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MACROSCOPIC PROBABILITY FOR RATES OF CHEMICAL REACTIONS
CORRELATED WITH ELECTROSTATIC POTENTIALS OF THE TRANSIT AND REACTANT STATES

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Microscopic Reversibility for Rates of Chemical Reactions Carried
out with Partial Resolution of the Product and Reactant States*

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ABSTRACT

Applications of the principle of microscopic reversibility are considered for rates of reactions measured in experiments that reveal some of the dependence on the rotational, vibrational, and/or translational states of the reactants or products. Each type of measurement establishes a characteristic set of quantum states for the reactants and products, suggesting the removal of trivial statistical factors (densities of states) from the data to retrieve a purely dynamical quantity $\bar{\omega}(E)$, the state-to-state reaction rate suitably averaged over the initial and final sets of states at fixed total energy E . This quantity is fully symmetric with respect to the direction of the reaction--either the forward or reverse rate coefficient can be obtained by multiplying $\bar{\omega}$ with the proper density of final states. Thus $\bar{\omega}$ reflects the intrinsic probability of the process, disregarding the statistical bias introduced by the nature of the experiment itself. Methods of accurate computation of state-densities appropriate to several kinds of detailed kinetic measurements currently feasible are given.

I. Introduction

Despite the impressive successes of traditional chemical kinetics in accounting for the gross features of chemical reaction rates such as their variation with temperature, our understanding of the relative importance of translational, rotational, and vibrational degrees of freedom in reaction processes has remained highly speculative. It was realized early, to be sure, that unimolecular processes require the participation of internal degrees of freedom¹, but the implications of this fact have been extensively exploited only in models adopting a statistical viewpoint at the outset to avoid consideration of fine-grained details². The difficulty in establishing experimentally the effects of the different degrees of freedom originates in the indeterminacy of the initial and final molecular states in most experiments: The reactant states are usually unspecified except as they are weighed by the Boltzmann distribution, and the product states are restricted only by the conservation of energy.

Experimental techniques capable of resolving the states of the reactants and/or products are needed to expose the more detailed aspects of the reactions. Although the reactant translational motion can be well controlled in molecular beam experiments and widely varied with the use of special techniques such as supersonic or charge-exchanged beams³, there is no useful method at the present time for selecting internal states of the reactants over a wide range of internal energies. Results have, however, begun to appear on partially resolved analyses of the states of the products of bimolecular reactions studied by (a) infrared

chemiluminescence⁴, (b) chemical lasers⁵, and (c) velocity- or state-analysis of the products in crossed molecular beam reactions⁶.

The reactions studied by these techniques are typically quite exoergic, so that any of the contributions to the total energy of the products is free to range over a span much larger than the variation allowed by the experimental conditions in the total energy itself. One of the infrared chemiluminescence reactions^{4c}, $\text{Cl} + \text{HI} \rightarrow \text{HCl} + \text{I}$, serves as an example. If a crude line-of-centers model is used to account for this reaction's roughly 0.7 kcal/mole Arrhenius activation energy, it is predicted that over 90% of the reactions occur with reactant energies (translational plus rotational) in the range 2.5 ± 1.5 kcal/mole. Relative to the product ground state, which lies 31.7 kcal/mole below that of the reactants, the energy is therefore 34.2 ± 1.5 kcal/mole.

The principle of microscopic reversibility⁷ permits the transformation of data on product state distributions into information about the dependence of the rates of the reverse (endoergic) processes on the division of the available energy among rotational, vibrational, and translational modes. This is not merely an academic exercise giving nothing more than a different representation of the same data: In general only "atypical" reactions (low thresholds, large cross-sections) can be studied by these new techniques. The reverse reactions, having thresholds at least equal to their endoergicities, are much more likely to be representative of the majority of chemical processes. Data on unusual reactions are thus exchanged for data on more ordinary ones.

Each experimental technique reveals different aspects of the distributions, some of them more detailed than others. In applying the micro-reversibility principle to the best advantage, it is important to incorporate all the details produced by a given experiment while excluding all those that are not. The purpose of this paper is to outline these considerations for a number of experimentally interesting cases, and to derive working equations for each. The fully resolved infrared chemiluminescence experiments have already been analyzed in two papers by Anlauf, Maylotte, Polanyi, and Bernstein⁸ and by Polanyi and Tardy⁹, but will also be included here.

II. Microscopic Reversibility

Symmetries in the equations of motion of a dynamic system generate restrictions on the solutions of these equations, usually in the form of conservation laws. The power of these relations lies in their general ability to limit possible kinds of solutions or to establish relationships between solutions even though none of the actual solutions may be known. When the Hamiltonian is invariant to time-reversal¹⁰ a second solution to the time-dependent Schrodinger equation (or classical equations of motion), differing only in the direction of the motion, can be immediately obtained from any given solution by the operation of time-reversal on the original state-vector (or trajectory)¹¹. The expression of the consequences of time-reversal symmetry in terms of transition rates is known as the "principle of microscopic reversibility". Although such a principle can be formulated for any kind of process, our

discussion will be restricted to binary collisions:



The "products" C and D can either be the same chemical species as the "reactants" A and B (inelastic scattering) or different from them (chemical reactions).

Our system will be assumed to be enclosed by a finite container, but one whose size is large enough that the allowed translational energies are essentially continuous. Presently, in fact, we shall adopt a continuous description of the translational motion, which is equivalent to allowing the container to become infinite. It is convenient, however, to be able initially to specify unambiguously a normalizable state of the reactants or products by a composite discrete label γ . γ includes a set of internal quantum numbers n describing the electronic, vibrational, and rotational state of the pair of molecules and three translational quantum numbers τ describing their relative translational motion. This description is appropriate for the observable states of the system, i.e., before or after a collision has occurred, but since it does not take the interaction into account it cannot properly describe the system during a collision. Hence, the states so described are not stationary states of the Hamiltonian. If the system is prepared at time $t=0$ in one of these states γ its wave function will evolve in time, developing amplitudes in other states γ' having the same total energy. The squares of the amplitudes are the probabilities for transitions from γ to γ' ,

$p(\gamma \rightarrow \gamma'; t)$. The principle of microscopic reversibility requires that at all times $p(\gamma \rightarrow \gamma'; t) = p(\tilde{\gamma}' \rightarrow \tilde{\gamma}; t)$, where $\tilde{\gamma}$ is the state obtained by time-reversal of γ , etc. This relationship obviously also holds for the transition rate, $w = (dp/dt)_{t=0}$:

$$(1) \quad w(\gamma \rightarrow \gamma') = w(\tilde{\gamma}' \rightarrow \tilde{\gamma})$$

I.e., the rate of transition between two given states in the forward direction is the same as the rate of transition in the reverse direction for the time-reversed states. It is essential to include the operation of time reversal of the states for the reverse process. There is no necessary relation between $w(\gamma \rightarrow \gamma')$ and $w(\gamma' \rightarrow \gamma)$ unless required by additional symmetry properties. Figure 1, following a similar figure of Blatt and Weisskopf¹², illustrates the distinction between the two different inverse processes.

Although the complete symmetry of Eq. 1 is extremely appealing, it implies a perfect knowledge of the initial and final states, including their translational quantum numbers. For all experimentally interesting situations, however, the translational states are so closely spaced in energy that their complete quantum specification is out of the question; and, what is more serious, our knowledge of the internal states is also usually incomplete. We wish to construct relationships that reflect the exact state of our knowledge so that all the known details can be utilized without resorting to guesswork on the undetermined ones. A measurement that fails to provide a complete quantum specification of the state of the system establishes instead a set of states, any one

of which may be the real state of the system. Such a set of states would contain all the fully described states whose properties are consistent with the measurements. Since all the information about the state of the system should be incorporated into the description of the set of states, no distinctions are possible among the members of the set.

We will denote by Γ the set of initial (reactant) states and by Γ' the set of final (product) states established by any experiment. Since a given molecule can be in only one of the initial states at time $t=0$ (even though we have no way of knowing which one) but develops simultaneously amplitudes into all the final states, the physically meaningful rate is the average over the initial set Γ and the sum over the final set Γ' . This sum-average will be indicated by a superior bar:

$$(2) \quad \bar{w} = N_{\Gamma}^{-1} \sum_{\gamma} \sum_{\gamma'} w(\gamma \rightarrow \gamma')$$

The sum extends over all values of γ in Γ and of γ' in Γ' . N_{Γ} is the number of values of γ in the set Γ --the "size" of the set.

For the reverse process the roles of the two sets are interchanged: we must average over Γ' (now the initial states) and sum over Γ (now the final states). In terms of \bar{w} the law of microscopic reversibility becomes

$$(3) \quad \bar{w}(\Gamma \rightarrow \Gamma') / N_{\Gamma'} = \bar{w}(\tilde{\Gamma}' \rightarrow \tilde{\Gamma}) / N_{\Gamma}$$

Since time-reversal symmetry guarantees a one-to-one correspondence between each state and its time-reverse no distinction is needed between N_{Γ} and N_{Γ}^{∞} , etc.

For an arbitrarily large container the translational states approach a continuum. This allows the convenience of treating the translational motion in terms of continuous variables, but at the cost of the ability to distinguish individual states and hence of the ability to count states. Instead, the number of translational states included within given intervals of the chosen variables must be obtained from the product of the density of states with respect to these variables times the differential ranges of all the variables:

$$dN_{\Gamma} = P_{\Gamma}(\alpha, \beta, \dots) d\alpha d\beta \dots$$

The expression for the density of states P_{Γ} depends on the particular choice of independent variables, but in any case it is proportional to the volume of the container. For a given density of particles the total transition rate is also proportional to the container's size. Hence, it is customary to use, rather than the (divergent) density of states or transition rate for all space, the density of translational states per unit volume ρ_{Γ} and the transition rate per reactant pair per unit volume κ . $\kappa = v \sigma$ is the product of the relative speed v and the cross-section σ of the process of interest. Averaging of κ over a Boltzmann distribution of initial states and summing it over all possible final states produces the thermal rate coefficient $k(T)$.

The independent variables to be used in our description of

the translational motion are the relative kinetic energy E_T and the direction $\hat{\Omega}$ of the relative velocity. The number of translational states per unit volume within the ranges dE_T and $d^2\hat{\Omega}$ is independent of the direction. Hence it is given by the fraction of a sphere occupied by the incremental solid angle $d^2\hat{\Omega}$ times the total number of translational states in the interval dE_T : $d^3N_T = (d^2\hat{\Omega}/4\pi) \times (\rho_T dE_T)$. Here $\rho_T(E_T)$ is the density of translational states with respect to E_T irrespective of the direction of the relative motion¹³:

$$(4) \quad \rho_T(E_T) = \pi^{5/2} \mu^{3/2} E_T^{1/2} h^{-3} = A_T E_T^{1/2}$$

where μ is the reduced mass of the colliding molecules. The quantity A_T , defined by Eq. 4, is introduced to simplify expressions appearing below.

The set of initial or final states distinguished by any measurement process will consist of certain combinations of continuous translational states and discrete internal states. The appearance of the translational variables always removes the possibility of counting the states in the sets, so that densities of states are called for. With the incorporation of internal states into the description, however, the total energy E (relative to the reactant ground state) becomes a more convenient continuous variable than E_T since the various sets do not necessarily span simply-connected intervals in the translational variables. In Equation 3 N_T must be replaced by $dN_T = \rho_T dE$ where $\rho_T(E)$ is the density of states (per unit volume) in the initial set with respect to E . Similarly, N_T' becomes $dN_T' = \rho_T' dE'$ (where E' is the total energy of the products relative to their ground state), so that the

law of microscopic reversibility becomes:

$$(5) \bar{k}(r \rightarrow r') / \rho_{r'} = \bar{k}(r' \rightarrow r) / \rho_r = \bar{\omega}(r, r')$$

The differentials dE and dE' , which must be equal to satisfy energy conservation, have been cancelled out of Eq. 5. Equation 5 relates the forward and reverse \bar{k} 's only at a fixed total energy and cannot be expected to say anything about the dependence of either coefficient on the total energy.

The fully symmetric quantity $\bar{\omega}(\Gamma, \Gamma') = \bar{\omega}(\Gamma', \Gamma)$, defined in Eq. 5, is the state-to-state transition rate ω (per unit volume for each reactant pair) averaged over both the initial and final sets of states. It is a fundamentally dynamical quantity, not presently calculable theoretically. The densities of states, on the other hand, are purely static entities determined only by the spectroscopic properties of the reactants or products and the precise descriptions of the sets of states. In the following sections we show how they can readily be computed to a high degree of accuracy for several currently feasible experiments, and how they are to be used in connection with existing experimental data to extract information about the $\bar{\omega}$'s.

From Eq. 5 we can see that the ambiguities inherent in the initial and final sets of states in any experiment effect the observed \bar{k} in two essential ways: (1) Any variation of the basic dynamical quantity ω within these sets is obscured by the averaging over both sets. (2) The measurable quantity \bar{k} is proportional to

the density of final states. In some cases the latter statistical effect is sufficient to bias measurements towards predetermined qualitative trends almost independent of the variation of ω . The following section, where specific examples are considered, should clarify these effects.

III. Definitions of State Densities for Specific Sets of States

A. Completely Determined States

In the ideal collision experiment, we would know everything possible within the limits imposed by quantum mechanics about the initial states and learn everything possible about the final states. The internal states of the reactants and products would be fully determined, even to substate within a degenerate level; the relative incident translational kinetic energy E_T would be specified to within a small range dE_T ; and the direction of the relative momentum would be known to within a small solid angle $d^2\hat{\Omega}$. This ideal has actually been approached in the preparation of state- and velocity-selected beams of CsF in one set of experiments¹⁴ and in the analysis of CsF products from the reaction $\text{Cs} + \text{SF}_6$ in another study¹⁵. The extremely difficult internal state determination was accomplished by simultaneous use of inhomogeneous electric fields to focus given J,M states (certain values of M only) then microwave or RF resonance to "flop-in" or "flop-out" molecules in definite vibrational states (as in molecular beam electric resonance experiments). At this early stage in the development of these arts for collision studies, it is difficult to

foresee how widely the techniques will be applicable.

In this type of determined situation, the only density functions needed would originate in the impossibility of making dE_T or $d^2\hat{\Omega}$ exactly zero, i.e., the density of translational states defined in Eq. 4, $\rho_T(E_T)$.

B. Temperature or Total Energy Determined

At the other extreme in resolution are experimental situations in which only the temperature is known. If the reaction proceeds slowly with respect to all other relaxation processes, equilibrium Boltzmann distributions apply to all degrees of freedom of the reactants and products¹⁶. In this case the thermal rate coefficient $k(T)$ is given by:

$$(6) k(T) = \sum_n \frac{g_n \exp(-\beta E_n)}{Q_I(T)} \iiint_{\hat{\Omega}, E_T} \frac{dE_T d^2\hat{\Omega} \rho_T \exp(-\beta E_T)}{4\pi Q_T(T)} \bar{k}(n, E_T, \hat{\Omega})$$

where g_n is the degeneracy of the internal state n , and E_n its energy. $Q_I(T) = \sum_n g_n \exp(-\beta E_n)$ is the internal partition function; ρ_T is the density of translational states (Eq. 4), and $Q_T(T) = (2\pi\mu k_B T)^{3/2} h^{-3}$ is the translational partition function (per unit volume). β is $(k_B T)^{-1}$ where k_B is the Boltzmann constant. Final state variables have been left out of the notation for \bar{k} to simplify the expression. Eq. 6 involves two different kinds of averaging--one in which some experimental influence can be exerted by varying the temperature and another, involving averages of terms with the same Boltzmann factor, that cannot be externally varied. This distinction becomes more apparent if the total energy $E = E_T + E_n$

is used as the independent variable and Eq. 6 is written as

$$(7) \quad k(T) = \int dE \bar{Q}_{TOT}^{-1}(E) \rho_{TOT}(E) \exp(-\beta E) \bar{K}(E)$$

Here $\rho_{TOT}(E)$ is the total density of states at (total) energy E:

$$(8) \quad \rho_{TOT}(E) = \sum_n g_n \rho_T(E - E_n)$$

The sum in Eq. 8 runs over all n for which $E_n \leq E$, and \bar{K} is defined below. Figure 2 indicates the contributions from rotational sublevels of a particular vibrational state to the total density at energy E. $Q_{TOT}(T) = Q_I(T)Q_T(T)$ is the total partition function, and $\bar{K}(E)$ is defined by

$$(9) \quad \bar{K}(E) = \sum_n \iint \frac{d^2\hat{\Omega}}{4\pi} g_n \rho_T(E - E_n) \kappa(n, E - E_n, \hat{\Omega}) \\ \times \left[\sum_n \iint \frac{d^2\hat{\Omega}}{4\pi} g_n \rho_T(E - E_n) \right]^{-1}$$

The integral $\iint d^2\hat{\Omega}/4\pi$ is unity, so the denominator of Eq. 9 is $\rho_{TOT}(E)$. $\bar{K}(E)$ is the average of $\kappa(n, E - E_n, \hat{\Omega})$ over the set of all states whose total energy is E. It is possible (in principle) to extract the energy dependence of $\bar{K}(E)$ from knowledge of the temperature dependence of $Q_{TOT}(T)$ and $k(T)$ ⁷, but the relative contributions to $\bar{K}(E)$ from different subsets of states at that total energy are not obtainable even in principle without additional information.

For most physically reasonable ways in which $\bar{F}(E)$ depends upon E , the strong damping of the Boltzmann factor forces all the appreciable contributions in thermal averages such as Eq. 7 to come from energies within a range of at worst a few times $k_B T$ of an energy closely related to the energy threshold of the reaction. In these cases the total energy of the reactants (and hence of the products) can be regarded as determined to within that accuracy. For highly exoergic reactions, this can mean a small fractional uncertainty in the total energy as measured from the ground state of the products as our Cl+HI example above demonstrates. Two recent papers¹⁸ have examined, under the assumption of no participation of internal degrees of freedom, the relationships between the Arrhenius activation energy and the excitation function $\sigma(E_T) = (\mu/2E_T)^{1/2} \bar{F}(E_T)$. For a wide variety of functional forms for σ , the activation energy is approximately the threshold energy when $k_B T$ does not exceed the threshold energy by a large factor. The qualitative results of these studies also support the assertion at the beginning of this paragraph that most of the contributions to k come from a small range of energies, and it is reasonable to presume that this would also be true for systems where the internal states also participate.

C. Intermediate Resolution

Assuming the total energy to be known, we can consider a number of possibilities for intermediate resolution between the two extremes just discussed. For simplicity, our treatment will be

restricted to collisions in which the reactants as well as the products consist of an atom and a diatomic molecule. The variables needed to describe the reactants or products are then the vibrational and rotational quantum numbers of the diatomic molecule (V and J), the projection of the molecular angular momentum on an external axis (M), the relative kinetic energy E_T , and the direction of the relative momentum $\hat{\Omega}$. Although directional variation of rate coefficients can be measured in molecular beam experiments, this presentation will assume in the interest of simplicity that all quantities are averaged over angles, so that $\hat{\Omega}$ can be dropped from consideration. Each of the cases described below corresponds to definite assumptions about the measurement process, i.e., which of the remaining variables are determined in an experiment and which are not. The correct density accompanying any given description of a set of states is, of course, independent of whether these are the initial or final states in a process. In discussing specific experiments, however, it is sometimes necessary to distinguish between the reactant and product states. Therefore, where it is appropriate to make such distinctions, the initial state variables will appear unprimed and the final state variables primed. E and E' will denote, respectively, the total energy relative to the reactant and product ground states: $E' = E + \Delta D_0$, where ΔD_0 is the ground-state to ground-state exoergicity of the reaction.

For each of the cases discussed a correct quantum mechanical expression will be given for the state density. In practical applications, however, it will quite often be true that such a pre-

scription cannot be followed, either because the energy-level spectrum is insufficiently well-known or because the experimental energy resolution is not sharp enough to warrant a fully discrete description of the internal states. For these instances, it is desirable to have approximate expressions obtained from continuous approximations to the rotational and/or vibrational levels.

Within the continuous assumption itself several levels of approximation can be distinguished for the densities of rotational/vibrational states. Even when the internal levels are all known accurately, smoothly varying "average" densities may be desirable for treating experimental data taken at such low resolution that the quantum spikes in the true densities are unresolvable. These densities can be obtained by differentiation of surfaces (or curves) through the $E_I(V, J)$ points as functions of V and J . (E_I is the internal energy relative to the ground state.) In this approximation the density of rotational states for a fixed V , $\rho_J(V)$ would be given by

$$(10) \quad \rho_J(V, E_I) = (2J+1) \left(\frac{\partial J}{\partial E_I} \right)_V = \left\{ \frac{\partial E_I}{\partial [J(J+1)]} \right\}_V^{-1}$$

and the density of vibrational states for a fixed value of J , $\rho_V(J)$, would be

$$(11) \quad \rho_V(J, E_I) = \left(\frac{\partial E_I}{\partial V} \right)_J^{-1}$$

Figure 3 shows the rotational densities of Eq. 10 for the various vibrational states of the electronic ground state of H_2 . All the rotation-vibration states are known in this case from exact numerical solution of the Schrodinger equation¹⁹ for a highly accurate interatomic potential function²⁰. The 3 to 1 ortho/para weighting factor arising from nuclear spin statistics is absent in the figure. It can be taken into account for treating ortho-para H_2 mixtures simply by multiplying the densities shown by a factor of three for the odd rotational levels (dark circles in the figure).

Except for a few molecules containing hydrogen or deuterium, there are insufficient data on the energy levels for application of formulas such as Eqs. 10 and 11. For many molecules, however, the interatomic potentials may be well established from Rydberg-Klein-Rees fits to spectroscopic data or less well from some other source. Useful and highly accurate densities can be obtained in these cases from semi-classical theory. All these expressions originate in the WKB equation relating V , J , and the corresponding energy level $\mathcal{E}_I(V,J)$. Derivations of expressions for the various densities in the WKB approximation are given in the Appendix. The symbol \mathcal{E} is used here and in the following energy levels rather than E to indicate that they are measured relative to the minimum in the potential rather than from the quantum-mechanical ground state, i.e., the zero-point vibrational energy is included in \mathcal{E} .

For many purposes a crude, easily computable approximation is sufficient. Such an approximation is obtained by a "continuous rigid-rotor-harmonic-oscillator" (RRHO) model, assuming the internal levels

to be given by

$$(12) \quad \mathcal{E}_I(V, J) = h\nu_0 V + hc B_e J(J+1)$$

with V and J regarded as continuous rather than discrete variables.

Again, \mathcal{E}_I denotes the energy relative to the potential minimum. In this approximation the density of rotational states ρ_J has the same value $(hcB_e)^{-1}$, for all vibrational states. The density of vibrational states is also a constant: $\rho_V = (h\nu_0)^{-1}$ for all values of J . The density of internal states (both rotational and vibrational) at a given internal energy is, in this approximation, given by

$$(13) \quad \rho_I(\mathcal{E}_I) = (h^2 c \nu_0 B_e)^{-1} \mathcal{E}_I$$

Expressions for the other various densities are easily derivable from these and will be given in the appropriate section below. Although the RRHO estimates are crude, they give the correct general trends, and even the quantitative agreement is acceptable for many molecules. In the sections below where individual experimental cases are discussed many of the state densities will be reported in the form of a correction factor ρ^* that must be applied to the RRHO estimate to give the correct values: $\rho^* = \rho(\text{actual}) / \rho(\text{RRHO})$.

Figure 4 shows the corrections to the total density of states,

ρ^*_{TOTAL} for H_2 in the true quantum case and in the WKB approximation and the WKB result for the Rydberg-Klein Rees I_2 potential²¹. The

ordinate is the ratio of the total energy to the dissociation energy (both measured from the potential minimum).

1. $V, J,$ and E_T Known but not M : Infrared Chemiluminescence

Over the past dozen years or so J. Polanyi and co-workers have perfected the techniques for observation of infrared chemiluminescence⁴ to the point that now they can observe the radiation emitted from newly-formed chemical products before their vibrational or rotational distributions are appreciably relaxed. The reactants (atom + diatomic molecule) in these experiments issue from a pair of mixing jets giving essentially thermal distributions for the reactant variables. The reactions studied are mostly quite exoergic, so that the total energy of the products is known to reasonably good fractional accuracy as previously discussed. The measurements determine the relative rates of formation of the various rotational and vibrational states of the products (J' and V' , but not M'). The relative kinetic energy can be obtained (with some uncertainty) by difference: $E'_T = E' - E'_I(V', J')$. These measurements on the product states represent the closest approach accomplished at the present time to the ideal of complete determination. They do not, however, give any information about the angular distribution of products.

Since no details are known about the reactant states, the appropriate density of states for them is the total density of states at energy E (relative to the ground state of the reactants). The observed rate coefficients are averages over all reactant states having the given

energy (see Eq. 9). For the products, the only unspecified variables are the angular momentum projection quantum number M and the direction of the relative momentum $\hat{\Omega}$. Therefore the density of the final set of states is the product of the translational density at each internal level and the degeneracy of that level

$$(14) \rho_{\Pi'}(E', V', J') = (2J'+1) \rho_{\tau} [E' - E'_I(V', J')]$$

$E'_I(V', J')$ is the internal energy of the V', J' vibration-rotation state relative to the ground state of the products.

Figure 5 shows $\bar{\omega}$ values for the reaction $\text{Cl} + \text{HI} \rightarrow \text{HCl} + \text{I}$ as functions of the fractions of the total energy of the products in translational, rotational, and vibrational degrees of freedom at the fixed value of the total energy corresponding to average thermal internal and translational energies above the threshold. These values were obtained from Eq. 5, using the density of states defined in Eq. 14 with the data of Maylotte and Polanyi^{4c}. The quantities displayed in this figure are the same as are shown in a different method of presentation in figure 1a of ref. 8a. Since there was only a single set of initial states for these experiments the $\bar{\omega}$'s are proportional to the rate coefficients for the reverse process.

2. E and V known but not E, J, or M: Chemical Lasers and Early Infrared Chemiluminescence

Rotational relaxation usually occurs two or three orders of magnitude more rapidly than vibrational relaxation. This makes it

possible to observe reaction products with essentially completely relaxed rotational degrees of freedom but with the vibrational populations unaltered by relaxation. This was the case in infrared chemiluminescence^{4a} experiments prior to the most recent improvements in techniques, and is the current capability of chemical lasers⁵. In both these types of experiments the reactants are thermal (internally and translationally).

This situation differs from the one previously discussed only in the loss of knowledge of the product rotational state distribution. Therefore the density of the product states is the sum of the densities given in Eq. 16 over all rotational states with the given vibrational quantum number that are accessible at the existing total energy E' :

$$(15) \quad \rho_{\Pi'}(E', V') = \sum_{J'=0}^{J^*} (2J'+1) \rho_{\tau} [E' - E'_{\text{I}}(J', V')]$$

where J^* is defined by $E'_{\text{I}}(V, J^*+1) \geq E' > E'_{\text{I}}(V, J^*)$. In the RRHO approximation, this becomes:

$$(16) \quad \rho_{\Pi}(\mathcal{E}, V) = \frac{2}{3} (hc\beta_e)^{-1} (\mathcal{E} - h\nu_0 V)^{3/2} = \frac{2}{3} (hc\beta_e)^{-1} [\mathcal{E}(1-f_v)]^{3/2}$$

where $f_v = h\nu_0 V / \mathcal{E} = V/V^*$ is the fraction of the total energy \mathcal{E} in vibration. Fig. 6 illustrates the dependence on f_v of the quantity

$$\rho_{\text{RC}}^{\circ} \equiv \frac{3}{2} hc\beta_e \mathcal{E}^{-3/2} \rho_{\Pi}(\mathcal{E}, V) .$$

The solid curve is the RRHO

value $(1-f_v)^{3/2}$, and the points are for HF at two different energies, computed with discrete rotational-vibrational energy levels

obtained from the spectroscopic constants given by Webb and Rao²².

The RRHO approximation is seen to be quite good for this case.

The chemical laser results of Parker and Pimentel⁵ for the relative rates of formation of HF in different vibrational states from the reaction $F+H_2 \rightarrow HF(V') + H$ are $k(V'=2)/k(V'=1) \approx 5.5$, $k(V'=3)/k(V'=2) \approx 1.6$. Assuming the total energy of the products to be the sum of the reaction exoergicity, the Arrhenius activation energy, and average thermal contributions from translation and rotation ($E' = \Delta D_0 + E_a + 5/2RT = 34.8$ kcal/mol), and using the RRHO values for the densities of states, we can estimate that $\bar{\omega}(V'=2)/\bar{\omega}(V'=1) \approx 14$ and $\bar{\omega}(V'=3)/\bar{\omega}(V'=2) \approx 20$. The first of these ratios follows much more reliably from the Parker and Pimentel data than the second because the $V'=3$ level has such a large fraction of the total energy in vibration that estimates of the density of states for product molecules with that vibrational quantum number are extremely sensitive to the value of the total energy assumed. The data themselves may be questionable. Polanyi and Tardy⁹ have studied the same reaction by infrared chemiluminescence. They find the same qualitative trend in vibrational populations but their ratios are quantitatively different.

3. E_T and E Known but not V, J, or M: Molecular Beam Velocity Analysis

Since the actual internal levels of a given molecule are separated by discrete intervals, it is, strictly speaking, only possible to have at any given total energy those values of E_T for which the difference $E - E_T$ corresponds to one of the internal energies. The joint density of states per unit volume (with respect

to both E and E_{τ}) is given by:

$$(17) \quad d^2 N_{\tau}(E, E_{\tau}) / dE dE_{\tau} = \rho_{\tau}(E_{\tau}) \sum_{V,J} (2J+1) \delta [E - E_{\tau} - E_I(V,J)]$$

(units $\text{erg}^{-2} \text{cm}^{-3}$). For an absolute evaluation of the density of states with respect to E alone, it would be necessary to integrate Eq. 17 over a range of translational energies (dictated by the experimental conditions) while holding the total energy constant. For relative evaluations, however, the average of $d^2 N / dE dE_{\tau}$ over the range of E_{τ} suffices:

$$(18) \quad \rho_{\tau}(E, E_{\tau}) = \langle \rho_{\tau}(E_{\tau}) \rho_{IQ}(E - E_{\tau}) \rangle_{E_{\tau} \text{ Avg.}}$$

where $\rho_{IQ}(E_I)$ is the quantum density of internal states (the delta-function sum of Eq. 17).

If the experimental resolution were good enough to distinguish the contributions from the individual internal levels, a knowledge of the spectrum of the molecule would allow assignment of V, J quantum numbers to the states and only M would remain undetermined. This case has been treated in the discussion of the infrared chemiluminescence experiments. In practice, however, measurements of E_{τ} even at the best resolution presently attainable call for averaging over a large number of internal levels. Within the range of translational energies of the averages ρ_{τ} does not change appreciably, but the spiky structure in

ρ_{IQ} is smoothed out, giving

$$(19) \quad \rho_{I'}(E, E_{\tau}) = \rho_{\tau}(E_{\tau}) \rho_I(E - E_{\tau})$$

where ρ_I is the average density of internal states, smoothed over several internal levels.

Since the translational density of states can always be expressed exactly, the reliability of any evaluation of Eq. 19 depends upon the estimate used for ρ_I . The RRHO expression for the internal state density is, as previously noted, $(h^2 c \nu_0 B_e)^{-1} \mathcal{E}_I$. Fig. 7 shows some correction factors $\rho_I^* = \rho_I / \rho_I(\text{RRHO})$ as functions of the ratio of the internal energy to the dissociation energy (from the potential minimum). The values shown are for the exact H_2 levels¹⁹ smoothed over rotational but not vibrational states, WKB values for the true H_2 potential, WKB values for a Morse function fit to the H_2 potential and WKB for the I_2 RKR potential²¹. The WKB expression for the internal state density

$$(20) \quad \rho_I^{\text{WKB}}(\mathcal{E}_I) = 8\pi^2 (2\mu)^{3/2} \int_{R_1}^{R_2} R^2 [\mathcal{E}_I - \phi_0(R)]^{1/2} dR$$

is discussed in detail in the Appendix. It reproduces the trend of the correct result even for as strongly quantum a molecule as H_2 . For diatomic molecules with reduced masses greater than a few atomic mass units, the WKB approximation is probably quite good at all energies above the ground state.

Use of the RRHO expression for ρ_I gives the following

estimate for the density defined in Eq. 19:

$$(21) \rho_r(\mathcal{E}, E_T) = 3^{-3/2} 2^{1/2} A_T \mathcal{E}^{3/2} \rho^{\circ}(\text{TRANS-INT})$$

where A_T is the quantity defined in Eq. 4, and $\rho^{\circ}(\text{TRANS-INT})$ is a factor containing the dependence on $f_T = E_T/\mathcal{E}$, the fraction of the total energy in translation:

$$(22) \rho^{\circ}(\text{TRANS-INT}) \equiv 3^{3/2} 2^{-1/2} f_T^{1/2} (1-f_T)$$

This quantity is shown in Fig. 8. Although the figure is not to be believed in detail owing to the crudeness of the RRHO approximation, its qualitative features are correct: the density $\rho_r(\mathcal{E}, E_T)$ will be small when f_T is near either zero or unity and its maximum will occur near $f_T = 1/3$. Here we have a good example of a statistical bias introduced by the experiment. Whatever the dependence of $\bar{\omega}$ on E_T for a given reaction, the measurable rate coefficient \bar{k} in velocity analysis experiments, being the product of $\bar{\omega}$ and the density of final states, (see Eq. 5) will tend to peak at intermediate values of f_T . Reduction of the data to $\bar{\omega}$ thus has two virtues: It gives a fully symmetrical quantity from which either the forward or reverse rate can be obtained simply by multiplying by the appropriate density of states, and it extracts from the measurements a purely dynamical quantity from which the trends forced by the nature of the experiment have been removed.

Fig. 9 shows $\bar{\omega}$ vs. f_T for the reaction $K+I_2 \rightarrow KI+I$, obtained using Eq. 20 (the RRHO expression) with the molecular beam velocity analysis

data of Gillen and Bernstein^{6d}. Fig. 10 is a similar graph for the reaction $K+HBr \rightarrow HBr+H$, taken from the data of Gillen, et. al^{6c}. The $K+I_2$ results are an example of a strongly varying $\bar{\omega}$ that opposes the statistical factor contained in the density of states. $\bar{\omega}$ for this reaction is sharply peaked at a small value of f_τ , but not so strongly that it keeps the experimental \bar{K} (also shown in the figure) from going to zero as f_τ goes to zero. Figure 9 also shows the $\bar{\omega}$ that would result from either of two limiting assumptions, i.e., that all the internal energy be in the form of either (a) rotational or (b) vibrational excitation (but not both). (The seeming ability to arrive at two contradictory $\bar{\omega}$'s from the same set of data is not the paradox it first appears to be. In each case, the average transition probability of some sets of states Γ and Γ' is obtained. The set of product states associated with the more detailed information is smaller in accord with the more specific description. The average of that $\bar{\omega}$ over all combinations of product rotational-vibrational states having a given internal energy would reproduce the less detailed $\bar{\omega}$. Most of the combinations would, however, have contributed nothing to the average, since the internal energy would not all be concentrated entirely into the assumed mode.)

The $K+HBr$ reaction (fig. 10) shows a much less dramatically varying $\bar{\omega}$, so that the dependence of \bar{K} is largely governed by that of $\rho(E, E_\tau)$. It may even be true that the $K+HBr$ data could have been fit by constraining \bar{K} to have the E_τ dependence of the density of states (Eq. 21). The blowup at $f_\tau \rightarrow 1$ is associated with the lack of perfect knowledge of the total energy. The large values arise

from division of rapidly decreasing experimental values (see fig. 12 of ref. 24) by even more rapidly decreasing state densities.

4. Rotational State Determined: Molecular Beam State Analysis

Static four-pole or ten-pole electric fields can be used to focus molecular beams of polar diatomics in definite J, M states²². Assuming that no further details are known except for the total energy E , the set of states indicated by the measurement consists of all the accessible vibrational states (each accompanied by the translational energy required to keep the total energy fixed at E). The density of this set of states is defined by

$$(23) \quad \rho(E, J, M) = \sum_{v=0}^{v^*} \rho_{\tau} [E - E_{\tau}(v, J)]$$

where v^* satisfies $E_{\tau}(v^*, J) \leq E < E_{\tau}(v^*+1, J)$. If M were also undetermined, the density would have to be summed over all the possible values of that parameter, giving an additional factor of $(2J+1)$:

$$(24) \quad \rho(E, J) = (2J+1) \rho(E, J, M)$$

In the RRHO approximation, the densities of Equations 23 and 24 become:

$$(25) \quad \rho(E, J, M) = \frac{2A_{\tau}}{3h\nu_0} E^{3/2} [1 - f_R(J)]^{3/2}$$

$$(26) \quad \rho(E, J) = 2A_{\tau} [3h\nu_0 (hcB_e)^{1/2}]^{-1} E^2 f_R^{1/2} (1 - f_R)^{3/2}$$

where $f_R(J)$ is the fraction of the total energy in rotation:

$$f_R = hcB_e J(J+1) / \mathcal{E} \quad [\text{in Eq. 26, the difference between } (J+\frac{1}{2})^2 \text{ and}$$

$J(J+1)$ has been ignored]. WKB approximations to these densities are discussed in the Appendix. Fig. 11 shows the f_R dependence of Eq. 26,

$$P^{\circ}(V-r) = f_r^{1/2} [1-f_R]^{3/2} \quad \text{and, in the upper part correction factors}$$

P^* for the actual HF molecule and for a discrete rigid-rotor-harmonic-oscillator approximation to the HF levels (i.e., using the B_e and ν_0 of HF) at two different energies.

No data are yet available for either of the analyses discussed in this section, but such measurements are within technical capabilities and will certainly be reported in the near future.

Acknowledgements

I am deeply indebted to Prof. R. B. Bernstein for many stimulating discussions and for his constructive suggestions regarding this manuscript. I would also like to thank all the members and staff of the University of Wisconsin's Theoretical Chemistry Institute for their hospitality during my stay there.

Appendix I: Semi-classical Densities of States

In the WKB approximation, the vibrational and rotational "quantum numbers", V and J , of a diatomic molecule are related to the internal energy \mathcal{E}_I by the following equation

$$(A1) \quad V + \frac{1}{2} = \frac{2}{\hbar} m^{1/2} \int_{R_1}^{R_2} [\mathcal{E}_I - \phi_J(R)]^{1/2} dR$$

$\phi_J(R)$ is the usual effective interatomic potential, given in terms of the actual potential $\phi(R)$ by

$$(A2a) \quad \phi_J(R) = \phi(R) + \frac{\hbar^2 (J + 1/2)^2}{8\pi^2 m R^2}$$

if the Langer correction is made in the WKB approximation, or by

$$(A2b) \quad \phi_J(R) = \phi(R) + \frac{\hbar^2 J(J+1)}{8\pi^2 m R^2}$$

if the correction is not made. R_1 and R_2 are the classical turning points. They depend both on \mathcal{E}_I and on J . m is the reduced mass of the diatomic system. \mathcal{E}_I , as previously noted, is measured relative to the minimum of $\phi_0(R)$.

For a fixed value of J , the density of vibrational states can be obtained by differentiation of Eq. A1:

$$(A3) \quad \rho_V(\mathcal{E}_I, J) = \left(\frac{\partial V}{\partial \mathcal{E}_I} \right)_J = (2m)^{1/2} \hbar^{-1} \int_{R_1}^{R_2} [\mathcal{E}_I - \phi_J(R)]^{-1/2} dR$$

The expression for the density of rotational states for a fixed value of V involves two WKB integrals

$$\begin{aligned}
 (A4) \quad \rho_J(\mathcal{E}_I, V) &= (2J+1) \left(\frac{\partial J}{\partial \mathcal{E}_I} \right)_V \\
 &= 8\pi^2 m h^{-2} \int_{R_1}^{R_2} [\mathcal{E}_I - \phi_J(R)]^{-1/2} dR / \int_{R_1}^{R_2} R^{-2} [\mathcal{E}_I - \phi_J(R)]^{-1/2} dR
 \end{aligned}$$

The particular value of J at which Eq. (A4) is to be evaluated must be the one giving the chosen value of V in Eq. A1.

The total density of internal states, rotational and vibrational, at a given internal energy can be obtained by integrating $\rho_V(\mathcal{E}_I, J)$ over all values of J for which it is positive.

$$\begin{aligned}
 (A5) \quad \rho_I(\mathcal{E}_I) &= \int_0^{J^*} \rho_V(\mathcal{E}_I, J) (2J+1) dJ \\
 &= \int_0^{J^*} (2J+1) \left\{ \int_{R_1}^{R_2'} [\mathcal{E}_I - \phi_J(R)]^{-1/2} dR \right\} dJ
 \end{aligned}$$

at $J = J^*(\mathcal{E}_I)$, the minimum of ϕ_J is \mathcal{E}_I above the minimum of $\phi_0(R)$. With some care, the order of integration

in Eq. A5 can be reversed to produce the following one-dimensional quadrature for ρ_I :

$$(A6) \rho_I(\mathcal{E}_I) = 8\pi^2 (2m)^{3/2} \hbar^{-3} \int_{R_1}^{R_2} R^2 [\mathcal{E}_I - \phi_0(R)]^{1/2} dR$$

The density of vibrational-translational states for a given value of J (See Eq. 23) can be defined in the semi-classical approximation by:

$$(A7) \rho_{V\tau}(\mathcal{E}, J) = \int_{\mathcal{E}_0}^{\mathcal{E}} \rho_V(\mathcal{E}', J) \rho_{\tau}(\mathcal{E} - \mathcal{E}') d\mathcal{E}'$$

There is a finite lower limit in Eq. A7 because the minimum internal energy is not zero but $\mathcal{E}_I(V=0, J) = \mathcal{E}_0$. Putting the expression from Eq. A3 for ρ_V and that of Eq. 5 for ρ_{τ} into A7, and reversing the order of integration, we obtain

$$(A8) \rho_{V\tau}(\mathcal{E}, J) = 4\pi^2 \mu^{3/2} m^{1/2} \hbar^{-4} \int_{R_1}^{R_2} [\mathcal{E} - \phi_J(R)] dR$$

(m is the diatomic reduced mass, μ that of the atom-diatom pair).

No correspondingly simple expression has been found for the joint rotation-translational density for a given V , defined by

$$(A9) \rho_{ROT-\tau}(\mathcal{E}, V) = \int_{\mathcal{E}_0}^{\mathcal{E}} \rho_J(\mathcal{E}', V) \rho_{\tau}(\mathcal{E} - \mathcal{E}') d\mathcal{E}'$$

The semi-classical evaluation of this density can be accomplished either by determining ρ_J as a function of \mathcal{E}' and performing the integration as written in Eq. A9 or by replacing the summation of Eq. 17 with integration using WKB values for $\mathcal{E}_I(V, J)$.

The total density of states (translational and internal) of the atom-diatom system (see Eq. 8) is defined semi-classically by

$$(A10) \quad \rho_{TOT}(\mathcal{E}) = \int_0^{\mathcal{E}} \rho_I(\mathcal{E}_I) \rho_T(\mathcal{E} - \mathcal{E}_I) d\mathcal{E}_I$$

Using ρ_I from Eq. A6, ρ_T from Eq. 5 and, as before, inverting the order of the \mathcal{E}_I and R integrations, we obtain the following simple form

$$(A11) \quad \rho_{TOT}(\mathcal{E}) = 16 \pi^4 (m\mu)^{3/2} h^{-6} \int_{R_1}^{R_2} R^2 [\mathcal{E} - \phi_0(R)]^2 dR$$

All the state densities not involving translational energy have cgs units of erg^{-1} . When translational degrees are included, as in Eq's. A8-A11, the densities are per unit volume, so that the cgs units are $\text{erg}^{-1} \text{cm}^{-3}$.

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Figure Captions

- Fig. 1: Figure taken from Blatt and Weisskopf¹² showing the difference between two possible kinds of inverse processes. The two upper sections illustrate processes that are the true time-inverses of each other. The lowest section illustrates a process that is in general unrelated to the other two.
- Fig. 2: Schematic illustration of the contributions from the rotational sub-levels of a particular vibrational state to the total density of states at some total energy E relative to the ground state.
- Fig. 3: Semi-logarithmic plot of the densities of rotational states for various vibrational states of the ground ($1\Sigma_g^+$) electronic state of H_2 , computed from Eq. 10. Open circles are for the even J states, dark circles for the odd J states. The energy (given relative to the ground state) is in units of cm^{-1} , hence the units of ρ are cm .
- Fig. 4: Correction factor for obtaining the total density of states from the RRHO approximation value, plotted vs. the ratio of the total energy to the dissociation energy (both measured relative to the potential minimum). The full curve is the quantum result for H_2 , and the dashed curve is the WKB approximation to it. The lower (long-

dashed) curve is the analogous WKB result for I_2 .

Fig. 5: Triangular plot of $\bar{\omega}$ for the reaction $Cl+HI \rightarrow HCl+I$ as a function of the fractions of the total energy in rotation (R), vibration (V), and translation (T). The $\bar{\omega}$ is averaged over all states of the assumed total energy for the reactants, and over the M substates for a given V' and J' of the products. The out-of-plane scale is linear. The numbers accompanying each cut identify the various vibrational states V' of the HCl molecule. The data used in constructing this figure are those of ref. 4(c).

Fig. 6: Dependence on the fraction of total energy in vibration on the density of rotational-translational states for fixed vibrational quantum number. The full curve is the RRHO result. The open circles are quantum values of ρ_{RT}° (see text) for the HF molecule at a total energy of $20,000 \text{ cm}^{-1}$ above the ground state, and the full circles are the quantum results for HF at a total energy of $40,000 \text{ cm}^{-1}$ above the ground state.

Fig. 7: Correction factors ρ_I^* for obtaining densities of internal states from the RRHO estimates. The upper set of curves is for the H_2 molecule in various approximations as labelled. EXACT means that the exact H_2 levels, smoothed over rotational but not vibrational states were used. MORSE-WKB means that a Morse function

fit to the true H_2 potential was used in the WKB computation. The lower curve shows the WKB result for the true I_2 potential, analogous to the WKB curve above for H_2 .

Fig. 8: Dependence on the fraction of the total energy in translation of the density of states of Eq. 19 (the one appropriate for velocity analysis experiments). The curve shown is the RRHO approximation, arbitrarily normalized to unity at its maximum.

Fig. 9: The full curve is the primary \bar{K} data for the reaction $K+I_2 \rightarrow KI+I$ from ref. 6(d), normalized to unity at its maximum. The dashed curve is the $\bar{\omega}$ obtained from these data (also normalized to unity at its maximum) using the density of states of Eq. 21 in Eq. 4. The dotted curve is the result for $\bar{\omega}$ that would be obtained from the original data if it were also determined that all of the internal energy of the products was to be found in either rotational or vibrational energy, but not both (see discussion in text).

Fig. 10: $\bar{\omega}$ obtained from the molecular beam velocity analysis experiments of ref. 6(c) plotted vs the fraction of the total energy in translation. The blowup near $E_T/E=1$ is spurious. It is mainly attributable to uncertainty in the total energy.

Fig. 11: The lower figure is the RRHO density of states for experiments in which the rotational quantum number J is determined but nothing else is known except the total energy. (The curve is arbitrarily normalized to unity at the maximum--see Eq. 26). The upper curves are correction factors for obtaining the true density for this experimental situation from the RRHO estimate. Curves A and B are for discrete rigid-rotor-harmonic-oscillator levels computed with the ν_0 and B_e for HF at energies, respectively, of 5000 and 20000 cm^{-1} above the ground state. Curves C and D are for the true HF levels at, respectively, 5000 and 20000 cm^{-1} above the ground state.

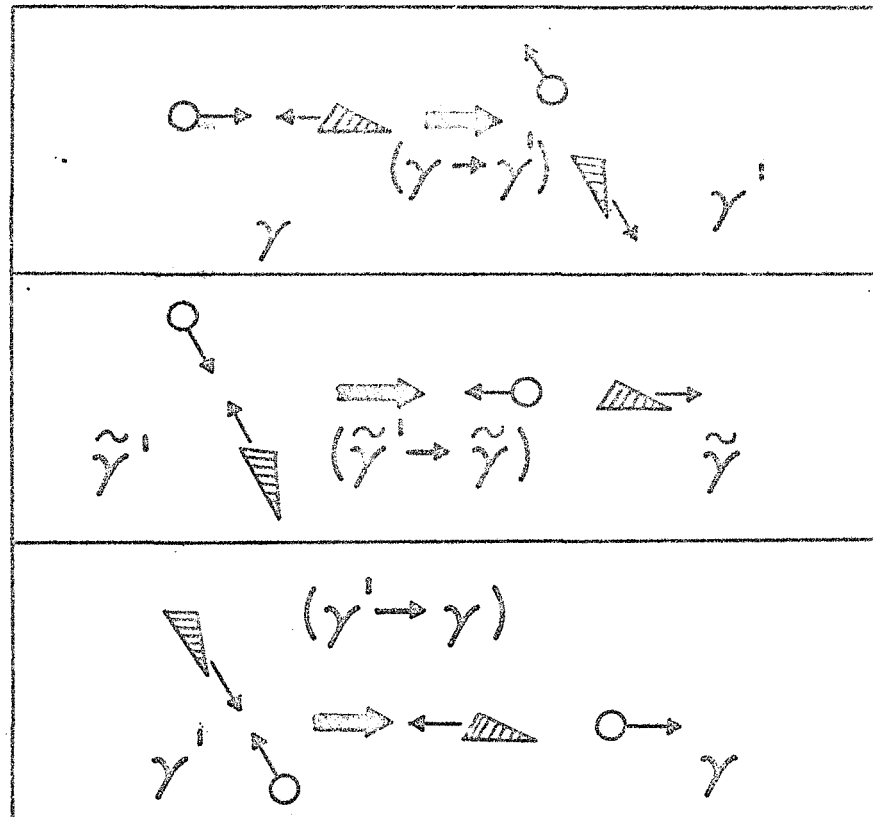


Figure 1

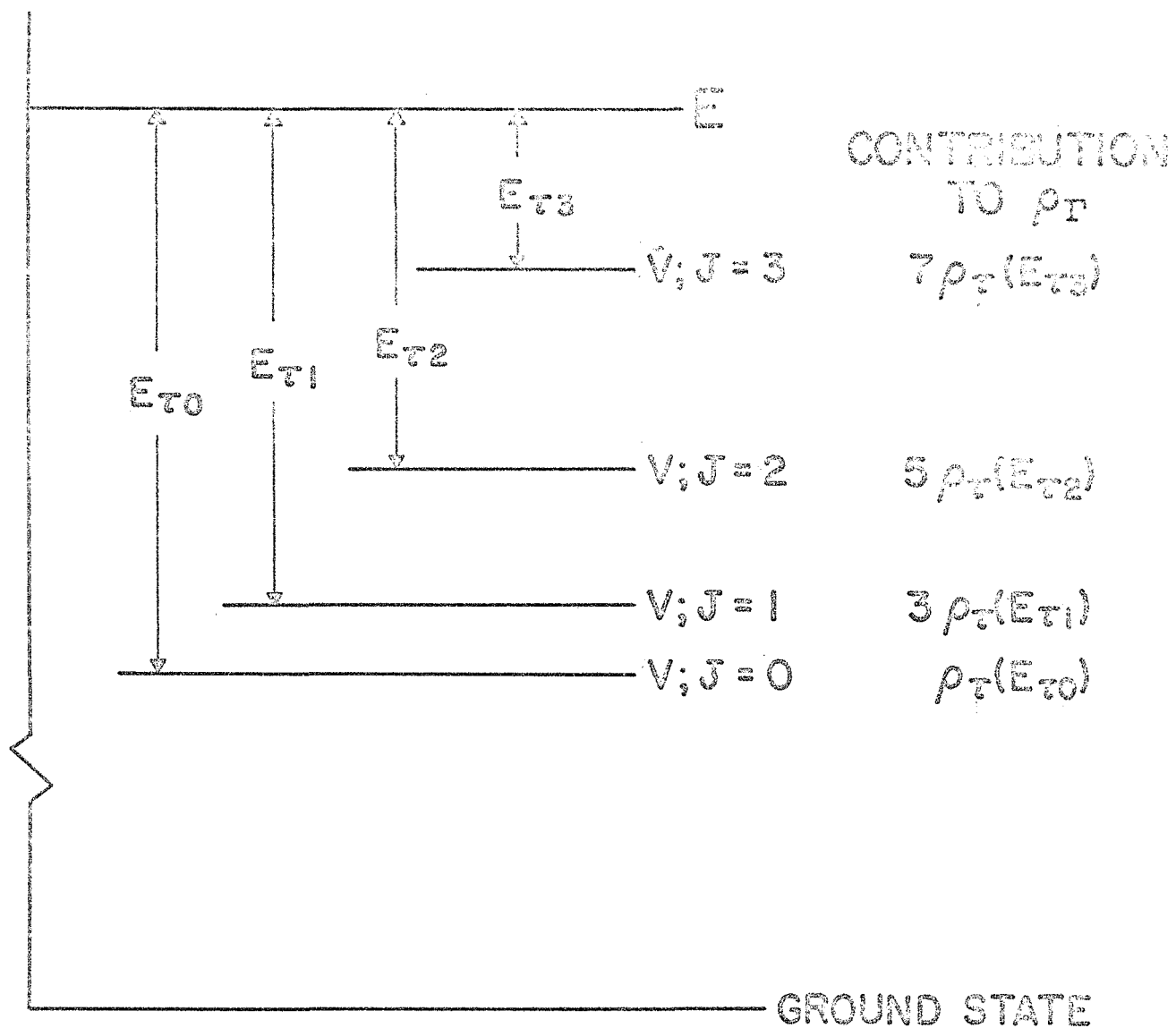


Figure 2

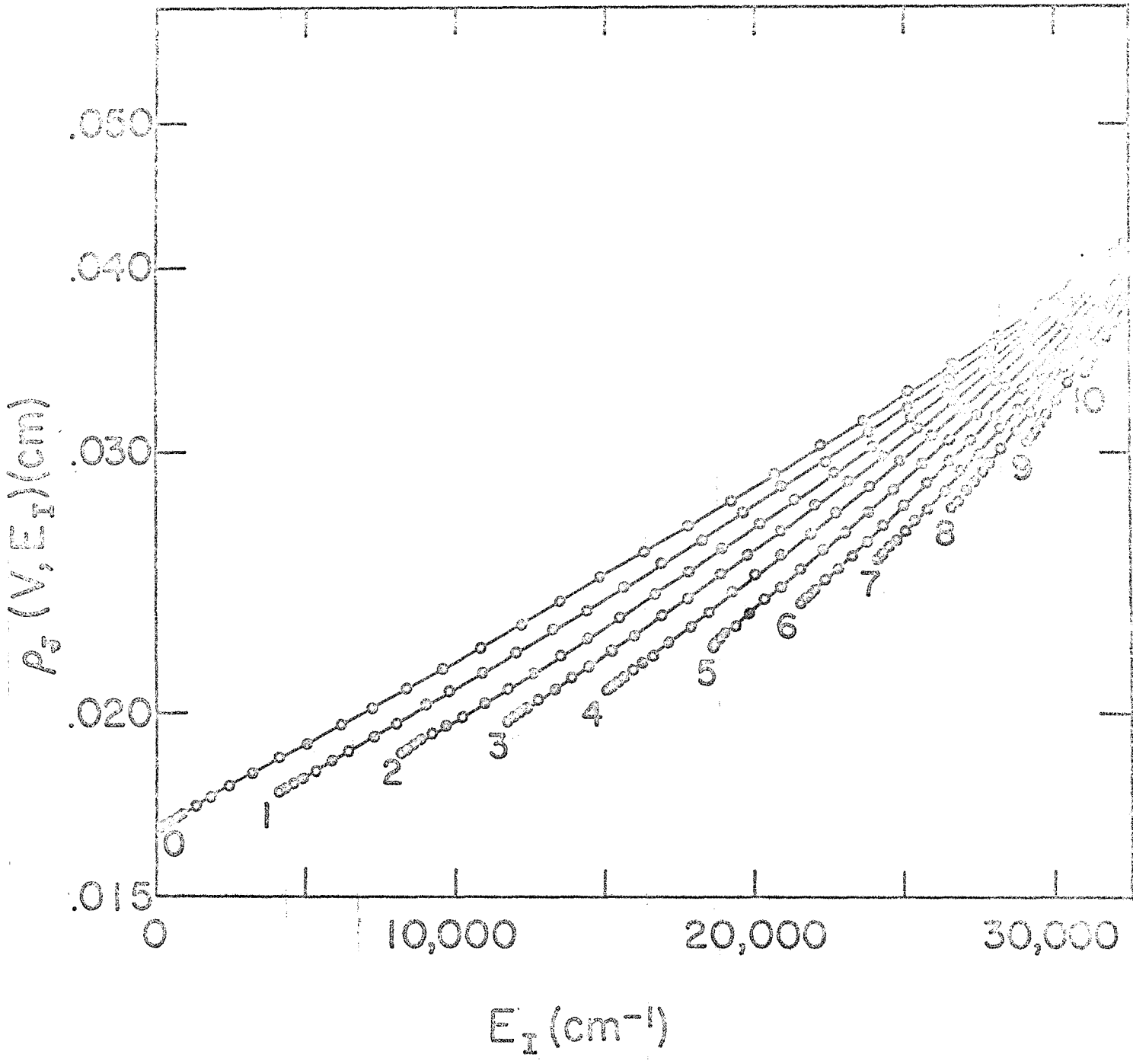


Figure 3

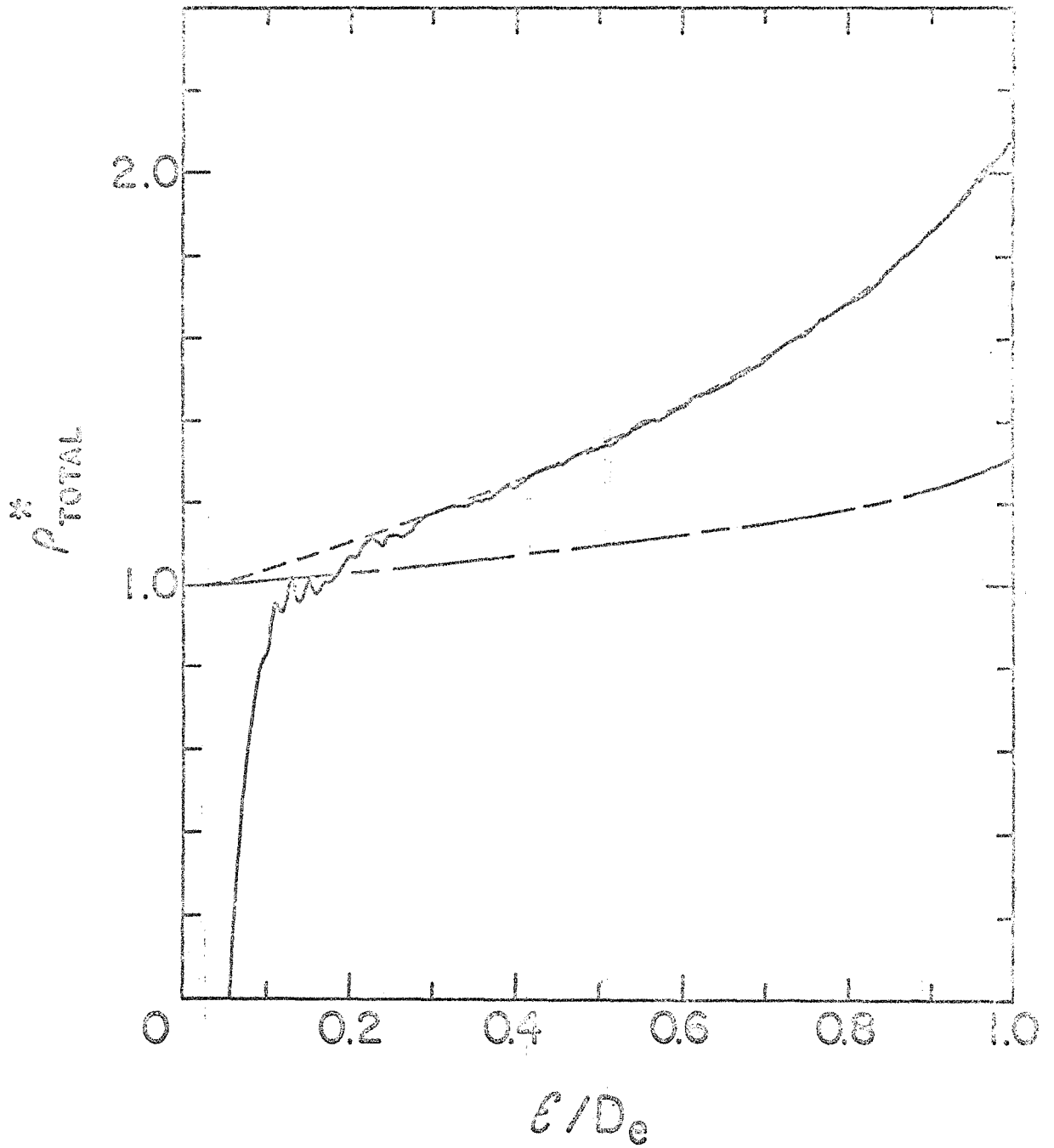


Figure 4

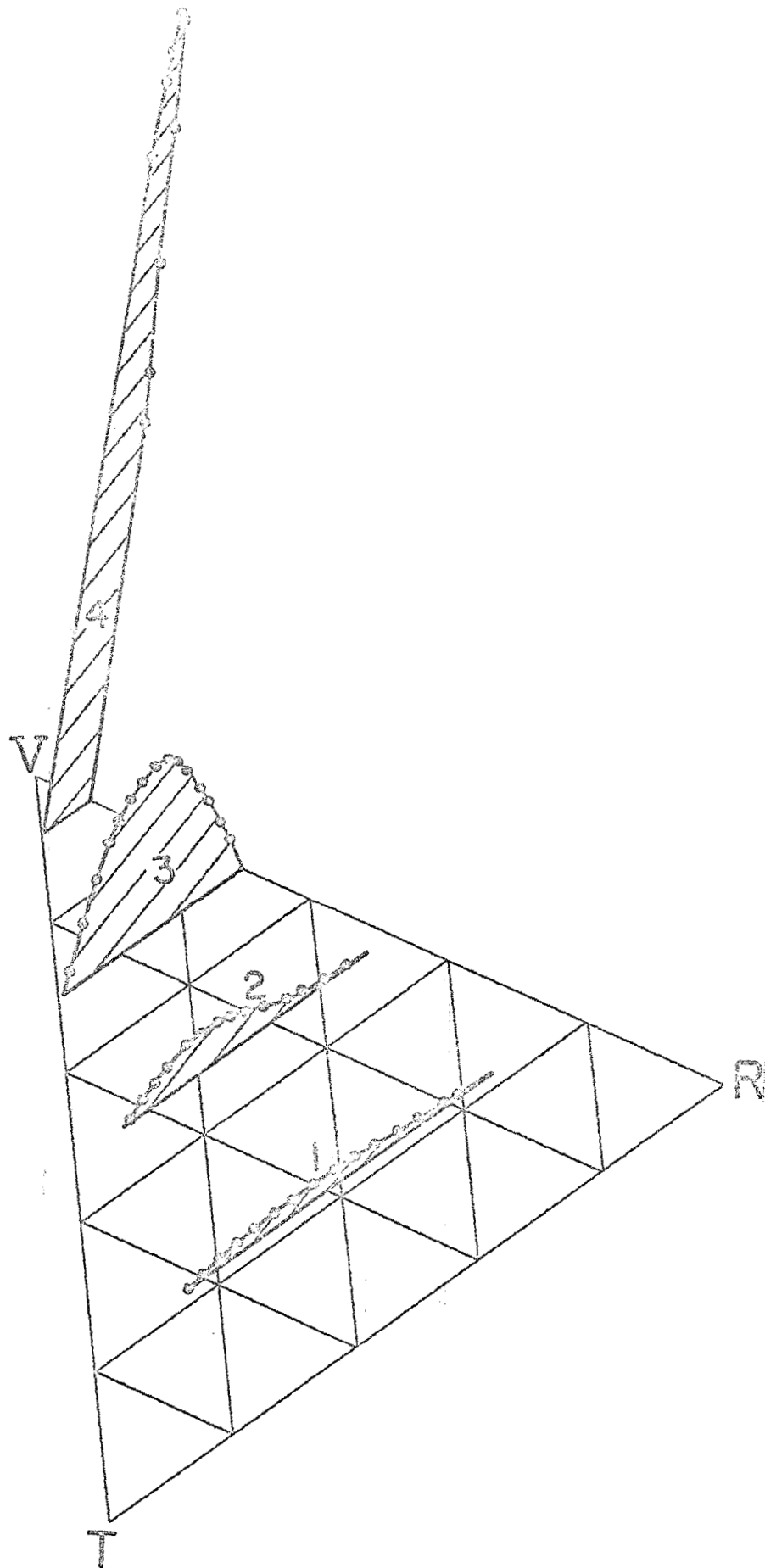


Figure 5

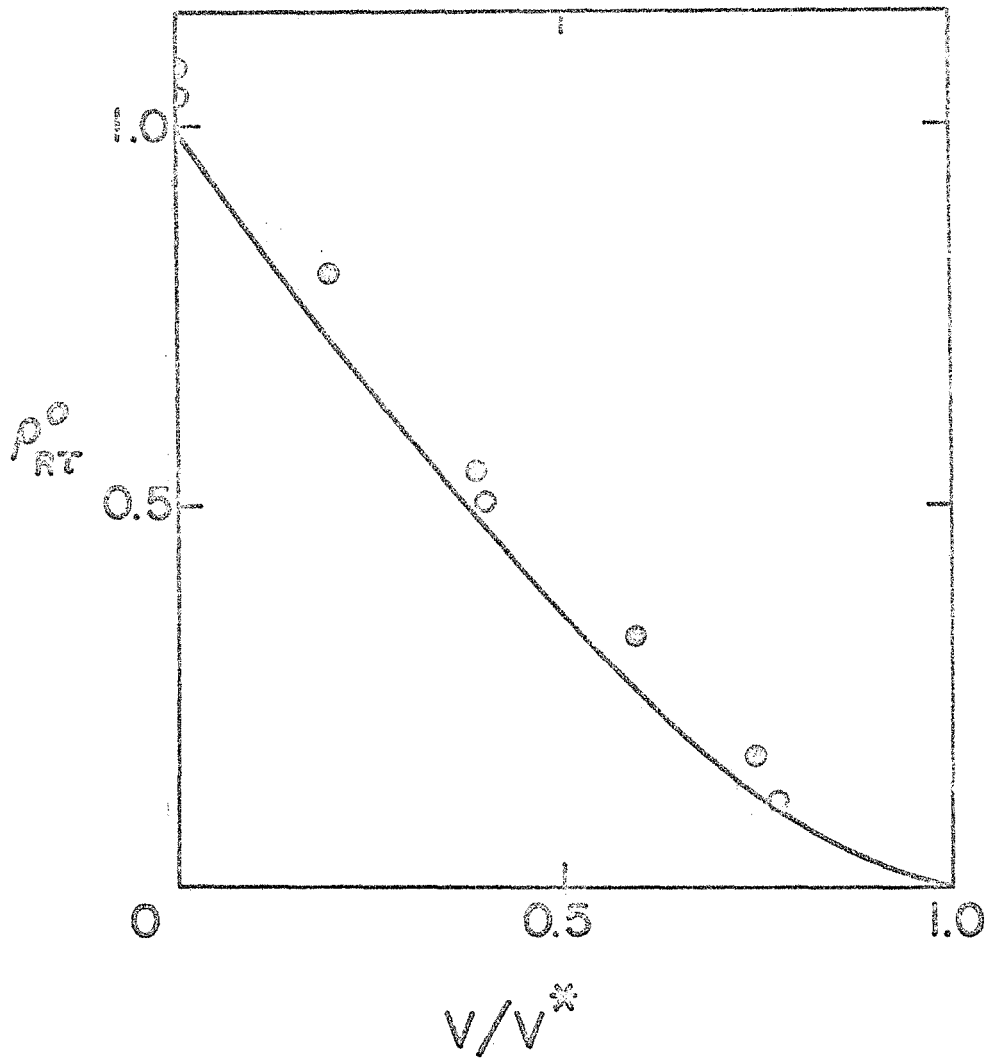


Figure 6

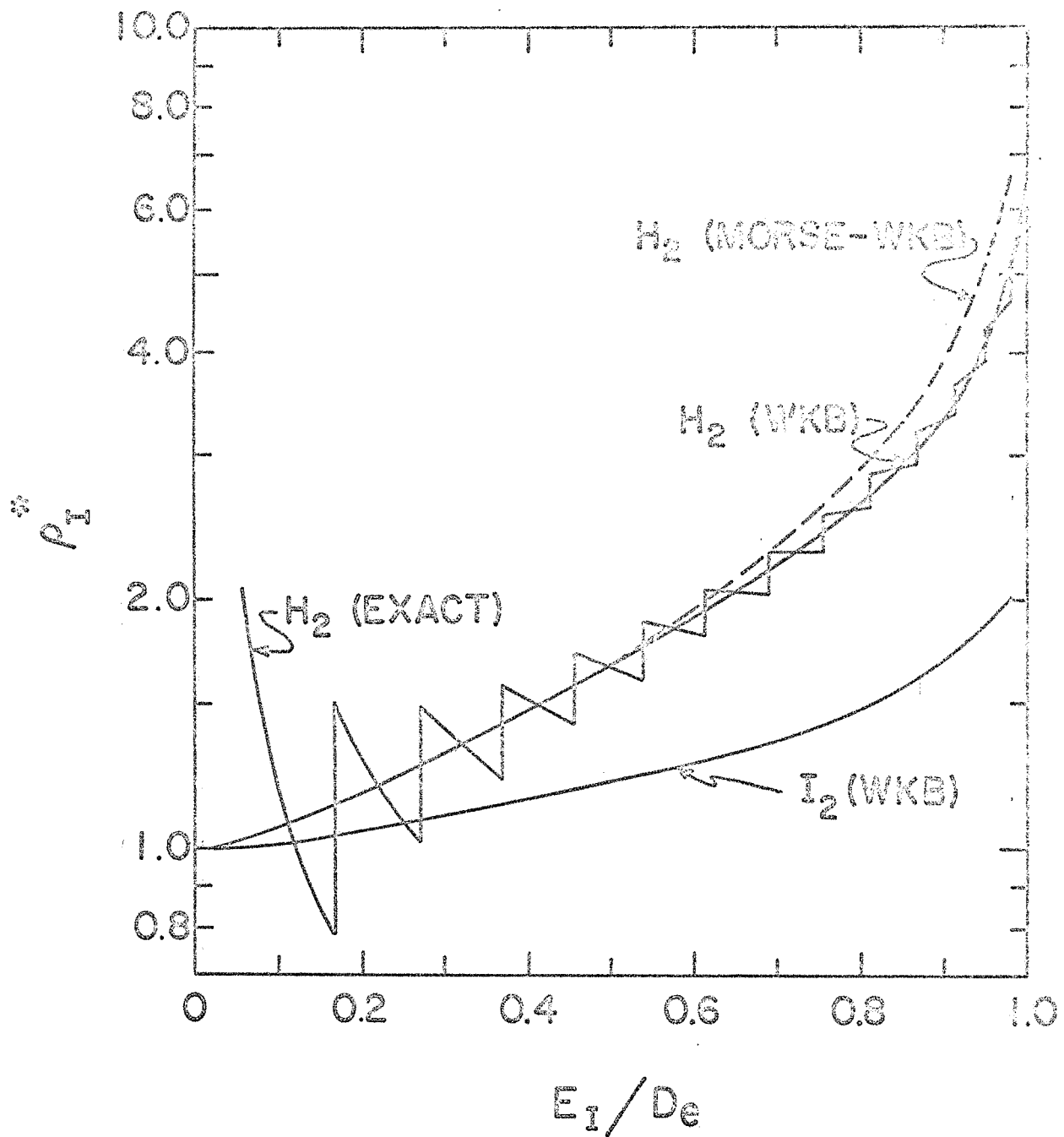


Figure 7

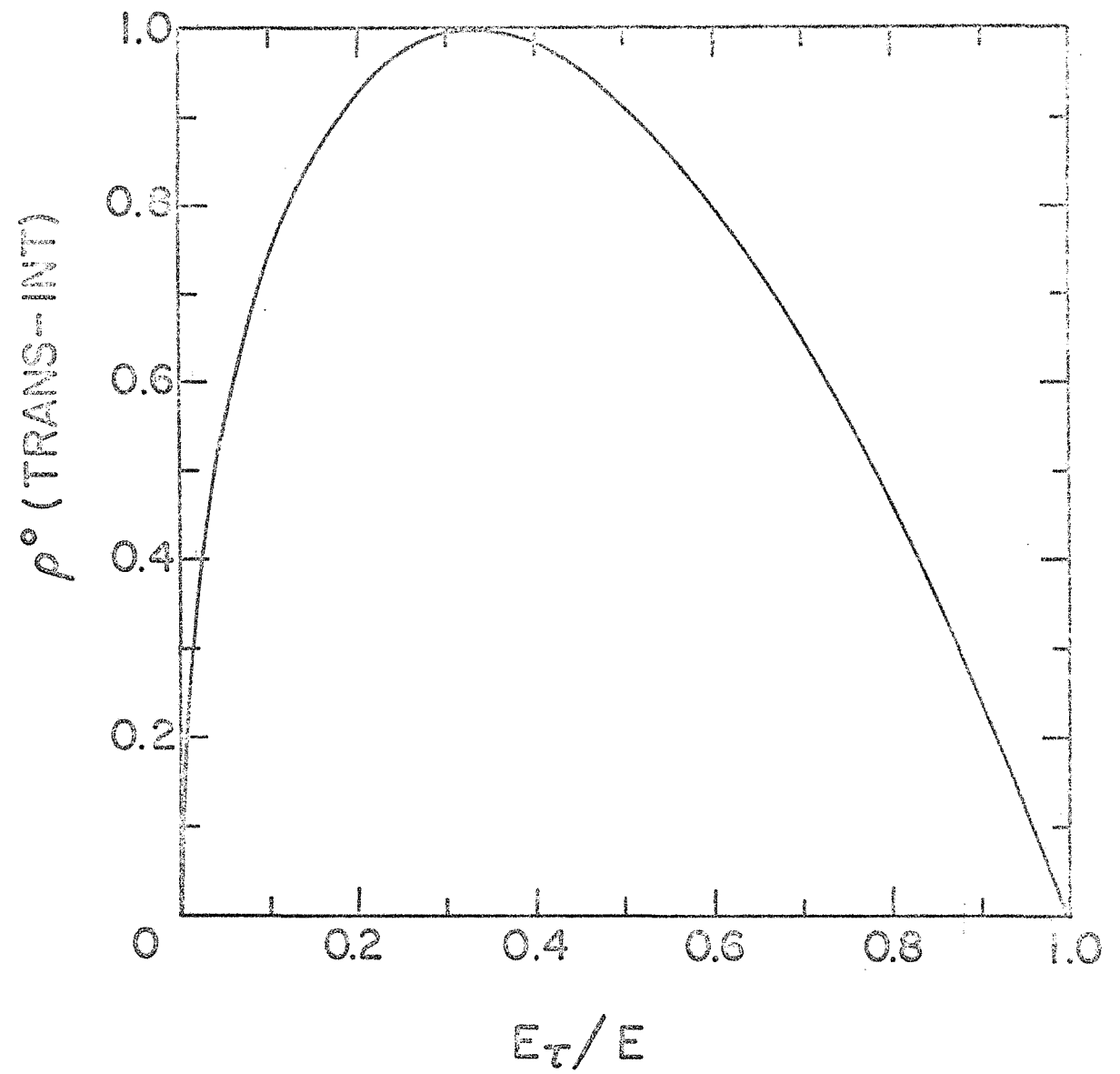


Figure 8

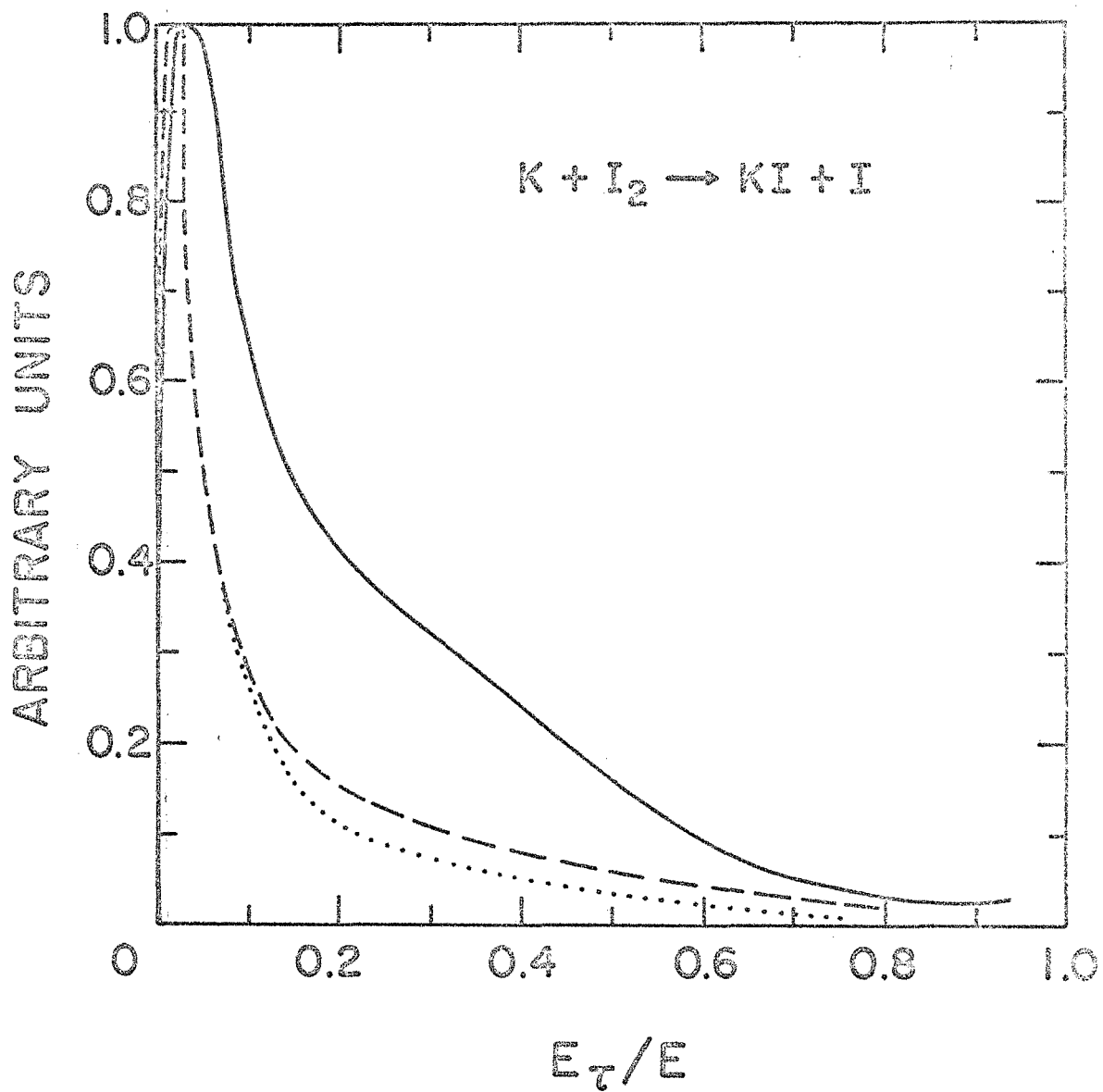


Figure 9

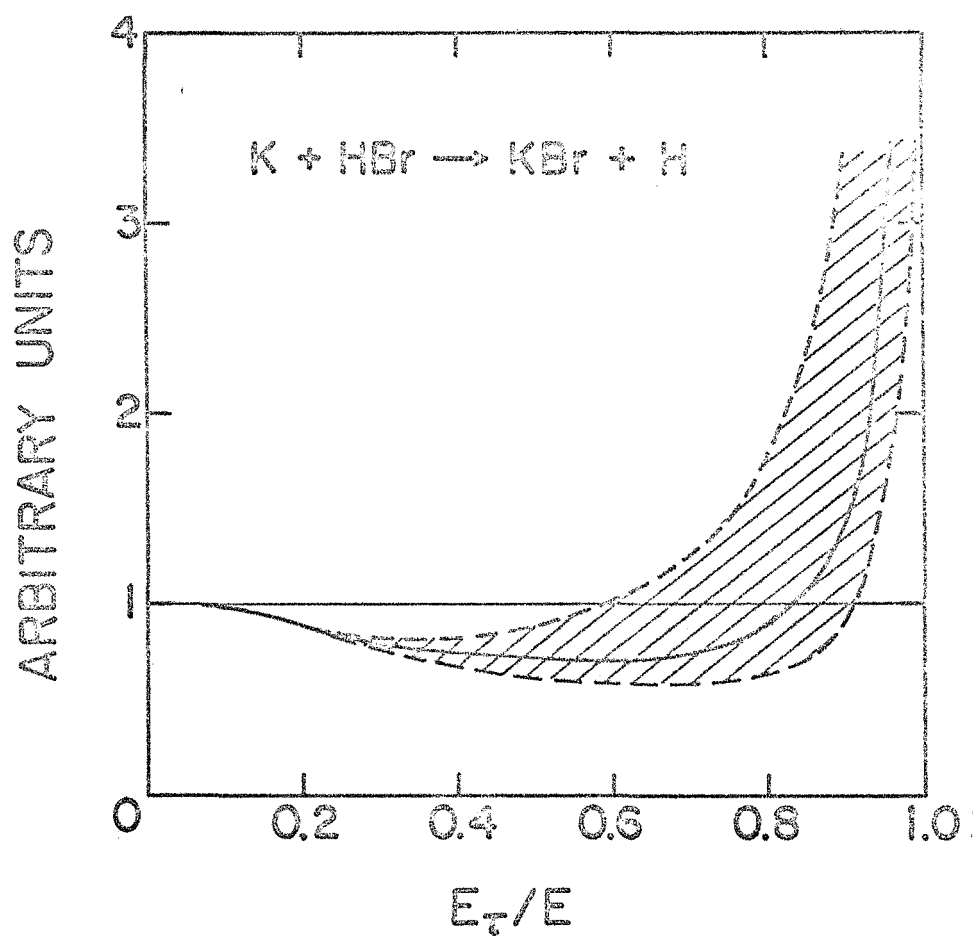


Figure 10

