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Structure-reactivity correlations in state-to-state chemistry

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The idea that a transition state is a "mixture" of reagents and products, previously used in the discussion of thermal structure-reactivity correlations ("Brønsted plots"), is now utilized to yield a simple, one-parameter analytical expression for the relative rate constants of state-to-state reaction series (i.e., where the initial or final internal state varies). The "weights" of reactants and products are determined by a maximal entropy or "thermodynamic-like" procedure. However, instead of using these weights to determine the free energy of activation, they are used directly in a novel statistical model for the reaction probability. The resulting equation is a generalization of the "exponential gap" law, which obtains when the parameter is very small. We demonstrate the utility of our correlation for both inelastic (energy-transfer) and reactive v to v' processes.

I. INTRODUCTION

One of the most significant achievements of modern gas-phase chemical kinetics is the development of state-selected chemistry.¹ Methods have been devised to follow the fate of specific quantum states and measure the detailed rate constants from/to a specified state.

The processes analyzed are of two major kinds. The first kind are inelastic (energy-transfer) processes, where the chemical identity of reagents and products is equal, and only the internal state changes. Rate constants for these processes are important for understanding bulk relaxation. Of the basic relations observed is an "exponential gap" law,² where the rate constant $k(s \rightarrow s')$ from initial internal state s to a final state s' depends exponentially on the energy gap [i.e., on the absolute value of the energy difference $\Delta E(s, s') \equiv E_{s'} - E_s$]:

$$k(s \rightarrow s') = Z \exp[-a |\Delta E(s, s')|] \quad (1)$$

(a and Z are constants typical to each specific system).

The second type of processes are reactive collisions, especially atom transfer reactions. For exoergic [$\Delta E(s, s') < 0$] reactions it is observed¹ that the population of the internal states (which reflects the rate constants into these states), immediately after the reaction and before any subsequent relaxation process occurred (the "nascent" population), may differ quite drastically from the thermal population reached after relaxation. For example, exoergic reactions tend to populate the higher vibrational levels (v') in the products, in contrast to the Boltzmann distribution, for which $v' = 0$ is the most significantly populated. This vibronic "population inversion" is the basis for the operation of IR chemical lasers.³ For the reverse, endoergic [$\Delta E(s, s') > 0$] reaction, a specificity of energy consumption is observed¹: The reactions are much more efficient if carried out from the higher vibrational levels. This specificity serves as a basis for isotope separation.⁴ However, it is not an independent phenomenon, but a consequence of the phenomenon of population inversion and the principle of detailed balance. This principle

states that the ratio of forward to reverse rate constants equals the appropriate equilibrium constant

$$k(s \rightarrow s')/k(s' \rightarrow s) = \exp[-\Delta E(s, s')/RT] \quad (2)$$

(R is Boltzmann's constant per mole and T is the absolute temperature). The equilibrium constant is more accurately written⁵ using the appropriate free energy term $\Delta G(s, s')$. However, the difference would usually be small for practical use.

Theories¹ of state-to-state rate constants may in general be divided into two types. The first type are dynamical calculations, where the complete knowledge of the potential energy surface is needed in order to solve the (classical or quantal) equations of motion for a large sample of initial conditions. However, it is seldom that the potential energy surface is known with reliable accuracy. Besides, extensive numerical work does not aid qualitative, intuitive insight. For these reasons a second type of theories is helpful. These include simplified models for reactive⁶ or inelastic⁷ collisions and statistical theories. Here use is made of limited information (sometimes, by introducing free parameters) to generate (at least approximate) results, and more important to explain the (above mentioned) trends in the rate constants.

Of statistical theories let us mention surprisal analysis,⁸ where the entropy of the nascent product population is maximized under constraints. These constraints vary from problem to problem. For example,^{8(a)} for reactive v to v' processes the constraint is usually found to be the average value of the vibrational energy $\langle E_v \rangle$. For inelastic v to v' processes the suggested^{8(b)} constraint is the average energy gap $\langle |\Delta E(v, v')| \rangle$.

Surprisal theory is especially helpful when the distribution of final states can be reproduced by a single constraint ("linear surprisal"). In such cases it affords a one parameter (the "Lagrange multiplier") fit to the relative rate constants. Linear surprisals are indeed found⁸ for many systems. There are, however, exceptions. For example,⁹ reactions of the type



where X and Y are halogen atoms, often show marked deviations from linear surprisals.^{9(a), 9(b), 9(f), 9(g)}

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The present work is a preliminary experiment to introduce into the field of state-to-state chemistry ideas which we¹⁰ have previously found fruitful in the field of (thermal) structure-reactivity correlations. By this terminology is meant the functional dependence of the (thermal) rate constant (or the free energy of activation G_a) on the free energy change ΔG in a series of reactions. (In the field of proton transfer reactions such correlations are known as "Brønsted plots"¹¹). We suggest that the basic idea,^{10(a)} that a "transition state" is a "mixture" of reagents and products (Sec. II), can be carried on from thermal (Sec. III) to state-to-state processes (Sec. IV), whereas the postulates of transition-state theory cannot, and must be replaced by other statistical assumptions (Sec. IV). Applications (Sec. V) to reactive and nonreactive $v \rightarrow v'$ processes are presented.

II. THE CRITICAL CONFIGURATION AS A MIXTURE OF REAGENTS AND PRODUCTS

In this section we wish to determine the critical configuration n^* for the transition from reagents to products. This transition would be described by a parameter n , which assumes the value zero for reagents, $0 < n^* < 1$ for the critical configuration, and unity for products. In a reaction of the type $A + BC \rightarrow AB + C$, n can be interpreted as the bond order of the newly forming AB bond, and $1 - n$ as that of the weakening BC bond, so that along the reaction coordinate the total bond order is conserved.¹² Such an interpretation is plausible but not essential in the following derivation; hence, we shall not allude to it.

The idea of a critical configuration is central in many theories of chemical reactivity.¹³ It is usually calculated as an extremum of some function, be it potential or free energy along the reaction coordinate for transition-state theory^{13(a)} or the flux (number of states) along the reaction coordinate for microcanonical variational transition-state theory.^{13(c)} In the present formulation n^* would be a maximum of a "Lagrangian." This Lagrangian can be interpreted as the free energy profile along the reaction coordinate. However, for reasons to be clarified below, we wish to divorce our presentation from such an interpretation.

We determine the critical configuration as follows: Any configuration n , intermediate between reagents and products, has a reagent-like or product-like character as measured by $n_1 \equiv 1 - n$ and $n_2 \equiv n$, respectively. Let us think of the two numbers n_1 and n_2 as the "probabilities" of the asymptotic structures, "reagents" and "products" in the intermediate configuration. It is natural to measure the extent to which these two asymptotic structures are mixed by an "entropy" or "mixing" function¹⁴ $M(n)$. This function is a symmetric, convex function of n , has a maximum at $n = \frac{1}{2}$, and obeys $M(0) = M(1) = 0$. Such properties of $M(n)$ are discussed in length elsewhere.^{10(d),10(e)} One mixing function common in statistical thermodynamics^{14(c)} is the Shannon entropy^{14(b)}

$$M(n) = -n \ln n - (1 - n) \ln(1 - n). \quad (4)$$

Another plausible example is^{10(d)}

$$M(n) = [n(1 - n)]^{1/2}. \quad (5)$$

Let us designate the energies of reactants and products (as measured from a common zero) by E_1 and E_2 , respectively. The "average energy" at the intermediate configuration is $\bar{E} = \sum_i n_i E_i = E_1 + n\Delta E$, where $\Delta E \equiv E_2 - E_1$. The most mixed configuration n^* for given values of ΔE and \bar{E} is given by the distribution of maximal entropy^{14(c)-(e)} subject to the "constraint" \bar{E} .¹⁵ By introducing a Lagrange multiplier λ , one maximizes the Lagrangian

$$G(n) \equiv n\Delta E + \lambda M(n). \quad (6)$$

Hence, n^* is determined from

$$0 = \Delta E + \lambda M'(n^*) \quad (7)$$

(a prime denotes differentiation). For example, for $M(n)$ given by Eq. (4) one has

$$n^* = [1 + \exp(-\Delta E/\lambda)]^{-1}. \quad (4')$$

Alternatively, from Eq. (5) follows:

$$n^* = \frac{1}{2} [1 + \Delta E/(\Delta E^2 + \lambda^2)^{1/2}]. \quad (5')$$

λ in the above equations is seen to be an analog of temperature, as it measures the width of the distribution (n_1^*, n_2^*). For example, from Eq. (4') we have that $n_2^* - n_1^* = \tanh(\Delta E/2\lambda)$. Hence, the smaller λ is, the wider the distribution. λ also determines the sensitivity of n^* to a change in ΔE : The smaller λ is, the larger the sensitivity.

As the value of \bar{E} is unknown, we cannot determine λ . However, if we define a "reaction series"^{10(d)} as a family of reactions where n^* depends only on ΔE , we have $\lambda = \text{const.}$ for such a series. This enables one to correlate critical configurations of various reactions in a series. The usefulness of such a definition lies in the fact that reaction series do exist.¹⁰ A "thermal reaction series" would be obtained by considering the effect of substitution [e.g., varying X or Y in Eq. (3)] on the thermal reaction probability. A "state-to-state reaction series" is obtained by considering the effect of variation of an internal state [e.g., v' in Eq. (3)] on the state-to-state transition probability. In what follows we shall use the expressions derived for n^* to correlate rate constants in such series.

III. THERMAL STRUCTURE-REACTIVITY CORRELATIONS

We wish to evaluate a reaction probability $P(1 \rightarrow 2)$ for a process symbolically written as

$$1 \rightarrow \# \rightarrow 2. \quad (8)$$

Evidently, $P(1 \rightarrow 2) + P(1 \rightarrow 1) = 1$, where $P(1 \rightarrow 1)$ is the "no-reaction probability." Reaction probabilities are equivalent to (normalized) relative rate constants. The absolute rate constant $k(1 \rightarrow 2)$ is obtained by multiplying the reaction probability by the collision rate constant Z :

$$k(1 \rightarrow 2) = ZP(1 \rightarrow 2). \quad (9)$$

In the following we discuss $P(1 \rightarrow 2)$ in terms of the two stages of the process (8): The probability for going from reagents to $\#$ is denoted by $P(1 \rightarrow \#)$, and that for going from $\#$ to products by $P(\# \rightarrow 2)$. If these two

stages are independent, $P(1 \rightarrow 2) = P(1 \rightarrow \#)P(\# \rightarrow 2)$.

First consider the basic assumptions of transition-state theory (TST)^{13(a)}: $\#$ and "1" are assumed to be in thermal equilibrium; hence,

$$P(1 \rightarrow \#) = \exp(-G_a/RT), \quad (10a)$$

where G_a is the free energy of activation. Next, $\#$ is assumed to be a configuration of no return; hence,

$$P(\# \rightarrow 2) = 1. \quad (10b)$$

These two assumptions combined given the TST reaction probability.

A possible approach^{16,10} to structure-reactivity correlations is to calculate G_a from a function $G(n)$ interpreted as the free energy profiles along the reaction coordinate [e.g., Eq. (6)]. By this approach one correlates thermal rate constants. It is indeed known that the above formulation of TST is hard to generalize to state selected processes. Hence, we shall try to divorce the following presentation from the assumptions (10): In the present section we will examine an alternative to Eq. (10a), whereas in Sec. IV we will consider a suitable substitute also for Eq. (10b).

An alternative to Eq. (10a) is obtained by realizing that a barrier's location can serve as a measure of reactivity instead of its height. The more $\#$ resembles 1 (i.e., the smaller $n^\#$), the larger $P(1 \rightarrow \#)$. In the limit where $\#$ is identical with reagents, this probability is by definition unity. Hence, we replace the equilibrium assumption of TST by the assumption that $P(1 \rightarrow \#)$ is a monotonic function of $n_1^\# \equiv 1 - n^\#$. One possible function of this sort is

$$P(1 \rightarrow \#) = n_1^{*A}, \quad (11)$$

where the power $A > 0$.

Next, suppose one still retains Eq. (10b). Then $P(1 \rightarrow 2) = n_1^{*A}$ and $P(2 \rightarrow 1) = n_2^{*A}$. From detailed balance [cf. Eq. (2)], assuming a common Z for reactions in both directions, we have

$$A = -\Delta E / [RT \ln(n_1^\# / n_2^\#)]. \quad (12)$$

For the sake of comparison with the previous approach, we take Eq. (10a) as a definition of G_a ; hence,

$$G_a = -RT \ln P(1 \rightarrow 2) = \Delta E \ln n_1^\# / \ln(n_1^\# / n_2^\#). \quad (13)$$

It is also instructive to consider the Brønsted slope $\alpha \equiv dG_a/d\Delta E$. As previously noted,^{17,16,10} the assumption that $G(n)$ is given by Eq. (6) and that $G_a \equiv G(n^\#)$ suffice to show [cf. Eq. (7)] that for any $M(n)$ one has $\alpha = n^\#$. Hence, the Brønsted slope is a measure of the location of the transition state, which is Leffler's postulate.¹⁸ It follows that α changes from zero (for very exothermic reactions) to unity (for very endothermic reactions). The last statement can also be demonstrated for Eq. (13), by writing its asymptotic form

$$\begin{aligned} \Delta E \ll 0 &\Rightarrow 1 \approx n_1^\# > n_2^\# \approx 0 \Rightarrow G_a \approx -\Delta E \frac{\ln n_1^\#}{\ln n_2^\#} \approx 0, \\ \Delta E \gg 0 &\Rightarrow 0 \approx n_1^\# < n_2^\# \approx 1 \Rightarrow G_a \approx \Delta E \frac{\ln n_2^\#}{\ln n_1^\#} = \Delta E. \end{aligned} \quad (13')$$

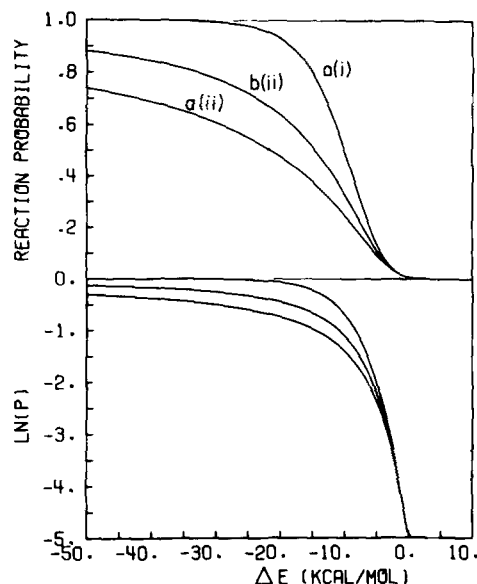


FIG. 1. Three functions for thermal structure-reactivity correlations. Curves denoted by (a) are from inserting an expression for G_a in Eq. (10); those denoted by (b) are by inserting an expression for $n^\#$ in Eq. (11). (i) and (ii) refer to calculating the above expressions using $M(n)$ from Eqs. (4) and (5), respectively, a(i) and b(ii) are equivalent, see the text. $G_a^0 = 3$ kcal/mol for all three plots. The difference between these plots is not as small as it seems when drawn in a smaller scale^{20(a)}; however, it decreases for smaller G_a^0 .

In deriving Eq. (13') we have used the fact that $n^\#$ is a monotonic function of ΔE . This version of Hammond's postulate¹⁹ follows from Eq. (7) for $M(n)$ with the correct properties.^{10(d)-10(f)}

Once a specific form for $M(n)$ is assumed, the dependence of $n^\#$ on ΔE is determined (cf. Sec. II), and therefore also the ΔE dependence of G_a , A , or $P(1 \rightarrow 2)$. For example, in the case that $M(n)$ is given by Eq. (4) one has that $n_1^\# / n_2^\# = \exp(-\Delta E / \lambda)$, $A = \lambda / RT$ is independent of ΔE , and therefore [cf. Eq. (13)] $G_a = -\lambda \ln n_1^\#$. ($\lambda \ln 2$ is seen to be the free energy of activation G_a^0 for the $\Delta E = 0$ reaction.) The same result is obtained by using $n^\#$ of Eq. (4') in $G_a = G(n^\#)$ [$G(n)$ is given by Eq. (6)]. Hence, for the Shannon entropy (4) the two approaches coincide. This is not so for $M(n)$ from Eq. (5). Then the maximum of the free energy profile is

$$G_a = G(n^\#) = \frac{1}{2}[\Delta E + (\Delta E^2 + \lambda^2)^{1/2}] \quad (5'')$$

($G_a^0 = \lambda/2$ is seen to be free energy of activation for the $\Delta E = 0$ reaction). Equation (5'') is not equivalent to Eq. (13) with $n^\#$ from Eq. (5'). [Here $G_a^0 = (\lambda/2) \ln 2$ is seen to be the free energy of activation for the $\Delta E = 0$ reaction.] Therefore, using the two examples of $M(n)$ in the two approaches generates three structure-reactivity plots, as shown in Fig. 1. All three functions are qualitatively alike—an indication that the replacement of Eq. (10a) by Eq. (11) was not by itself a very drastic step.

IV. STATE-TO-STATE STRUCTURE-REACTIVITY CORRELATIONS

Let us now consider a state-to-state reaction series where the variation in $\Delta E \equiv \Delta E(s, s')$ is achieved by a

change in an internal state of the products. In the example of Eq. (3), the final vibrational state of HX varies. Other examples may be nonreactive, inelastic (energy-transfer) collisions.

In deriving Eq. (11) for "thermal structure-reactivity correlations" we assumed [cf. Eq. (10b)] that the critical configuration \neq in Eq. (8) is a "configuration of no return,"¹³ and have therefore set $P(\neq \rightarrow 2) = 1$. This postulate clearly fails when the configuration "2" is an internal state of the products, and one wishes to compare the probability of its formation to that of other possible internal states. Once a transition state \neq is reached, it is still to be determined into what internal state s' of the products the system proceeds. Hence, $P(\neq \rightarrow 2)$ is not unity but varies with s' , a variation which has a decisive role in determining the final state distribution. This intuition is also behind several "retreat coordinate" models⁶⁽¹⁾ for state-to-state processes.

We suggest a substitute to Eq. (10b) which follows from the same argument which has led to Eq. (11). The critical configuration was interpreted as a "resonance structure" with weights n_1^* and n_2^* . This suggests that the probability that \neq disintegrates to give the asymptotic structure i is simply n_i^* . Hence,

$$P(\neq \rightarrow 1) = n_1^*, \quad P(\neq \rightarrow 2) = n_2^*. \quad (14)$$

The probabilities for the reverse processes (into \neq) follow from the argument leading to Eq. (11):

$$P(1 \rightarrow \neq) = n_1^{*A}, \quad P(2 \rightarrow \neq) = n_2^{*A}, \quad (14')$$

where the power $A > 0$. Finally, if the two stages in Eq. (8) are independent, we have for the reaction probability

$$P(1 \rightarrow 2) = P(1 \rightarrow \neq)P(\neq \rightarrow 2) = n_1^{*A} n_2^*. \quad (15)$$

Detailed balance [i.e., Eq. (2) assuming $\bar{Z} = \bar{Z}$] implies

$$A = -\Delta E / [RT \ln(n_1^*/n_2^*)] + 1, \quad (16)$$

which should be compared with Eq. (12). Also

$$G_a \equiv -RT \ln P(1 \rightarrow 2) = \Delta E \ln n_1^* / \ln(n_1^*/n_2^*) - RT \ln(n_1^* n_2^*), \quad (17)$$

which should be compared with Eq. (13).

Clearly, $P(1 \rightarrow 2)$ in Eq. (15) has a maximum as a function of ΔE or, equivalently, G_a in Eq. (17) has a minimum. This stems from the properties of $M(n)$, which ensure that n_2^* is monotonically increasing with ΔE and therefore n_1^* is monotonically decreasing.^{10(d)-10(f)} Multiplying Eq. (11) by n_2^* produces a maximum in $P(1 \rightarrow 2)$. Equivalently, the additional term in Eq. (17) produces a minimum in G_a .

Inserting Eq. (4) for $M(n)$ gives

$$A = \lambda / RT + 1, \quad (16')$$

$$G_a = -(\lambda + RT) \ln n_1^* - RT \ln n_2^* \\ = (1 + RT/\lambda) \Delta E - (\lambda + 2RT) \ln n^*, \quad (17')$$

where $n^* \equiv n_2^*$. The equivalent of the Brønsted slope is

$$\alpha \equiv \frac{dG_a}{d\Delta E} = n^* - \frac{RT}{\lambda} (1 - 2n^*). \quad (18)$$

From Eq. (18) the asymptotic behavior is transparent:

$$\alpha \rightarrow \begin{cases} -RT/\lambda, & \Delta E \rightarrow -\infty, \\ 1 + RT/\lambda, & \Delta E \rightarrow +\infty. \end{cases} \quad (19)$$

The similarity with the thermal correlations (10) or (11) is that α is asymptotically constant, i.e., $\ln k(1 - 2)$ is asymptotically linear. However, the asymptotic values of α are not 0 and 1, but rather < 0 and > 1 (for $\lambda > 0$). The location of the maximum is at $n^* = kT/(\lambda + 2RT) < 1/2$, i.e., at a negative ΔE value.

It is instructive to examine Eq. (17') also as a function of λ . When $\lambda \rightarrow \infty$ (practically $\lambda \gg RT$), $G_a \rightarrow -\lambda \ln n_1^*$, which is the thermal correlation (cf. Sec. III). Equivalently, one has from Eq. (18) that $\alpha \rightarrow n^*$, or from Eq. (19) that the asymptotic values of α tend (from below and above, respectively) to 0 and 1. In the other extreme, when $\lambda \rightarrow 0$, the maximum in $P(1 \rightarrow 2)$ moves to $\Delta E = 0$ and the asymptotic slopes tend to be equal and large. Hence, in this limit our expressions simply reduce to the exponential gap law (1).

V. APPLICATIONS FOR $v \rightarrow v'$ PROCESSES

In this section we demonstrate the utility of the correlation (15) for reactive and nonreactive bimolecular collisions of a diatom in a vibrational state v with an atom (or molecule), giving as products a diatom in a vibrational state v' . In the following examples we use Eq. (4') for n^* and for ΔE we take the energy difference of initial and final vibrational levels

$$\Delta E(v, v') = -\Delta D_e - E_v + E_{v'}. \quad (20)$$

Here $\Delta D_e \equiv D_{e2} - D_{e1}$, where D_{e1} and D_{e2} are the diatomic well depths of reactants and products, respectively. (For nonreactive collisions $\Delta D_e = 0$.) The vibrational energies E_v and $E_{v'}$ are calculated from the bottom of the diatomic well:

$$E_v = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2, \quad (21)$$

using the experimental spectroscopic constants²¹ ω_e and $\omega_e x_e$.

The reaction series considered are such that v is kept constant and v' varied. The population of final vibrational states $p(v')$ is calculated by normalizing Eq. (15), i.e., $p(v') = n_1^{*A} n_2^* / Q$, where $Q = \sum_v n_1^{*A} n_2^*$. The absolute rate constant is $p(v')$ multiplied by the total rate constant for reaction from v , by $Z \equiv k(v \rightarrow)$. Hence,

$$k(v \rightarrow v') = Z p(v') = Z n_1^{*A} n_2^* / Q. \quad (22)$$

Here Z is independent of v' by its definition and λ by the definition of a reaction series.^{10(d)} $G_a^0 = (\lambda + 2RT) \ln 2$ is the value of G_a [cf. Eq. (17)] for $\Delta E = 0$ and termed¹⁶ the "intrinsic barrier." $2RT \ln 2$ is taken as an "entropic" contribution to G_a^0 ; hence, $E_a^0 \equiv \lambda \ln 2$. E_a^0 and Z are the parameters appearing in the fits to the absolute rate constants.

In Eq. (22), E_a^0 and Z (and also Q) are all functions of v . These functions are not uncorrelated: We expect their variation with v to conform to the "dynamical selectivity-reactivity principle."²² This means that the

larger the total reactivity as measured by $Z(v)$, the smaller the final state selectivity, i. e., the width of $p(v')$ is larger, implying a larger $E_a^0(v)$. It was also found^{22(b)} that reasonable bounds for total reaction probability as a function of total energy can be generated from the final state distributions at those energies. In the present context this means that one should be able to generate $Z(v)$ by the same procedure which generated $p(v')$. This follows by replacing Eq. (22) with the stronger statement

$$k(v \rightarrow v') = \bar{Z} n_1^* n_2^*, \quad (22')$$

where $\bar{Z} \equiv Z(v)/Q(v)$ is independent of both v' and v . This leaves us with only one v dependent parameter $E_a^0(v)$. An increase of $E_a^0(v)$ with v (i. e., with total energy) makes $p(v')$ flatter, and therefore increases $Q(v)$ and the total reactivity $k(v \rightarrow) = \bar{Z} Q(v)$.

The following examples are divided into (A) nonreactive and (B) reactive $v \rightarrow v'$ processes. Each fit shows $k(v \rightarrow v')$ vs $\Delta E(v, v')$ in both a linear and a logarithmic scale. These fits were actually made in the logarithmic scale, which is equivalent to minimizing relative deviations.²³ A logarithmic representation stresses the be-

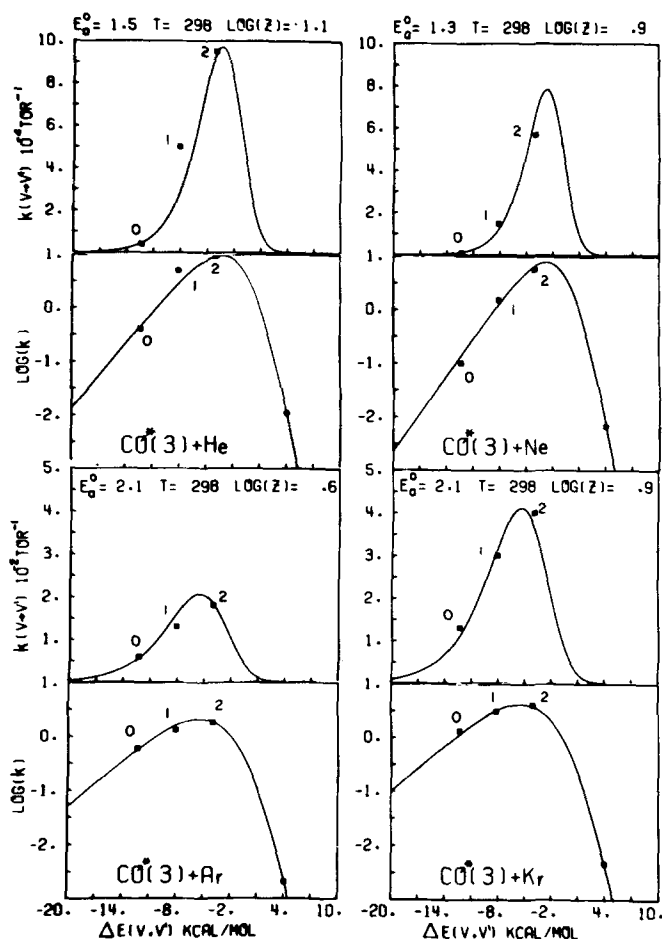


FIG. 2. A fit [cf. Eqs. (15) and (4')] to the final state distribution in Reaction (23a).^{24(a)} v' is marked in each panel. E_a^0 seems to depend on the rare gas M. [In a surprisal analysis^{3(b)} of the same reaction series, the Lagrange parameter adjoint to the constraint $|\Delta E(v, v')|$ was also found to depend on M.] Notations in the figure are explained in the text.

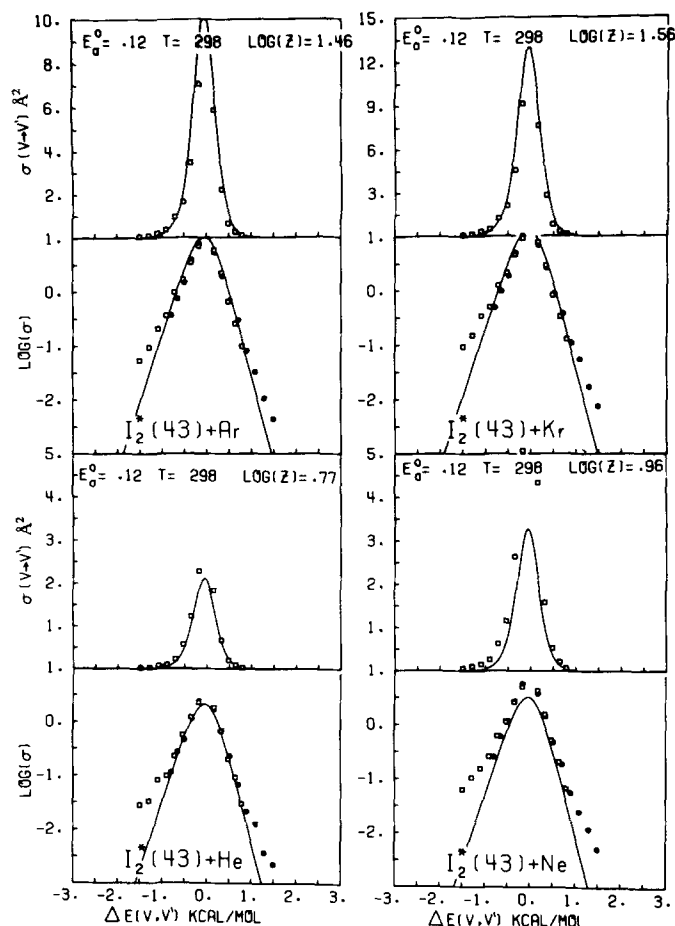


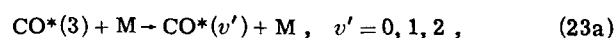
FIG. 3. Final vibrational distribution in Reaction (23b).^{24(b)} $k(43 \rightarrow 43)$ could not be measured. The line is a fit to Eqs. (15) and (4'). See the text for discussion.

havior in the "tail" of the distribution, where $p(v')$ is very small. In each figure the experimental points are marked by squares, the lowest v' being the leftmost square. Shown in the logarithmic plots are rate constants for the reverse processes (circles), as calculated from the experimental results by detailed balance (2). In each figure we give the value of the temperature T of the rotational-translation degrees of freedom (in K), as well as E_a^0 (in kcal/mol) and $\log Z$ (base 10). Z has the same units as the corresponding rate constants.

A. Nonreactive $V-T$ and $V-V$ processes

1. $V-T$ processes

Examples are collisions of electronically (*) and vibrationally excited diatomic molecules with rare gas atoms²⁴:



Rate constants for Reactions (23) are inferred²⁴ from the quenching by addition of M of the (electronic vibration-rotation) emission intensity.

A fit to Reaction (23a)^{24(a)} is shown in Fig. 2. The

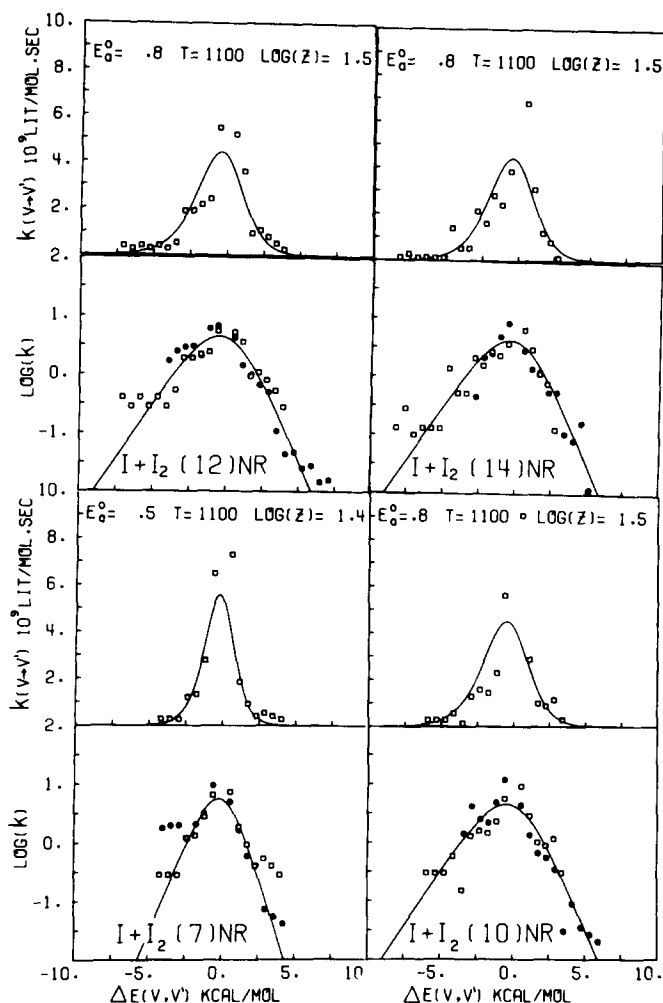
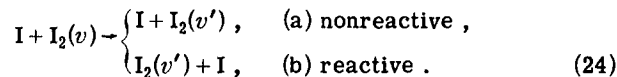


FIG. 4. 3D trajectory calculations²⁷ of final vibrational distribution in Reaction (24a). See the text for discussion.

lack of experimental points on the endoergic branch ($v' > 3$) renders our parameters uncertain. More complete are results for Reaction (23b),^{24(b)} which include data for $v' > 43$ as well as for $v' < 43$. We find that all rare gases share the same value of $E_a^0 = 0.12$ kcal/mol. They differ only in the value of Z . This may reflect a variation in the collision cross section with increasing size of M . To check this point, we treat I_2 as a mass point, and assign to M an effective radius for collision r_M . We assume that r_M is proportional to the radius \bar{r}_M of maximal radial density in the ns orbital ($n = 1, 2, 3$, or 4).²⁵ If cross sections for collision are of a "hard sphere" from $\sigma = \pi r_M^2$, we have $Z = Cr_M^2$ where C is common to all rare gases.²⁶ Results with $C = 66$ (for r_M in Å) are shown in Fig. 3, which demonstrates the effectiveness in the reduction of number of parameters. However, the value of Z for Ne is too low, and there is a downward deviation for the lowest v' states.

A similar fit for $M = H_2$, CO, and I_2 ^{24(b)} can be found elsewhere.^{10(f)} The small value for the intrinsic barrier in all cases is in agreement with the exponential gap law limit of Eq. (17'), discussed at the end of Sec. IV.

To demonstrate this point, that nonreactive collisions are characterized by a smaller intrinsic barrier G_a^0 than reactive collisions, let us consider a system which may also be reactive:



A fit to extensive 3D classical trajectory calculations²⁷ is shown in Fig. 4 for the nonreactive channel and in Fig. 5 for the reaction channel. (In each plot v is fixed and v' varied.) The Monte Carlo procedure for selecting initial values introduces considerable statistical errors in the trajectory calculation, resulting in large error bars for our parameters. It is nevertheless clear that E_a^0 for the nonreactive channel is much smaller than that of the reactive channel.

It is also instructive to consider the values of the parameters (E_a^0 and $\log Z$) as a function of v . From the limited available results it seems that these parameters increase with v when v is small (e.g., $v = 7$), and reach a constant value for large v (e.g., $v = 10, 12$, and 14). Similar results²⁷ for Cl replacing I are shown elsewhere.^{10(f)} These results are in accord with the selectivity-reactivity principle discussed above. To

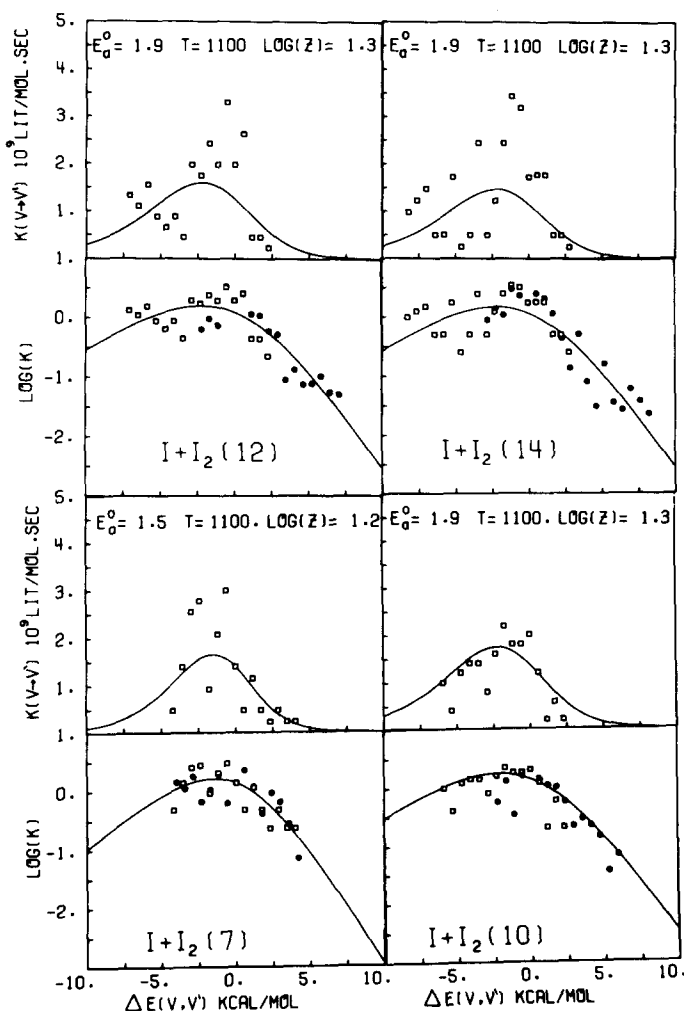


FIG. 5. Same as Fig. 4, but for the reactive channel (24b).²⁷

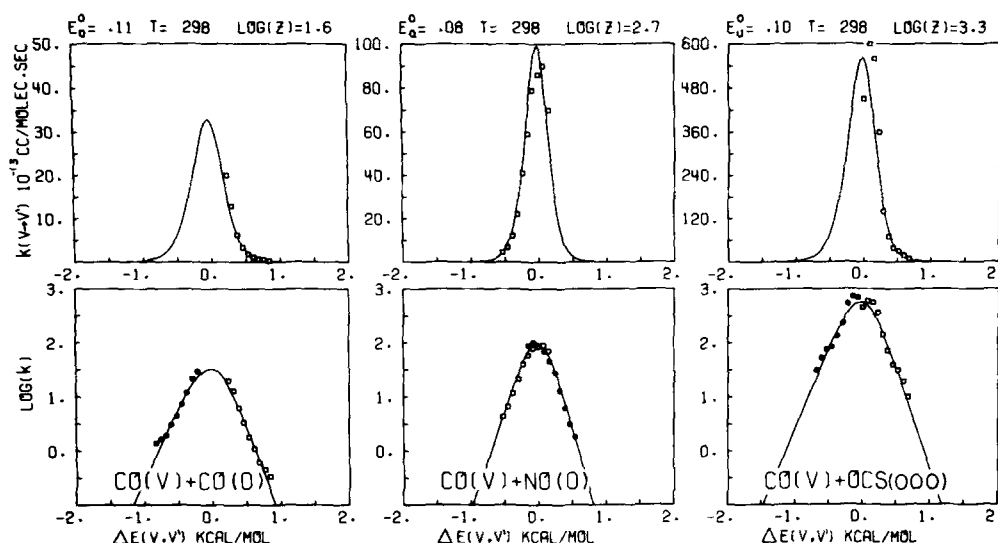
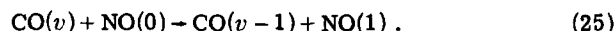


FIG. 6. A fit of Eqs. (15) and (4') to the rate constants of the V - V process (25).²⁸

check the validity of Eq. (22') we have calculated $Q(v)$ to an error < 0.001 . For $v=7, 10, 12$, and 14 we find that $\log Q(v) = 0.04, 0.11, 0.12$, and 0.12 , respectively, for Reaction (24a), and $\log Q(v) = 0.16, 0.22, 0.25$, and 0.28 , respectively, for Reaction (24b). The trend indeed parallels that of $\log Z(v)$ for these reactions. Results from lower v levels are needed for a complete verification.

2. V - V transfer

Here the diatom collides with another molecule whose internal vibrational state changes upon collision, e. g.,²⁸



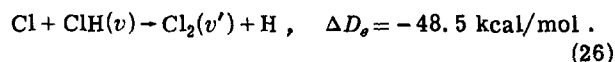
V - V processes are very efficient in comparison to V - T processes,¹ resulting in a large Z (Fig. 6). The small value for the intrinsic barrier is a quantitative expression for the importance of a resonance condition ($v' \approx v$) in V - V energy transfer.

B. Reactive collisions

We divide the examples into two: endoergic and (very) exoergic collisions.

1. Endoergic (and ergoneutral) reactions ($\Delta D_e \leq 0$), with an initial vibration $v > 0$

Here mainly trajectory results are available. Results for Reaction (24b) were shown in Fig. 5. Similar results for $\text{Cl} + \text{Cl}_2$ are shown elsewhere.¹⁰⁽⁷⁾ Shown in Fig. 7 is a fit for the endoergic reaction²⁹



The remarks made on Reaction (24) are valid here: There is a statistical noise in the trajectory calculation due to the Monte Carlo procedure. However, a trend in the values of the parameters is still observed: They rise with v for low v and reach a constant value when v is large. The selectivity-reactivity principle is again sustained, and $\log Q(v) = -0.31, -0.17, -0.10$,

and -0.08 for $v=7, 8, 9$, and 10 , respectively, in qualitative agreement with the trend in $\log Z(v)$.

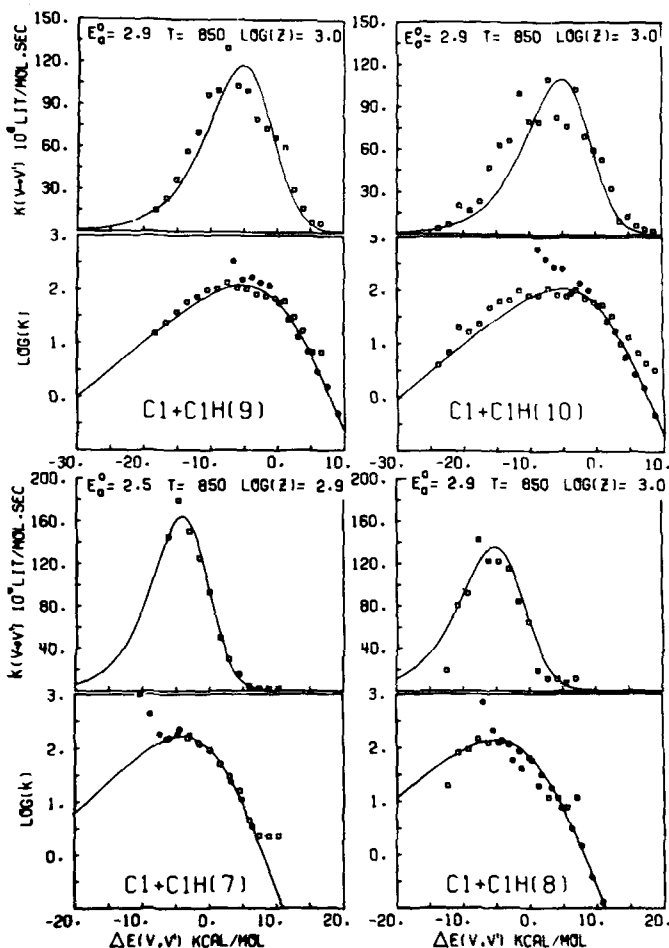


FIG. 7. A fit of Eqs. (15) and (4') to the final state distribution in Reaction (26), as determined from a 3D classical trajectory calculation.²⁹

2. Exoergic reactions

Reactions of this type are of great interest, as they are the key to the operation of chemical lasers.³ There is much experimental data for the nascent product vibrational distribution, immediately after such a reaction and (hopefully) before any relaxation process takes place. The reactants are usually taken from a thermal heat bath at room temperature. Hence, v is effectively zero and $T=300$ K. When the measurement^{9(b)–9(e),30} is done by following the IR emission of the product diatom, it is not possible to determine the population in $v'=0$. In such cases we use extrapolation by Eq. (17'). By the chemical laser method^{9(e),31} the ground state population becomes experimentally accessible.

We consider two major types of exoergic reactions: halogen and hydrogen transfer. Halogen transfer reactions usually show marked deviations from linear surprisals.^{9(a),(b),(f),(g)} They seem to fit Eq. (15), as seen in Figs. 8 and 9. The two Cl transfer reactions in Fig. 8 have very similar ΔD_e values and identical intrinsic barriers; the two F transfer reactions in Fig. 9 have different ΔD_e and E_a^0 values: The more exoergic reaction has a larger intrinsic barrier, and hence a broader v' distribution. This is yet another version of the selectivity–reactivity principle,²² where the total available energy is varied by a variation in ΔD_e .

The success of fitting these vibrational populations to Eq. (15) is, however, limited. Some experimental results do not fit unless we also let the temperature (or rather $A=\lambda/RT+1$) be a free parameter. An example^{9(b)} for Cl and Br transfer is shown in Fig. 10. Also, an alternative measurement^{9(c)} of the reaction $H+ClF$ (cf. Fig. 8) fits Eq. (15) with an unrealistic value of $T=95$ K.²³ The problem is demonstrated for the hydrogen transfer reaction

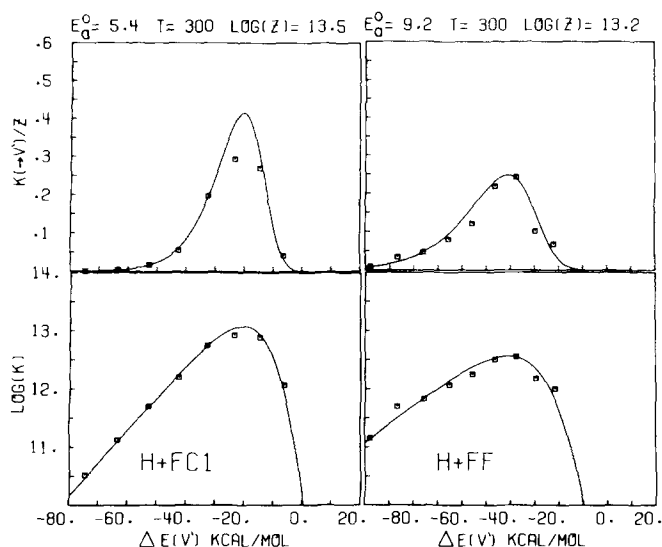


FIG. 9. Same as Fig. 8 for HF vibrational distribution in two F transfer reactions.^{9(c),9(d)} ΔD_e ($H+FC1$) = 74.8 kcal/mol. ΔD_e ($H+F_2$) = 98 kcal/mol. For the $H+FC1$ reaction, not only the population in $v'=0$, but also that of $v'=1,2$, was determined by extrapolation. Other measurements^{9(e)} of the same systems give similar results with slightly different parameters.



Panel (a) of Fig. 11 shows classical 3D trajectory results,^{30(a)} which fit reasonably well. Panel (b) shows an attempt to fit experimental results³¹ with $T=300$ K. Finally, panel (c) shows how these results can be fitted with $T \approx 1600$ K. The main difference between the trajectory calculation and the experiment is that the latter has a larger relative population in $v'=0$ and 1. This

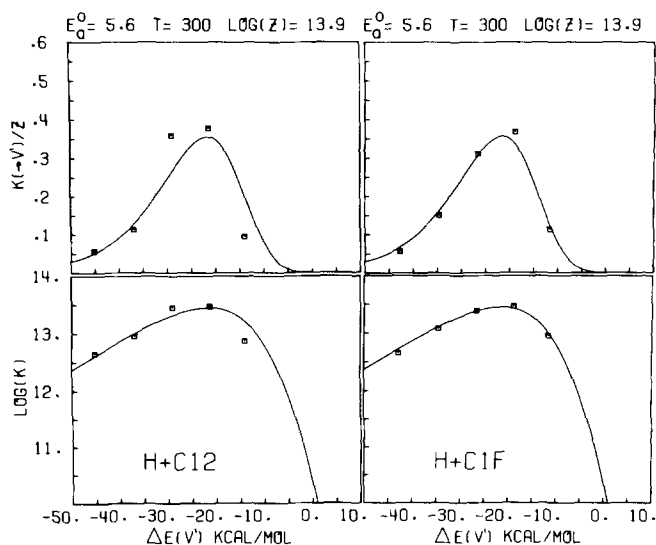


FIG. 8. A fit of Eqs. (15) and (4') to the final HCl vibrational distribution in two Cl transfer reactions.^{9(e)} The population in $v'=0$ (leftmost square in each panel) was determined by extrapolation. ΔD_e ($H+Cl_2$) = 45.2 kcal/mol. ΔD_e ($H+ClF$) = 42.8 kcal/mol. Note that the two distributions, and hence the parameters used in the fit, are practically identical. Note that in the upper panel k is divided by the calculated value of Z .

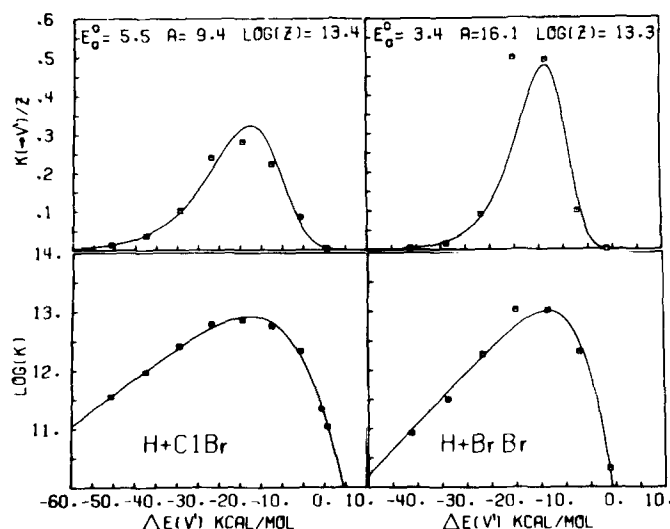


FIG. 10. Similar to Fig. 8 for Cl and Br transfer reactions.^{9(b)} To distinguish this example, where T is taken as a free parameter, from the previous ones, where T assumes its experimental value, we present the value of the parameter A [related to T via Eq. (16')]. ΔD_e ($H+ClBr$) = 50.7 kcal/mol. ΔD_e ($H+BrBr$) = 41.2 kcal/mol.

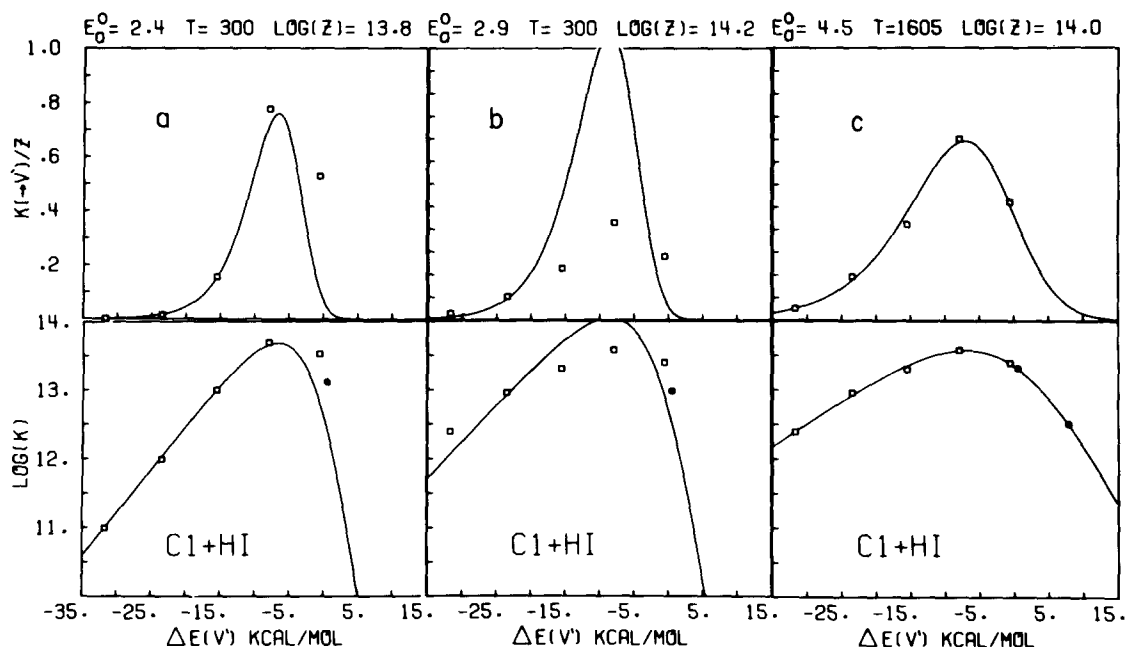


FIG. 11. Final vibrational distribution of the HCl product in the H transfer reaction $\text{Cl} + \text{HI}$ ($\Delta D_e = 31.7$ kcal/mol). (a) A good fit to 3D classical trajectory calculations.^{30(a)} (b) A bad fit to experimental results.³¹ (c) A good fit to the same³¹ experimental results when we give the temperature a value of 1605 K. [The circles for the reverse reactions in this panel were calculated from Eq. (2) assuming $T = 1605$ K.] The population of $v' = 0$ was measured experimentally, not extrapolated.

difference suffices to introduce a drastic change in the parameters.

A final example, shown in Fig. 12, is for the reaction series $\text{F} + \text{HX}$.^{30(b)} This is also a final example of the selectivity–reactivity principle as discussed above: The more exoergic the reaction, the less drastic the population inversion.

VI. CONCLUSION

We have demonstrated a possible extension of thermal structure–reactivity correlations to state-to-state chemistry. The analytic, one-parameter relation, obtained for the relative final population, describes both exponential gap behavior in nonreactive collisions and population inversion as observed in reactive v to v'

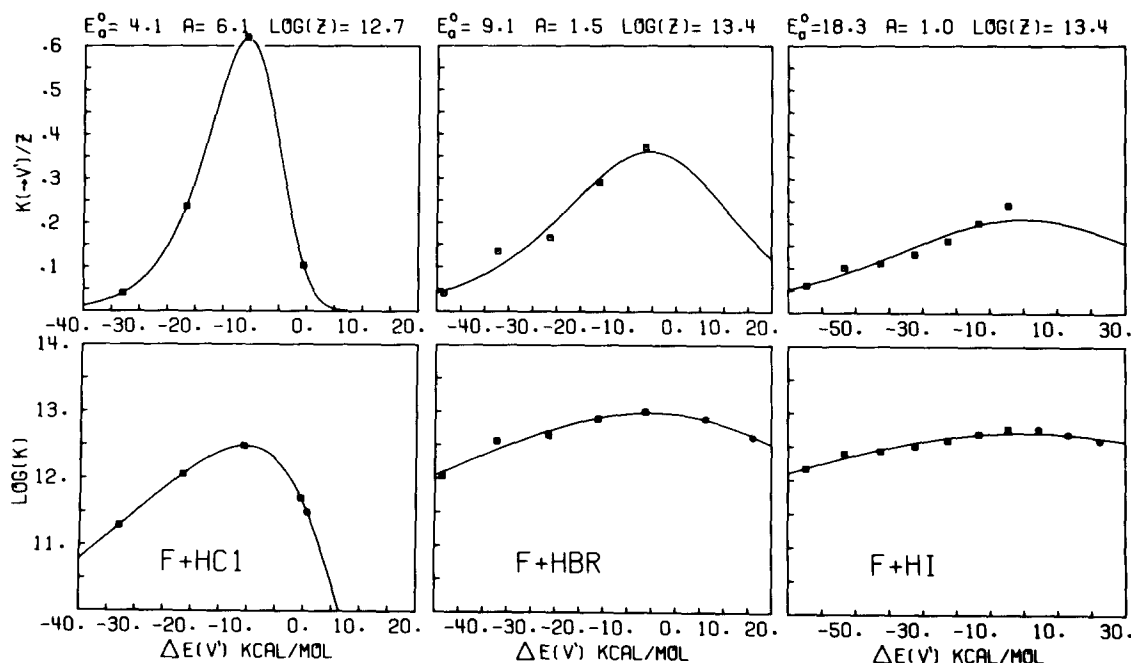


FIG. 12. Final HF vibrational distribution for $\text{F} + \text{HX}$ reactions, where $\text{X} = \text{Cl}$, Br , and I .^{30(b)} $\Delta D_e = 32.9$, 48.5 , and 64.7 kcal/mol, respectively. The fit to Eq. (15) uses A as an additional parameter. This series is an example of the selectivity–reactivity principle.²²

processes.

In the theory the main question is whether it is possible to present a unified framework for both thermal and state-to-state correlations and to obtain a functional dependence of E_a^0 on v and ΔD_e . In application the main problem encountered is that $p(v')$ for some of the exoergic reactions can be fitted only by assuming that the temperature is different from its experimental value.

ACKNOWLEDGMENT

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