case are given in Fig. 5 [i. e., Eqs. (3.19) and (3.22) for the general case and Eqs. (A1) and (A5) for the  $l \gg j$  case], and some tabulation is given in Table I. In Fig. 6 the results from phase space theory and tight transition state theory with full angular momentum restrictions are compared with experiment. A decrease in the barrier  $U^\ddagger$  in the exit channel by 1.4 kcal/mole for the  $l \gg j$  case in Fig. 5 roughly caused a shift of the entire curve to the left, by 1.4 kcal/mole.

It is clear that the addition of exit channel dynamical effects in the present form for methyl elimination reactions reduces the discrepancy between the statistical and experimental distribution. Other more dynamical theories may, of course, give somewhat similar results but any theory should include some discussion of the dynamical evolution of bending vibrations of the exit channel transition state into other degrees of freedom of the products, and may include the interactions of the translational motion with the other internal degrees of freedom in this exit channel. In contrast, all of these interactions vanish when the exit channel transition state is loose.

### ACKNOWLEDGMENT

We are pleased to acknowledge a helpful discussion with Professor Donald Secretst of this department on numerical methods for solving integral equations, and to acknowledge support of the present research by a grant from the National Science Foundation.

### APPENDIX A. LOOSE AND TIGHT TRANSITION STATE THEORY WHEN $l \gg j$

In this Appendix the results of previously derived equations are listed for convenience.<sup>4</sup> They also follow



from the general equations of Sec. III, as is shown below by assuming  $l \gg j$ .

The loose transition state distribution can be obtained by assuming  $l \gg j$  for a phase space distribution or by using RRKM theory with full angular momentum restrictions. The result for the distribution is<sup>4</sup>

$$d\sigma_{E_p, j_0 n_0 E} / dE_p = \sigma_0 \int_{u=0}^{E-E_p} \rho_1(u) \rho_2(E-E_p-u) A(E_p) du / \sum_{\alpha} N_{J\alpha}^{\dagger}, \quad (\text{A1})$$

where  $\rho_1$  and  $\rho_2$  refer to the individual vibrational-rotational density of states of each of the product molecules. Rigorously,  $\rho_1$  and  $\rho_2$  are sums of delta functions centered at each energy level; however, a good approximation is obtained by using the semiempirical quantum mechanical relations of Whitten and Rabino- vitch. The  $J$  in  $N_{J\alpha}^{\dagger}$  can be taken to be an average  $J$  if one wishes, since  $N_{J\alpha}^{\dagger}$  is usually weakly dependent on  $J$ .  $A(E_p)$  is unity when  $l_m > l_{0m}$  and equals  $(l_m/l_{0m})^2$  when  $l_m \leq l_{0m}$ .

It is instructive to show that Eq. (A1) follows from Eq. (3.22) when  $l \gg j$ . From Eqs. (3.1), (3.2), and (3.21) it is found that

$$d\sigma_{E_p, j_0 n_0 E} / dE_p = \sigma_0 \mathcal{F} \rho_v(E-E_p-E_R) \times \int_{j=|j_1-j_2|}^{j_1+j_2} dj \sum_{j=0}^{J_<} \left[ (2J+1)/l_{0m}^2 \left( \sum_{\alpha} N_{J\alpha}^{\dagger} \right)^{-1} \times h(l_{<} - |J-j|) (l_{<} - |J-j|) \right], \quad (\text{A2})$$

where  $w_{JnIE}^{\dagger} = h(E_p - B_J^{\dagger})$  for a loose transition state,  $\mathcal{F}$  is defined by Eq. (3.5), the sum over  $J$  has been extended to  $J_{<} = \min\{l_{0m}, l_m + j\}$  without changing the value of  $d\sigma_{E_p, j_0 n_0 E} / dE_p$ , and the various other symbols were defined in Sec. III. If it is assumed that  $l \gg j$ , then  $J_{<} \cong \min\{l_m, l_{0m}\}$ ,  $|J-j| \cong J-j$ ,  $l_{<} \cong J+j$ , and  $(l_{<} - |J-j|) \cong 2j$ . Upon introducing these approximations into Eq. (A2), integrating over  $j$ , and recalling that

$$\int_{j=|j_1-j_2|}^{j_1+j_2} 2j dj = 4j_1 j_2, \quad \sum_{j=0}^{J_{<}} (2J+1)/l_{0m}^2 \sum_{\alpha} N_{J\alpha}^{\dagger} \cong A(E_p) / \sum_{\alpha} N_{J\alpha}^{\dagger}$$

(where the  $J$  in  $N_{J\alpha}^{\dagger}$  is an average  $J$ ) and

$$\int_{u=0}^{E-E_p} \rho_1(u) \rho_2(E-E_p-u) du = \mathcal{F} [4j_1 j_2 \rho_v(E-E_p-E_R)],$$

Eq. (A2) reduces to (A1), the desired result.

The distribution of translational energy for product molecules that proceed through a tight exit channel transition state is the same as Eq. (A1) except now  $A_t(E_p)$  replaces  $A(E_p)$ , where<sup>4</sup>

$$A_t(E_p) = (1/l_{0m}^2) \int_{j^2=0}^{l_{0m}^2} w^{\dagger}(E_p - B_J^{\dagger}) dJ^2 \quad (l_m > l_{0m}) \\ = (1/l_{0m}^2) \int_{j^2=0}^{l_m^2} w^{\dagger}(E_p - B_J^{\dagger}) dJ^2 \quad (l_m < l_{0m}) \quad (\text{A3})$$

and where<sup>4</sup>

$$w^{\dagger}(E_p - B_J^{\dagger}) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} (Q_{J\alpha}^{\dagger} / \beta Q) \exp[\beta(E_p - B_J^{\dagger})] d\beta, \\ Q_{J\alpha}^{\dagger} = \int_0^{\infty} (dN_{J\alpha}^{\dagger}(x)/dx) \exp(-\beta x) dx, \quad Q = Q_1 Q_2, \quad (\text{A4}) \\ Q_1 = \int_0^{\infty} \rho_1(x) \exp(-\beta x) dx, \quad Q_2 = \int_0^{\infty} \rho_2(x) \exp(-\beta x) dx.$$

$Q_{J\alpha}^{\dagger}$  defined in Eq. (A4) is the vibrational-rotational partition function of all the active modes of the transition state, excluding the  $2J+1$  degeneracy which is absent from both sides of Eq. (3.3), and  $Q$  defined in Eq. (A4) is the vibrational-rotational partition function of all active modes of the product molecules.

If one assumes much cancellation in  $Q_{J\alpha}^{\dagger}/Q$  apart from the rotation of the products that appear as low frequency bending vibrations of the transition state, Eq. (A4) can be evaluated. By treating these bending vibrations classically we obtained the following from Eqs. (A3) and (A4):<sup>4</sup>

$$A_t(E_p) = (A^{\dagger}/6A) (l_m^2/2I^{\dagger})^2 (l_m/l_{0m})^2 \{1 - (1 - [l_{0m}/l_m]^2)^3\} \quad (l_m > l_{0m}), \quad (\text{A5})$$

$$A_t(E_p) = (A^{\dagger}/6A) (l_m^2/2I^{\dagger})^2 (l_m/l_{0m})^2 \quad (l_m < l_{0m}).$$

The  $A$  and  $A^{\dagger}$  in Eq. (A5) are numerical constants which depend on the structure of the transition state and of the separated product molecules.

The distribution of final translational energy for the product molecules having an exit channel tight transition state with  $l \gg j$  can be obtained by numerically evaluating Eq. (A1) noting that  $A(E_p)$  in Eq. (A1) is now to be replaced by  $A_t(E_p)$  defined in Eq. (A5).

It is interesting to show that the tight transition with  $l \gg j$  is a special case of the general tight transition state theory defined in Eq. (3.19). By comparing Eq. (3.19) with (A4) we must establish the following relation in order to show that Eq. (A4) follows from (3.19):

$$Q = \lim_{l \gg j} [\exp(\beta E_{1J}^{\dagger}) Q_v(\beta) \bar{G}^J(\beta)]. \quad (\text{A6})$$

The  $\exp(\beta E_{1J}^{\dagger})$  results in Eq. (A6) since  $Q_{J\alpha}^{\dagger}$  in Eq. (A4) is different from  $Q_{J\alpha}^{\dagger}$  in Eq. (3.18). The various symbols in Eq. (A6) were defined in Sec. III. Applying the convolution theorem to Eq. (A6) leads to

$$Q = \beta \lim_{l \gg j} \exp(\beta E_{1J}^{\dagger}) \mathcal{L}(1 * G^J * \rho_v), \quad \mathcal{L}(1) = 1/\beta, \quad (\text{A7})$$

where  $\mathcal{L}$  means Laplace transformation and  $*$  denotes a convolution. From Eqs. (3.3), (3.16), and (A6) one can show upon interchanging a  $j$  and  $l$  integral as described in Fig. 3 that

$$Q = \beta \lim_{l \gg j} \exp(\beta E_{1J}^{\dagger}) \mathcal{L} \left[ \int_{E_p-u}^E dE_p \mathcal{F} [\rho_v(E-E_p-E_R)] \times \int_{j=|j_1-j_2|}^{j_1+j_2} dj h(l_{<} - |J-j|) \int_{l=|l_1-j_1|}^{l_{<}} h(E_p - B_l^{\dagger}) dl \right], \quad (\text{A8})$$

where the various symbols are defined in Sec. III. By interchanging the order of the limiting process and the

Laplace transform we find  $l_{\zeta} \cong J+j$ ,  $|J-j| \cong J-j$ ,  $h(l_{\zeta} - |J-j|) \cong 1$ ,  $E_{1J}^{\dagger} \cong J^2/2I^{\dagger} = E_J^{\dagger}$ , and therefore Eq. (A8) becomes

$$Q = \beta \exp(\beta J^2/2I^{\dagger}) \int_{E-u^{\dagger}=0}^{\infty} e^{-\beta(E-u^{\dagger})} \times d(E-u^{\dagger}) \int_{E_p=u^{\dagger}}^E dE_p \rho(E-E_p) h(E_p - B_J^{\dagger}), \quad (\text{A9})$$

since

$$\rho(E-E_p) = \mathcal{F}[4j_1 j_2 \rho_v(E-E_p - E_R)]. \quad (\text{A10})$$

Evaluating the inner integral in Eq. (A9) gives

$$Q = \beta \exp(\beta E_J^{\dagger}) \int_{E-u^{\dagger}=0}^{\infty} \exp[-\beta(E-u^{\dagger})] N(E-B_J^{\dagger}) d(E-u^{\dagger}) \\ = \beta \int_{E-B_J^{\dagger}=0}^{\infty} \exp[-\beta(E-B_J^{\dagger})] N(E-B_J^{\dagger}) d(E-B_J^{\dagger}) = Q,$$

(A11)

where

$$N(E-B_J^{\dagger}) = \int_{x=0}^{E-B_J^{\dagger}} \rho(x) dx, \\ B_J^{\dagger} = E_J^{\dagger} + u^{\dagger},$$

and where  $N(y) = 0$  for  $y < 0$  since  $\rho(y) = 0$  for  $y < 0$ . Therefore, tight transition state theory with  $l \gg j$  as defined in Eq. (A4) follows from general tight transition state theory [Eq. (3.19)] when one assumes  $l \gg j$ .

## APPENDIX B. TIGHT TRANSITION STATE THEORY FOR THE ENTRANCE CHANNEL

In this section equations are derived for  $d\sigma_{E_p, j_0 n_0 E}/dE_p$  when both exit and entrance channels proceed through tight activated states. When the data become available the results of this section should be directly applicable. For simplicity the special case of  $l_0 \gg j_0$  and  $l \gg j$  is only considered.

The probability that a reacting pair prepared in state  $(\alpha_0 j_0 n_0 l_0 E)$  reacts is given by

$$w_{i_0 j_0 n_0 E} = \sum_{J=|l_0-j_0|}^{l_0+j_0} \frac{(2J+1)}{(2j_0+1)(2l_0+1)} w_{i_0 j_0 n_0 E}^J, \quad (\text{B1})$$

where  $w_{i_0 j_0 n_0 E}^J$  is the probability that a pair of reactants prepared in the state  $(\alpha_0 j_0 n_0 l_0 J E)$  react to produce a state of a given  $J$  and  $E$ . If one multiplies both sides of Eq. (B1) by  $(2l_0+1)$ , sums over  $l_0$  from 0 to  $\infty$ , and, finally, interchanges the order of the  $(J, l_0)$  sum we find

$$1 = \sum_{J=0}^{\infty} \sum_{l_0=|J-j_0|}^{J+j_0} [(2J+1)/(2j_0+1)] \\ \times w_{i_0 j_0 n_0 E}^J / \sum_{l_0=0}^{\infty} (2l_0+1) w_{i_0 j_0 n_0 E}.$$

(B2)

From Eq. (B2) the distribution of total angular momen-

tum is found to be

$$P_0(J) = \sum_{l_0=|J-j_0|}^{J+j_0} \frac{(2J+1)}{(2j_0+1)} w_{i_0 j_0 n_0 E}^J / \sum_{l_0=0}^{\infty} (2l_0+1) w_{i_0 j_0 n_0 E}.$$

(B3)

By using the standard relation<sup>24</sup>

$$\sigma_{0 j_0 n_0} = (\pi/k_0^2) \sum_{l_0=0}^{\infty} (2l_0+1) w_{i_0 j_0 n_0 E} \quad (\text{B4})$$

Eq. (B3) is written as

$$P_0(J) = [\pi/\sigma_{0 j_0 n_0} k_0^2 (2j_0+1)] \sum_{l_0=|J-j_0|}^{J+j_0} (2J+1) w_{i_0 j_0 n_0 E}^J. \quad (\text{B5})$$

The reaction probabilities in Eq. (B5) can be obtained by using microcanonical transition state theory together with the statistical adiabatic assumption. Since the details of the calculations are similar to those given in Part I for the exit channel, we merely give the final results for  $l_0 \gg j_0$  [see for example the derivation of Eqs. (6.6)–(6.9) in Part I]:

$$\left. \begin{aligned} w_{i_0 j_0 n_0 E}^J &= w^J(E_{p_0} - B_{i_0}^{0\dagger}) \\ &= \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} (Q_{J\alpha_0}^{0\dagger}/\beta Q_0) \exp[\beta(E_p - B_{i_0}^{0\dagger})] d\beta \\ Q_{J\alpha_0}^{0\dagger} &= \int_0^{\infty} [dN_{J\alpha_0}^{\dagger}(x)/dx] \exp[-\beta x] dx \\ Q_0 &= \int_0^{\infty} \rho_0(x) \exp(-\beta x) dx. \end{aligned} \right\} \quad (\text{B6})$$

$N_{J\alpha_0}^{\dagger}$  is the number of quantum states in the entrance channel activated complex for a given  $J$ ,  $M$ ,  $E$ , and  $\alpha_0$ , and  $\rho_0(x)$  is the vibrational-rotational density of states of the reactants. The other symbols are defined in the glossary of notation.

To calculate energy distributions one combines Eqs. (B5) and (B6) with Eqs. (3.1), (3.19), and (3.21).

## APPENDIX C. DERIVATION OF EQS. (3.16)–(3.17)

In this appendix we show that the error made in obtaining Eq. (3.16) [and hence (3.17)] from (3.14) is negligible for the present system.

One multiplies both sides of Eq. (3.14) by  $\exp[-\beta(E-u^{\dagger})]$  and, by integrating  $E-u^{\dagger}$  from 0 to  $\infty$ , finds

$$Q_{J\alpha}^{\dagger}(\beta)/\beta = \int_{E-u^{\dagger}=E_{1J}^{\dagger}}^{\infty} d(E-u^{\dagger}) \exp[-\beta(E-u^{\dagger})] \\ \times \int_{y=0}^{E-u^{\dagger}} dy \rho_v(y) \int_{z=0}^{E-u^{\dagger}-y} dz w^J(z) G^J(E-u^{\dagger}-y-z). \quad (\text{C1})$$

The  $Q_{J\alpha}^{\dagger}(\beta)$  in Eq. (C1) is defined in (3.18). By addition and subtraction Eq. (C1) is written as (C2):

$$\begin{aligned}
Q_{J\alpha}^{\dagger}(\beta)/\beta &= \int_{E-u^{\dagger}=0}^{\infty} \exp[-\beta(E-u^{\dagger})] d(E-u^{\dagger}) \int_{z=0}^{E-u^{\dagger}} dy \rho_v(y) \\
&\times \int_{z=0}^{E-u^{\dagger}-y} dz w^J(z) G^J(E-u^{\dagger}-y-z) - \int_{E-u^{\dagger}=0}^{E^{\dagger}} \exp[-\beta(E-u^{\dagger})] d(E-u^{\dagger}) \\
&\times \int_{z=0}^{E-u^{\dagger}} dy \rho_v(y) \int_{z=0}^{E-u^{\dagger}-y} dz w^J(z) G^J(E-u^{\dagger}-y-z).
\end{aligned} \tag{C2}$$

Equation (3.17) follows from (C2) by application of the convolution theorem if the second integral on the right hand side of Eq. (C2) is neglected.

To test this approximation we make some rough analytical calculations of the first and second integral in Eq. (C2) and show that the second integral is small for the system of interest, namely, Eq. (1.5). The error analysis will be performed in such a way as to obtain an upper bound on the error. It was found numerically that  $w^J(z)$  and  $G^J(E-u^{\dagger}-y-z)$  varied at least as  $C_1 z^2$  and  $C_2(E-u^{\dagger}-y-z)^2$ , respectively, where  $C_1$  and  $C_2$  are constants. The  $\rho_v$  in the first term on the right hand side of Eq. (C2) is, on the average, greater than

that in the second, since  $\rho_v(y)$  increases rapidly with increasing  $y$  for a molecule of 26 vibrational degrees of freedom. However, to obtain an upper bound on the error we assume that  $\rho_v(y)$  equals  $C_3 y$  ( $C_3$  is a constant) and so is the same in both terms. Some typical values of  $\beta$  and  $E_{1J}^{\dagger}$  are 1 and 1.5 kcal/mole, respectively. When this functional dependence of  $w^J(z)$ ,  $\rho(y)$ , and  $G^J(E-u^{\dagger}-y-z)$  is inserted into Eq. (C2), one finds that the first term of Eq. (C2) leads to a value of  $4C_1 C_2 C_3$  and the second term leads to a value of  $0.0007C_1 C_2 C_3$ . Thus, the percent error incurred in neglecting the second term in Eq. (C2) is 0.02%. This corresponds to making an error of 0.02% in the left hand side of Eq. (C2), and hence is negligible.

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