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AN INFORMATION THEORY APPROACH TO HYDROGEN HALIDE REACTION PRODUCT DISTRIBUTIONS

presented by

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has been accepted towards fulfillment of the requirements for

PH.D. degree in MECHANICAL ENGINEERING

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### AN INFORMATION THEORY APPROACH

### TO HYDROGEN HALIDE

### REACTION PRODUCT DISTRIBUTIONS

By

David H. Stone

#### A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Mechanical Engineering

#### ABSTRACT

# AN INFORMATION THEORY APPROACH TO HYDROGEN HALIDE REACTION PRODUCT DISTRIBUTIONS

By

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Chemical laser modeling is dependent on the reaction rate coefficients available from both experiment and theory. A statistical model is developed to correlate the relative rate coefficients for the laser pumping reactions: (I)  $F + H_2 \rightarrow HF(v,J) + H$ , (II)  $F + D_2 \rightarrow DF(v,J) + D$ , (III)  $H + F_2 \rightarrow HF(v,J) + F_1$  (IV)  $D + F_2 \rightarrow DF(v,J) + F_1$ (V) H + C1<sub>2</sub>  $\rightarrow$  HC1(v,J) + C1, (VI) D + C1<sub>2</sub>  $\rightarrow$  DC1(v,J) + C1, (VII)  $H + Br_2 \rightarrow HBr(v,J) + Br, and (VIII) D + Br_2 \rightarrow$ DBr(v,J) + Br. The detailed product distributions for reactions (IV) and (VIII) are generated by the model; these distributions have not yet been experimentally observed. The model uses surprisal analysis to transform the product translational distributions into an analytically tractable form. The translational surprisals are approximately quadratic in form and vary in width with vibrational energy. The surprisal widths are identified with product distribution entropy for use in developing the statistical collision

model. The model assumes a reaction complex interaction among nascent vibrational levels. The strength of the interaction determines the proposed degree of energy interchange among vibration, rotation, and translation. The logarithm of the number of nascent states involved in the interaction is identified as proportional to the translational distribution entropy. Relative values for the entropy are predicted and compared with the experimental data.

The statistical model is coupled to an algorithm which closely regenerates the reaction (III) product vibrotational distribution. Certain parameters are identified and assumed to be constant with respect to isotopically similar reactions. These parameters are incorporated into the model to predict the full vibrotational distributions for reactions (IV) and (VIII). The v = 1 rotational distribution for reaction (II) is predicted, since the reaction product data for that level was not accurately determined when these experiments were performed by Folanyi and others in 1972. The surprisal approach is also applied to HF vibration to rotation collisional relaxation. Surprisals are identified which correspond to recently reported trajectory studies and experimental data.

#### ACKNOWLEDGMENTS

"If any of you lack wisdom, let him ask of God, who giveth to all men liberally, and upbraideth not; and it shall be given him." (James 1:5) My gratitude goes first to my Lord Jesus Christ for calling me to this doctoral program, and for the ideas, support, and encouragement necessary for its completion. I also thank my precious wife, Bonnie, who "looketh well to the ways of her household" (Proverbs 31:27), thereby providing me the solidity at home essential to the development of this work.

I express my appreciation to my adviser, Dr. Ronald Kerber, for his guidance and abundant patience throughout the preparation of this dissertation. I thank the faculty members who served on my guidance committee: Dr. Thomas Kaplan, Dr. Jes Asmussen, Dr. Mahlon Smith, and Dr. John McGrath. Their reviews and critiques have been most valuable.

I am indebted to the United States Air Force for providing financial assistance and the opportunity to undertake this program.

I sincerely thank my parents, Robert and Suzanne Stone, and my pastor, Joseph Dedic, for their unfailing confidence in me. I also thank Mrs. Pat VanKirk for her invaluable assistance in the preparation of the final manuscript.

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# 1. THE STATISTICAL METHOD IN REACTION PRODUCT DISTRIBUTIONS

#### 1.1 Introduction

Chemical laser modeling is dependent on the reaction rate coefficients available from both experiment and theory. A comprehensive computer model must incorporate potentially hundreds of rates for the various pumping and relaxation mechanisms, in order to accurately predict laser performance. Available reaction rate data for HF (hydrogen fluoride) chemical lasers, for example, is usually taken from selected experiments and trajectory calculations as reviewed by Cohen and Bott in references 1 and 2. Not all reaction rates of interest in chemical lasers have been studied and significant uncertainties are present in many that are known. Techniques are needed to expand the data base from a few accurately measured reaction rates to a complete rate set. In this work the information theoretic or "surprisal" approach to reaction product distributions as developed by Bernstein, Levine, and Ben-Shaul (references 3-5) is applied in part to several reactions important in chemical laser development. Using the surprisal approach as a starting point, the reactions are then analyzed from the viewpoint of both reaction complex dynamics and statistical collision theory.

The experimental data which forms the basis of the analysis was obtained by Polanyi and other workers as cited below using reacting molecular beams. The reactions of primary interest in this work are the HF/DF laser pumping reactions, so-called because the reaction exothermicity "pumps" the molecular products into excited vibrational and rotational energy states. The product vibrational and rotational distributions were obtained by Polanyi, Woodall, and Sloan (references 6 and 7) for the reactions

$$F + H_2 \longrightarrow HF(v,J) + H$$
 (I)

$$F + D_2 \longrightarrow DF(v,J) + D$$
 (II)

$$H + F_2 \longrightarrow HF(v,J) + F$$
 (III)

where "v" is the vibrational quantum number and "J" is the rotational quantum number.

The objectives of this work are to develop a model which accurately predicts the features of the experimental distributions, and to develop a method to predict reaction product distributions which have never been measured experimentally. Of particular interest is an accurate prediction for the DF laser pumping reaction

$$D + F_2 \longrightarrow DF(v,J) + F$$
 (IV)

which has not been studied to any detailed extent experimentally.

To test the range of validity of the model and also for use in other types of chemical laser studies, the model is applied to the product distributions obtained by Anlauf, et. al. (reference 8) for the reactions

$$H + C1_2 \longrightarrow HC1(v,J) + C1$$
 (V)

$$D + C1_{2} \longrightarrow DC1(v, J) + C1$$
 (VI)

$$H + Br_{2} \longrightarrow HBr(v, J) + Br \qquad (VII)$$

The model is then used to predict the experimentally unknown product distribution for the reaction

$$D + Br_{2} \rightarrow DBr(v, J) + Br \qquad (VIII)$$

Each of the product distributions for reactions (I)-(VIII) will be transformed via the surprisal technique as modified in this work to make statistical analysis more tractable. Similarities are anticipated in the analysis for reactions (III)-(VIII) due to the character of the reactants, namely monatomic hydrogen and diatomic halide. The model incorporates the dynamical similarity of these reactions, but will be seen to exhibit sufficient flexibility to distinguish among these separate reactions.

The surprisal technique is also applied to vibration to rotation (V-R) relaxation processes in the HF molecule. Due to the lack of experimental data, a linear surprisal function is assumed. Results for different values of the surprisal slope are compared with trajectory calculations by Wilkins and recent limited experiments by Hinchen. 1.2 An Overview of the Information-Theoretic Approach to Reaction Product Distributions

Combining in part the developments from references 5 and 9, the basic concepts from information theory may be applied to reaction product distributions. The discussion is restricted to the "analytical route" which begins with observed experimental distributions and progresses toward understanding of the underlying reaction dynamics. This is in contrast to the "synthetic route" in which constraints to the product distribution are known or postulated. The form of the distribution is then synthetically obtained by maximizing the entropy subject to the given constraints. The analytical route is typically used by workers in this field to obtain these constraints given an observed distri-The present work diverges from this approach by bution. interpreting the observed distributions in terms of a modified statistical collision theory. The mathematical constraints of the distribution are not necessary here because useful results and predictions may be easily obtained without them, as will be shown later.

Consider an experiment which has n distinct possible outcomes which arise with equal probability. For example, we may choose any of reactions (I)-(VIII) and obtain a product distribution in n different vibrational levels. Let the measurement of the vibrational level for a given product diatomic molecule constitute a single experiment. Repeating this experiment N times will produce a particular sequence of n possible outcomes, arranged in a chain N items long. There

are evidently  $n^{N}$  different possible sequences, where each sequence item has a probability of 1/n. The actual sequence of outcomes is not particularly interesting compared with the number of events,  $N_{i}$ , which result in the i'th outcome, where i = 1,2,...,n. Any set of integers  $N_{i}$  which satisfies

$$\sum_{i=1}^{n} N_{i} = N \tag{1}$$

is a possible result. The number of such combinations of N objects taken in groups of  $N_1$ ,  $N_2$ ,..., $N_n$  is given by

$$W = N! / \prod_{i} N_{i}!$$
 (2)

If equation (2) is summed over all sets  $|N_i|$  that satisfy equation (1), the result must be  $n^N$ . Therefore the fraction of times, or probability, that a particular set  $|N_i|$  is observed is given by

$$P(\left|N_{i}\right|) = W/n^{N}$$
(3)

In any real experiment, the number of reactions, N, far exceeds the number of product levels, n. Stirling's approximation may then be used, such that in the limit where  $N \gg n$ ,

$$\ln P(|N_{i}|) = N\ln N - \sum_{i} N_{i}\ln N_{i} - N\ln(n)$$
$$= -N \left[ \ln(n) + \sum_{i} (N_{i}/N)\ln(N_{i}/N) \right]$$
$$= -N \left[ \ln(n) + \sum_{i} P_{i}\ln P_{i} \right]$$
(4)

where  $P_i = N_i/N$  is the observed probability of occurrence of

the i'th outcome. The information content of the distribution (ie., the particular set  $|N_i|$ ) is defined by

$$\mathcal{L} = -(1/N) \ln \left[ P(|N_i|) \right]$$
$$= \ln(n) + \sum_{i} P_i \ln P_i$$
$$= \sum_{i} P_i \ln \left[ P_i / (1/n) \right]$$
(5)

The information is a non-negative quantity and is always defined even if some outcomes are never observed, using the convention  $P_i lnP_i = 0$  when  $P_i = 0$  or 1. The smallest value of  $\mathcal{A}$  occurs when  $P_i = 1/n$  so that all possible outcomes arise with equal probability. The entropy of the distribution is defined as

$$H = -\sum_{i} P_{i} ln P_{i}$$
(6)

and is related to the information by

$$\mathcal{L} = \ln(n) - H \tag{7}$$

The entropy is also exclusively non-negative and attains its largest value, ln(n), for the distribution  $P_i = 1/n$ . The entropy is sometimes termed the "missing information," due to its complementary nature with respect to the information. The entropy of a distribution, H, is related to the thermodynamic entropy, S, by the gas constant: S = RH.

The physical significance of the information and entropy of distributions is explored in the following section. It is necessary to develop strict conditions governing the physical interpretation of these mathematical quantities. These conditions are fundamental to quantitative prediction and so form the framework of the model to be developed.

1.3 A Physical Interpretation of the Information Content of a Distribution

The relationship between entropy and information is provided by Brillouin in reference 10: "Entropy measures the lack of information; it gives us the total amount of missing information on the ultramicroscopic structure of the system." The structure of interest in this work is given by the details of the molecular reaction dynamics which produce the actual product distributions. Alternatively the term "structure" can be applied directly to the product distributions. This idea will be explored later in this section.

In the previous section, the information content of a known experimental distribution was derived. The form of equation (5) exhibits the averaging process which defines  $\mathcal{L}$ . In words, the information is the average difference between the logarithm of the observed probability,  $P_i$ , and the logarithm of a microcanonical distribution, 1/n. A microcanonical distribution is defined by the equality of each possible outcome. For chemical reactions of the types (I)-(VIII), a product microcanonical distribution is determined by calculating the number of allowed quantum states available to the products in terms of the total translational energy and the vibrational and rotational energies of the diatomic molecule. No change in electronic energy levels

is considered due to the limited amount of energy involved in these reactions.

The first excited electronic state of the HF molecule, for example, is 242 kcal/mole above the ground state (reference 11), whereas the total energy available to the products of reaction (III) is only 102 kcal/mole. Excited reactant electronic states are also too high in energy to influence product distributions under typical experimental conditions. In reaction (I), for example, the first F-atom excited state is 293 kcal/mole (reference 12) above the ground state while the first H<sub>2</sub> excited electronic state is 262 kcal/mole (reference 11) above its ground state. A review of the effect on product distributions of exciting vibrational modes in reactants for cases including reactions (II) and (V) is given in reference 13. These modes must be excited selectively since at T = 300K, for example, the v = 1 population of H<sub>2</sub> is only 0.15% of the v = 0 population, due to the energy difference in the Boltzmann factor of about 12 kcal/mole.

The product microcanonical distribution is called the "prior" distribution and is described in some detail in the next chapter. When the observed experimental distribution,  $P_i$ , corresponds to the prior distribution,  $P_i^0$ , the information is zero and the entropy is a maximum. The information can now be written

$$\mathcal{J} = \sum_{i} P_{i} \ln(P_{i}/P_{i}^{0})$$
(8)

It is convenient to define the "surprisal" by

$$I_{i} = -\ln(P_{i}/P_{i}^{0})$$
 (9)

which gives the local (ie., for outcome i) logarithmic deviation of the actual distribution from the prior distribution. Thus the information can also be written as

$$\mathcal{I} = -\sum_{i} P_{i} \ln I_{i}$$
(10)

Equations (8)-(10) must be subject to the constraint

$$\sum_{i} P_{i} = \sum_{i} P_{i}^{0} = 1$$
(11)

in order to satisfy non-negativity of the information. It is also necessary to identify a one-to-one correspondence among data points in the actual and prior distributions. Failure to satisfy equation (11) and/or to insure point-bypoint correspondence, as occurs occasionally in the literature, can lead to erroneous physical interpretations of experimental data as will now be shown.

As described in reference 10, information is the result of a choice which diminishes the number of possible outcomes. Information is not to be considered as the basis for a prediction in order to determine future outcomes. This is manifested in two principal ways: First, we must treat independent choices completely apart from each other. When specifying the product state of a diatomic molecule, such as produced by the reaction  $A + BC \rightarrow AB(v,J) + C$ , the vibrational distribution might first be determined. This "choice" increases our information toward determining the detailed product state which specifies vibrational,

rotational, and translational energies. The "choice" which determines the vibrational part of the product state is quite independent of the rotational distribution, however, except within the overall constraint of conserving total available energy. Therefore a prediction of the details of the rotational distribution cannot be made from any vibrational information obtained. Second, the averaging process of equation (10) produces a number independent of the symmetry or "structure" of a distribution. It may be desirable, for example, to use quantities like the mean product vibrational energy or the most probable product vibrational level as cornerstones of a dynamical theory. The information calculated by equation (10) may be used as a numerical measure of confidence in these desired quantities, if special conditions are invoked. These special conditions are now developed to make use of the information as a predictive tool.

Consider two hypothetical chemical reactions of the type A + BC  $\rightarrow$  AB(v) + C. The vibrational product distributions resulting from these similar experiments labeled "A" and "B" are shown in Figure 1. Also shown is the RRHO (rigid-rotor harmonic oscillator) prior distribution as a function of the fractional available vibrational energy. Distribution "A" is evidently more narrow than distribution "B". This seems intuitively related to the amount of "information" derived from performing the experiments. Applying equation (10) to these distributions, however, results in a value of  $\checkmark$  greater for "B" than for "A". This results



Figure 1. Vibrational distributions of different information content with respect to the prior distribution.

from both the averaging process and the use of the same prior distribution for both "A" and "B" which precludes point-by-point correspondence subject to equation (11).

The information as given by equation (10) can be made to exhibit predictive qualities subject to special conditions. In addition to normalization to satisfy equation (11), point-by-point correspondence must be imposed with respect to a fixed prior distribution. Use of a common prior distribution for different actual distributions enables identification of the width of a distribution with its entropy. This cannot be done in the example given because the product vibrational levels for "A" and "B" differ.

The functional form, or "class", of a distribution must also be specified. For a given class, the distribution sharpens as the information increases, subject to the conditions mentioned before. For complicated distributions, the turning points must also be specified. These occur where the slope of the surprisal changes sign. Simple distributions with one turning point are shown in Figure 2. The curve labeled "1" is the fixed prior distribution. As the curve number increases, so does the information via equation (10) and also the sharpness, or predictive quality of each distribution. All of the curves shown satisfy the constraints listed before and therefore exhibit a direct correlation between their information content and their predictive qualities.

For purposes of discussion, the class of a distribution is defined by the number of its turning points. Reactions



Figure 2. Probability distributions of increasing information content.

of the type  $H + BrC1 \rightarrow HC1 + Br$  exhibit bimodal rotational distributions, as discussed in reference 14. A typical bimodal distribution is shown in Figure 3. Also shown are the same data points arranged to form a one-peak distribution. Thus Figure 3 exhibits a Class 3 and a Class 1 distribution. For simplicity, the prior distribution is simply taken to be the reciprocal of the number of data points. It is evident that equation (10) is useless as a measure of predictive information to compare these distributions of different classes, since the same value of  $\mathcal{L}$  results from quite different physical results. It would be useful to find a function which is indifferent to the class of distribution while distinguishing among different physical results. In particular, a quantity is desired which measures the "structure" of a distribution.

A suggested candidate which measures the absolute deviation between the actual and prior distributions might be termed the "structural information", given by

$$\mathbf{d}_{s} = \ln \left[ \frac{|\mathbf{d}I/\mathbf{d}x|}{+1} \right]$$
(12)

Here the average value of the absolute surprisal slope is calculated with respect to an appropriate variable like fraction of energy in vibration,  $x = f_V$ , or rotation,  $x = f_R$ . Then

$$\frac{dI}{dx} = \frac{1}{n-1} \sum_{i} \frac{I(x_{i+1}) - I(x_{i})}{x_{i+1} - x_{i}}$$
(13)

where the sum runs over the n-1 intervals between the n data



Figure 3. Product populations of equal information content which represent different classes.

points. Equation (12) avoids the averaging process of equation (10), giving  $\mathcal{L}_s$  certain advantages over  $\mathcal{L}$ , although there are several mathematical properties satisfied by  $\mathcal{L}$  which do not apply to  $\mathcal{L}_s$ .

There are several useful features of the function  $\mathcal{A}_s$ . When the actual and prior distributions coincide, dI/dx = 0at each point and thus  $\mathcal{A}_{s} = 0$  which implies zero structure in a microcanonical distribution. If the actual distribution oscillates rapidly above and below a given prior distribution,  $\mathcal{L}_{c}$  can be quite large while the information,  $\mathcal{L}_{c}$ , may be quite small. Thus  $\boldsymbol{\mathcal{A}}_{s}$  is larger for the Class 3 distribution in Figure 3 than for the Class 1 distribution. The function  $\boldsymbol{J}_{\boldsymbol{z}}$ also has additivity characteristics due to the logarithm. Thus an experiment resolving both vibrational and rotational data can be described by two components of structure which can be summed to give a total measure of structure. It should be pointed out that calculating  $\mathcal{J}_{s}$  as a combined function of vibrational and rotational energies will give a number different from the sum of component values of  $\boldsymbol{\mathcal{A}}_s$ . This would, however, involve use of entirely different prior distributions which is not allowed according to the conventions cited earlier.

As an example of the property of additivity, consider experimental data consisting of detailed vibrational and rotational distributions. Let the vibrational distribution be characterized by the function

$$F_{V} = \left| \frac{dI(f_{V})}{df_{V}} \right| + 1$$
 (14)

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and the rotational distribution by

$$G_{R} = \left| \frac{dI(f_{R})}{df_{R}} \right| + 1$$
(15)

Then the complete vibrotational distribution may be characterized by

$$K_{V,R} = F_V G_R \tag{16}$$

The total "structural information" is then given by

$$\mathcal{L}_{s_{V}} = \ln K_{V,R}$$

$$= \ln F_{V}G_{R}$$

$$= \ln F_{V} + \ln G_{R}$$

$$= \mathcal{L}_{s_{V}} + \mathcal{L}_{s_{R}}$$
(17)

which illustrates the property of additivity due to the logarithmic definition of  $\mathcal{A}_s$ .

In the applications to follow, all experimental distributions to be analyzed are of the type Class 1 and thus may be handled subject to the conditions already discussed. The following chapter incorporates these conditions as a baseline for the analysis leading to a computational reaction model.

#### 2. SURPRISAL ANALYSIS

#### 2.1 Calculation of the Surprisal

To analytically describe and model the pumping distributions for reactions (I)-(VIII) the surprisals are now determined. The experimental rate coefficients, ie. the  $P_i$ , are those of references 6-8. The RRHO approximation is found to be quite sufficient for calculating the microcanonical, or prior, distributions  $P_i^0$ . For analytical simplicity, the prior distributions are calculated as functions of the fractional available energies in vibration, rotation, and translation, denoted  $f_V$ ,  $f_R$ , and  $f_T$  respectively. These quantities must therefore satisfy

$$f_V + f_R + f_T = 1$$
 (18)

for each reaction product distribution.

The fractional energies are determined with respect to the total energy available to the reaction products,

$$E_{total} = -\Delta H^{O} + E_{a} + \frac{3}{2}RT + RT$$
 (19)

The heat of reaction or exothermicity of the reaction is denoted "- $\Delta$ H<sup>O</sup>". This is added to the relative reactant translational energy,  $E_a + \frac{3}{2}$ RT, where  $E_a$  is the activation energy which must be overcome in order for each reaction to occur. Finally, an additional RT is available from the

internal energy of the incident diatomic molecule. It should be noted that these are molar quantities where the RT terms are the average thermal energies determined from statistical mechanics. Therefore the energy available in a particular molecular encounter may vary slightly about the statistical average per encounter.

The values of  $E_{total}$  for reactions (I)-(VIII) are given in Table 1.

Table 1. Total Available Reaction Product Energies

		REACTION		E <sub>total</sub> (kcal/mole)
F	+	$H_2 \rightarrow HF + H$		34.7
F	+	$D_2 \rightarrow DF + D$		34.4
Η	+	$F_2 \longrightarrow HF + F$		102.0
D	+	$F_2 \rightarrow DF + F$		103.0
Н	+	$C1_2 \rightarrow HC1 +$	C1	48.4
D	+	$C1_2 \rightarrow DC1 +$	C1	49.6
Η	+	$Br_2 \rightarrow HBr +$	Br	43.6
D	+	$Br_2^- \rightarrow DBr +$	Br	44.6

These values are approximate to typically 1-2 kcal/mole due largely to difficulties in determining the activation energy,  $E_a$ .

There are three forms of the surprisal of interest in this work, based on the prior distribution functions  $P^{O}(f_{V})$ ,  $P^{O}(f_{R})$ , and  $P^{O}(f_{T})$ . The development of these functions is given in some detail in reference 5, using the RRHO approximation to determine the density of product states at a particular fractional energy. The results are:

$$P^{O}(f_{V}) = \frac{5}{2}(1 - f_{V})^{3/2}$$
(20)

$$P^{O}(f_{R}|f_{V}) = \frac{3}{2} \frac{(1 - f_{V} - f_{R})^{1/2}}{(1 - f_{V})^{3/2}}$$
(21)

$$P^{o}(f_{T}) = c_{n} f_{T}^{1/2} (1 - f_{T})^{n}$$
(22)

The notation  $P^{O}(f_{R} | f_{V})$  denotes the prior distribution as a function of  $f_{R}$  once  $f_{V}$  is already specified. The coefficients  $c_{n}$  are given by

$$c_{n} = \frac{\Gamma(n + 5/2)}{n!\Gamma(3/2)}$$
(23)

where n = 1, 3, 4, and 6 respectively for products of the types A + BC, AB + CD, A + BCD, and AB + CDE. In this work all reaction products are of the form A + BC, so that n = 1.

The formulas (20)-(22) are smooth functions whose coefficients are determined by requiring the normalization

$$\int P^{0}(f_{x}) df_{x} = 1$$
(24)

This computation is not meaningful when dealing with quantized product levels. The forms of the prior distribution to be applied to reactions (I)-(VIII) are given as

$$P^{o}(f_{V}) = A(1 - f_{V})^{3/2}$$
(25)

$$P^{o}(f_{R}|f_{V}) = B \frac{(1 - f_{V} - f_{R})^{1/2}}{(1 - f_{V})^{3/2}}$$
(26)

$$P^{o}(f_{T}) = Cf_{T}^{1/2}(1 - f_{T})$$
(27)

where the coefficients A, B, and C are determined by the normalization of equation (11). This normalization facilitates physical interpretation of the surprisal distributions obtained from the experimental data.

The rotational surprisals,  $I(f_R) = -\ln P(f_R)/P^O(f_R)$ , for reactions (I)-(III) are shown in Figures 4-6. In developing the analytical model in the next chapter, the translational surprisals are found to be most useful and therefore only a few rotational surprisals are presented for descriptive purposes. The translational surprisals for reactions (I), (II), (III), (V), (VI), and (VII) are shown in Figures 7-12, respectively. Note that for each experimentally observed vibrational level there corresponds a rotational and translational surprisal distribution. The significance of the surprisals is discussed in the following section.

# 2.2 Comparison and Significance of the Surprisal Distributions

The complementarity of the rotational and translational surprisals is evident. The symmetry of the rotational curves with respect to each distribution maximum is reversed in the translational curves due to the relation

$$f_{T} = 1 - (f_{V} + f_{R}) = 1 - f_{internal}$$
 (28)

The translational surprisals are multi-peaked because the internal modes of energy are effectively lumped together when computing the prior distributions. The translational peaks for a given reaction are approximately equal in magnitude, however, due to the normalization of both the actual and prior rates for each vibrational level. The normalization thus has the desirable effect of removing the weighting effect of the vibrational distributions, which tend to be



Figure 4. Rotational surprisals for reaction (I).


Figure 5. Rotational surprisals for reaction (II).



Figure 6a. Rotational surprisals for reaction (III).



















Figure 10. Translational surprisals for reaction (V).







Figure 12. Translational surprisals for reaction (VII).

sharply peaked in the intermediate vibrational levels. This weighting effect would result in surprisal distributions of severely varying peak magnitudes and preclude meaningful physical interpretation. It would be mathematically produced by using the prior distributions given by equations (20)-(22) and neglecting the principle of point-by-point correspondence.

It is observed that the rotational surprisals have the same general form as the actual experimental rotational distributions. The actual distributions are the result of the particular combination of statistics and reaction dynamics peculiar to each reaction. The surprisal, however, is a quantitative measure of the deviation of the actual and statistical distributions. Therefore, in the surprisal, the "statistics" due to the density of available product states has been effectively subtracted from the actual distribution, leaving a distribution with principally dynamical information. This "subtraction," coupled with the logarithmic definition of the surprisal, results in relatively smooth curves of the same general form. The model developed in the next chapter identifies further statistical information peculiar to the dynamics of each reaction, now independent of the statistics already removed by calculating the surprisals.

There are two main features common to the surprisals shown in Figures 4-12. The first is the variation in the "widths" of the surprisals as functions of fractional vibrational energy. The width in each case is arbitrarily measured at I =  $\ln 2$ , where P =  $P^{O}/2$ . The units of surprisal

width are the dimensionless energies  $f_R$  and  $f_T$ . It is significant that the largest width systematically occurs in the intermediate vibrational levels, except for reaction (II). It is suspected that this exception occurs because of the uncertainty in the data presented in reference 6. The data for the second vibrational level "was determined with considerably less accuracy than the v = 3 and v = 4 levels due to a low signal-to-noise ratio." Furthermore, the v = 1 data was simply estimated. The model to be developed predicts a maximum width in the intermediate vibrational levels for reaction (II) and is used to generate rotational data for the product v = 1 level.

The second main feature of the surprisal distributions is the consistently skewed symmetry toward the high rotational (low translational) levels. There are generally a couple more J-levels found on the high rotational energy side of the most probable J-level (denoted  $\hat{J}$  or  $\hat{f}_R$ ). Coupled with the increased rotational level spacing at high energies characteristic of diatomic molecules, the effect is a pronounced asymmetry in rotational energy. The difference in rotational energy between  $\hat{f}_R$  and the value of the energy at I = ln2 is hereafter termed the surprisal "half-width". The notation " $\Delta$ " will refer to the "full-width" and " $\Delta_1$ " and " $\Delta_2$ " to the smaller and larger half-widths of each distribution, such that

$$\Delta = \Delta_1 + \Delta_2 \tag{29}$$

The full-widths in translational energy are shown for

reactions (I)-(III) and (V)-(VII) in Table 2.

Table 2. Translational Surprisal Full-Widths,  $\Delta(f_T)$ , at I = ln2

V-LEVEL										
REACTION	<u>1</u>	2	3	4	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>		
I	0.198	0.212	0.045							
ΙI	0.181	0.147	0.122	0.054						
III	0.036	0.048	0.065	0.068	0.064	0.068	0.030	0.017		
V	0.144	0.146	0.148	0.111						
VI		0.193	0.161	0.107	0.082	0.014				
VII	0.068	0.096	0.089	0.065	0.037					

An upper limit is automatically placed on each surprisal width due to the available rotational energy once a vibrational level is specified. For the lower vibrational levels of reactions (I)-(VIII) this upper limit in energy is much larger than the observed distribution widths. Restrictions from conservation of angular momentum account for the narrow range of observed product rotational energies. This is treated in some detail in reference 15. Physically, these restrictions are expected since the reactants must come close enough together to produce a reaction. This limits the impact parameter and therefore the range of initial angular momentum. A crude but illustrative calculation may be performed to approximate the magnitude of initial angular momentum as a function of impact parameter. This will lead into the discussion of reaction dynamics in the next chapter.

A simple parameter by which to visualize angular momentum in the reaction is the product rotational quantum number, J. In the rotational surprisals, data points at

 $f_R = 0$  correspond to J = 0 and subsequent data points correspond to J = 1, J = 2, etc. The angular momentum with respect to the center of mass of monatomic and diatomic reactants is given by

$$L = \mu v_{re1} b = h J (J + 1)^{1/2}$$
(30)

where  $\mu$  is the reduced mass of the reactants,  $v_{rel}$  is the relative velocity, and b is the impact parameter. A sample calculation for the H + F<sub>2</sub> reactant pair produces solutions for J for several values of the impact parameter, as shown in Table 3. The relative velocity is taken simply as the root mean square speed of a particle of reduced mass  $\mu$  at T = 300K. All reaction temperatures in this work are taken to be T = 300K unless otherwise specified.

Table 3. Initial Reactant Angular Momentum for Various Impact Parameters,  $H + F_2 \longrightarrow HF + F$ 

IMPACT PARAMETER "b"(A)	ANGULAR MOMENTUM QUANTUM NO. J*			
0.2	0.5			
0.4	1.3			
0.6	2.1			
0.8	2.9			
1.0	3.7			
1.2	4.6			
1.4	5.4			
1.6	6.3			
1.8	7.1			
2.0	7.9			

\* The fractional J-values shown are intended for descriptive purposes only.

For reaction to occur, as explained in reference 7, the impact parameter must be small. For reaction (III), the mean value of b is about 1.0Å. The maximum allowed b for this reaction to occur is about 2.0Å. It is evident from Table 3 that even for large values of the impact parameter, there is not enough initial rotational energy to excite very many J-levels in the product HF molecule. Theoretical work will be cited in the next chapter that indicates some correlation between the magnitude of the impact parameter and the final range of rotational level excitation. It may therefore be inferred that the small values of initial rotational energy are amplified by whatever process occurs within the reaction complex. Examination of this process is the subject of the next chapter.

## 3. A SEMI-EMPIRICAL MODEL TO CORRELATE TRANSLATIONAL SURPRISAL DISTRIBUTIONS

3.1 Review and Reinterpretation of Reaction Dynamics The surprisal distributions for reactions (I)-(VIII) are markedly similar, implying similarity in reaction dynamics. Particularly reactions (III)-(VIII) should exhibit similar dynamics due to the common monatomic hydrogen and diatomic halide reactants. In this section the fundamentals of reaction complex dynamics are reviewed and combined in such a way as to lead naturally to a statistical interpretation of the significant features of the surprisal distributions.

There are several features common to the experimental results for reactions (I)-(VIII) as outlined, for example, in reference 7. The products exhibit (a) relatively ineffcient vibrational excitation, (b) inefficient rotational excitation, and (c) not much increase in rotational excitation in successively lower vibrational levels. These effects are proposed in this work to be related to each other as described later in this chapter.

The inefficient conversion of available product energy into vibration can be explained via the "light-atom anomaly", as described in reference 14. This effect is pronounced in reactions (III)-(VIII), which involve a light attacking atom "A" incident on a heavy diatomic "BC". Each reaction may be

characterized by the degree to which the potential energy surfaces are "repulsive" or "attractive". Attractive surfaces produce energy release as the reactants A + BC approach each other. Repulsive surfaces produce energy as the products, AB + C, are separating. For reactants of approximately equal mass, the AB-C replusion occurs with the new A-B bond still extended. This is called "mixed energy release" on a repulsive surface. As a result, the repulsive energy produces large momentum of B and C, with consequent internal excitation of AB. In the case where A is very light compared to B and C, a "light-atom anomaly" may be encountered, if the surface is sufficiently repulsive in nature. Here the A atom approaches BC so rapidly that an AB bond effectively forms before the products can separate. With A and B close together, the B-C repulsion causes the AB product to recoil as a unit, producing large translational excitation but very little vibrational excitation. This light-atom effect will be used later to simplify model computations.

Low rotational excitation is particularly pronounced in reactions (III)-(VIII), due largely to the necessarily small initial orbital angular momentum as discussed in reference 7 and in the previous chapter. Although the impact parameter must remain small in order to insure reaction, there tends to be a correlation between its magnitude and the degree of product rotational excitation, as discussed in reference 16. In effect the energy release of the reaction may be thought of as amplifying the initial orbital angular momentum. This effect becomes more pronounced as the character of the potential

energy surface becomes more attractive. The more attractive reaction surfaces produce greater percentage rotational excitation, but also produce greater complexity in the reaction complex interaction. References 14 and 16-19 treat these effects and their implications in considerable detail, as summarized in the discussion to follow.

Larger degrees of complexity in the reaction complex interaction ultimately destroy smooth correlations between the impact parameter and the degree of rotational excitation. When the impact parameter is high and the potential energy surface is significantly attractive, there is a tendency for A to spiral in toward B and form AB with higher angular The three particles will spend a longer time tomomentum. gether on an attractive surface and therefore undergo multiple collisions with each other. The overall probability of reaction and the form of the product energy distribution become extremely sensitive functions of both the impact parameter and the initial energy. Thus molecular level variations about the ensemble average available energy may have significant effect on the form of the experimental product distributions.

The multiple collisions in the reaction complex fall into two general categories. A "clouting" encounter is typical of more repulsive surfaces and a "clutching" encounter is more probable for attractive surfaces. In the clouting encounter, atom A may spiral in toward B, begin to form a bond and induce rotational motion of the pair AB. The rotation brings A to a position where it "clouts" atom C before

the products separate. This collision tends to decrease the rotational energy possessed by AB as the products separate.

In a clutching encounter, atom A spirals in toward B as before, but the attractive surface induces reaction between A and C such that A is "clutched" by C away from B. This type of reaction is also termed a "migratory" encounter and tends to produce higher rotational excitation of the product AC. Clutching encounters also tend to destroy simple impact parameter correlations with product excitation.

A significant effect of both clouting and clutching secondary encounters is a tendency for the mean product vibrational energy to fall. Trajectory studies in the references cited show a definite correlation between this decrease and the degree to which secondary encounters occur. This drop in vibrational energy becomes especially significant as the attractive part of a potential energy surface is increased. The longer-lived and more complex the interaction becomes, implies transition to a statistical regime where correlations between initial and final states become too uncertain to allow for accurate dynamical study. In the limit of a truly long-lived complex, the dissociation of the A-B-C complex is governed by statistical considerations as explored in references 20-24. The product probabilities are then proportional to the amount of phase space accessible to the products as functions of internal and translational energies.

A primary consequence of the transition toward the statistical regime is a broadening of the product energy distributions. Energy lost from vibration must be transformed into some combination of rotational and translational energy. The evidence of low fractional rotational energy in low vibrational levels indicates that the primary conversion is to translational energy. The broadening is especially exhibited in the tails of the reported vibrational distributions toward low energies. These tails are also exhibited in the translational distributions, and in the rotational distributions with opposite symmetry. The degree of conversion to rotation is predicted in this work from statistical considerations later in this chapter.

A striking example of the effect of secondary encounters on the product distributions is presented in reference 16. Bimodal distributions in rotation for the lower vibrational levels are characteristic of the reactions

$$H + IC1 \longrightarrow HC1(v, J) + I$$
 (IX)

and

$$H + BrC1 \longrightarrow HC1(v, J) + Br$$
 (X)

The separation in the rotational peaks is especially pronounced for reaction (IX) and increases for both reactions as the vibrational level decreases. These reactions are examples of "microscopic branching" where the type of secondary encounter which occurs determines the domain of the reaction products.

The domain in low rotational energy evidently results from clouting encounters which tend to restrict product rotational energy. The high rotational energy domain results from migratory encounters following interaction with the monatomic product atom. It is significant that the separation in rotational domains is more pronounced in reaction (IX) than in reaction (X). This may be due quite simply to the size of the atoms involved, and hence the respective potential energy surfaces. The smaller size difference between the Br and Cl atoms evidently decreases the domain separation caused by the different types of secondary encounters. It is easily projected that the diatomic reactants of reactions (I)-(VIII) will exhibit even less separation, although the broadening effect will still occur.

In reviewing the surprisals of Figures 4-12, there is observed a correlation between the degree of asymmetry toward the high rotational levels and the magnitude of the attractive part of the potential energy surface. As described in references 25-27, the attractive percentage of the potential energy surfaces for reactions (III),(V), and (VII) is approximately 45%, 30%, and 45%, respectively. The balance of the percentage is primarily repulsive. It is observed that the surprisals exhibit considerably more asymmetry for reactions (III) and (VII) than for reaction (V). The larger attractive percentages result in more migratory encounters which produce the asymmetry.

A model incorporating the physical ideas presented in this section is now developed. Attempts are made to quantify

both the broadening effect of all secondary encounters and the degree of asymmetry of rotational distributions characterized by migratory encounters.

### 3.2 The Statistical Model

The discussion in Chapter 1 produced conditions under which the information content of a distribution, or conversely its entropy, takes on physical significance. The surprisal distributions in Figures 4-12 satisfy these conditions. Therefore the width of a given surprisal is directly related to the entropy of that distribution. As widths increase with respect to a fixed peak magnitude, so also does the entropy, corresponding to a lack of "predictive quality" in the data. An extremely important feature of the surprisals shown is the approximate equality in peak magnitudes for a given reaction, as discussed in the previous chapter. This enables comparison of translational surprisal entropies for each reaction, despite the lack of point-by-point correspondence as illustrated, for example, in Figure 2. If the peak magnitudes varied considerably, an analysis based on equation (12) would be necessary. Once making this straightforward connection between distribution width and entropy, a technique must be developed to predict the entropy of a distribution.

The fundamental assumption in statistical collision theory (references 20-24) is that the reaction complex is sufficiently long-lived to produce randomization between initial and final dynamical conditions. The product distributions are then basically microcanonical, although various

constraints may be invoked to add structure to the results. From the point of view of the reaction complex, the entropy of the product distribution is given by

$$H = \ln \Omega \tag{31}$$

where arOmega is the number of product states accessible from the complex.

If dynamical constraints are invoked, then some product states become more probable than others. Identifying the entropy, H, with the surprisal width,  $\Delta$ , the relation for this case becomes

$$\Delta = C \ln \Omega' \tag{32}$$

;

where  $\Omega'$  represents the constrained distribution of product states and C is a normalization constant to be determined empirically. The entropy was shown to increase positively with distribution width in Chapter 1. A simple linear relationship is assumed which will be shown to correspond to the experimental distribution widths.

Determination of the quantity  $\Omega'$  can be achieved by combining the dynamical ideas of the previous section. A schematic of the model is shown in Figure 13 which leads to a useful form for  $\Omega'$  and predictions of the distribution widths. (Hereafter the terms width and entropy as applied to product distributions are used equivalently.)

A three level product vibrational level distribution is used for simplicity in explanation. The physical example shown in Figure 13 also corresponds to the reaction (I)



Figure 13. Schematic of the reaction complex redistribution process.

product energy levels. As the reaction begins, a particular product vibrational energy becomes most probable depending on a given trajectory through the potential energy surface. This vibrational energy is characteristic of the initial A-B bond forming before any secondary encounters occur. The attractive part of the potential energy surface will produce initially high values of rotational energy by amplifying the initial orbital angular momentum. The secondary encounters then transform part of the vibrational energy into a mixture of rotation and translation. The strong repulsive part of the surface generates the majority of the translational energy and also causes a drop in rotational energy by the time the products are completely separated. This process is illustrated in Figure 13 by assuming that an initial reaction complex population forms with energy intervals of width  $\Delta$ ' centered about  $\hat{f}_{R}$  in each vibrational level. These populations in levels v = 2 and v = 3 are energy resonant with rotational levels diagonally below along the dashed lines. The actual quantum energy levels used for computation are those of the fully formed product diatomic molecule. The justification of this approximation to the very time-dependent energy eigenstates is the light-atom anomaly, which is quite applicable for reactions (III)-(VIII). Since both atoms of the reactant diatomic are identical, use of the product diatomic energy levels is proposed to be valid for both clouting and clutching encounters. In reactions of the types (IX) and (X) this would not be true. In reaction (IX),

for example, the HI energy levels would be quite different from the HC1 energy levels.

The secondary encounters are then assumed to mix the vibrational and rotational modes along the energy resonant diagonal lines. If the final encounter is clouting in nature, followed by repulsive release, populations in high rotational levels will effectively relax within a given vibrational level during the conversion to translational energy. If the final encounter is migratory, the A-C pair's rotational energy will be diminished by the B-C repulsion. This relaxation analogy is simply a descriptive summary of the reaction dynamics detailed in references 16-19. It is proposed in this work that the rotational energy relaxation in a migratory encounter takes place because repulsion occurs before A has time to rotate around C. The momentum contributed to C therefore opposes the rotational angular momentum imparted by the migration of A. The resulting decrease in product rotational energy is substantial, but evidently less than that produced by a clouting encounter. Instructive diagrams of these secondary encounters may be found in reference 19. The difference in rotational energy decrease produced by the two types of encounters is assumed in this work to account for the asymmetry of the significantly attractive reaction surface product distributions.

The reaction complex energy redistribution process is therefore assumed to take a path from vibration to rotation to translation. A simpler model based on a direct path from vibration to translation is analyzed in the next chapter and

is seen to be quite inferior to the present model in predicting the values of entropy for the reaction distributions of interest.

A given rotational distribution is assumed to be comprised of direct contributions plus population arriving as a result of the energy redistribution process. The v = 1population, for example, consists of molecules initially selecting that vibrational manifold, plus populations transferred from levels v = 2 and v = 3. Consider looking within the reaction complex from the energy point of view of the v = 1 level. The v = 1 product rotational entropy is dependent on the number of states ultimately accessible to that These states are assumed to be grouped within interlevel. vals of energy of width  $\Delta'$ , resonant in energy with the v = 2 and v = 3 initial vibrational populations. Each accessible state must be weighted, however, according to assumed constraints characteristic of the dynamics of the secondary encounters. The functional form of the weighting factors must be assumed and then tested via equation (32) against the measured surprisal entropy values.

The assumed form for the weighted number of states available to contribute to the entropy of a particular distribution is

$$Q'(v) = \sum_{\substack{\text{selected} \\ J-\text{levels}}} (2J + 1) P(E_{V-R}) e^{-\delta E/\alpha kT}$$
(33)

Here the sum runs over the J-levels found within each interval  $\Delta$ ' which is resonant with higher vibrational levels, as depicted in Figure 13.

The coefficient 2J + 1 is the degeneracy of each rotational level, ie., the number of separate quantum states allowed in each J-level. The quantity  $P(E_{V-R})$  is the arbitrarily chosen nascent vibrational distribution. It turns out that the results are not qualitatively affected by the specific form of this distribution. A convenient choice for the nascent vibrational distribution is the experimentally observed product distribution. When the model is coupled with an algorithm (to be developed in the next chapter), this choice of distribution produces favorable results in generating the full set of reaction rate coefficients. It would be expected that the redistribution process would greatly transform the nascent distribution as it progresses toward the final vibrational distribution. When the final vibrational data is normalized, however, the numerical differences between nascent and final distributions fall within experimental error. This was tested in detail when using the model to generate the reaction (III) rate coefficients.

Each state is also weighted by a factor  $e^{-\delta E/\alpha kT}$  which gives the effective probability of rotational to translational energy exchange. The temperature is taken as 300K and the quantity  $\delta E$  is the energy difference (see Figure 13) between the reaction complex rotational level and the peak of the rotational distribution in a given vibrational level. This is a simplification compared to the actual case of a variable energy distance between a selected rotational level in the resonant manifold and the multitude of allowed final J-levels.

The quantity  $\alpha$  is empirically determined to match the actual with the predicted distribution entropy values. The value of  $\alpha$  is interpreted as a measure of the magnitude of the effectiveness of the redistribution process produced by the secondary encounters characteristic of a particular reaction. The exponential form is used by analogy with collisional relaxation processes involving fully formed molecules. In particular,  $\alpha$  is analogous to the reciprocal of the constant quantity C<sub>2</sub> used by Polanyi and Woodall in reference 28 for HF collisional rotational relaxation,

$$P_{\hat{J}}^{J} = C_{1} \exp(-C_{2} \delta E/kT)$$
(34)

where

$$\delta E = E_{T} - E_{\hat{T}}$$
(35)

The process within the reaction complex is assumed to be analogous to collisional relaxation because of the apparent progression of energy from vibration to rotation to translation resulting from secondary collisional encounters.

Combining equations (32) and (33) for future reference produces the general form for prediction of distribution entropy as a function of vibrational level:

$$\Delta(v) = C \ln \left\{ \sum_{\substack{\text{selected} \\ J-1 \text{ evels}}} (2J + 1) P(E_{V-R}) e^{-\delta E/\alpha kT} \right\}$$
(36)

### 4. APPLICATION OF THE MODEL TO HYDROGEN HALIDE PRODUCT DISTRIBUTIONS

# 4.1 Prediction of the Entropy and Asymmetry of Product Distributions

Equation (36) is now used to predict the translational distribution entropy values for reactions (I)-(III) and (V)-(VII), for comparison with experimental data. Arguments will be made in the next chapter to enable prediction of the entropy values for reactions (IV) and (VIII). The translational distributions are chosen for quantitative analysis because the corresponding prior distributions are computed by considering vibration and rotation as simply components of the internal energy. This approach is in accordance with the model just presented which postulates mixing between vibrational and rotational energies, prior to release of translational energy.

To make use of equation (36) a matrix of the molecular product rotational levels is arranged as shown schematically in Figure 13 in the last chapter. The energy levels are computed according to the spectroscopic data in reference 11. The peak of each surprisal distribution is taken as the energy about which approximately resonant states are selected in lower vibrational levels. This peak is usually, but not necessarily, the most populated rotational level within a given vibrational level. The surprisal peak might

occasionally be shifted slightly from the population peak depending on the functional form of the prior distribution. The nascent vibrational distribution,  $P(E_{V-R})$ , is applied as a weighting factor to each state found along the diagonal resonance. The values of the rotational peaks,  $\hat{J}$ , and the nascent distributions,  $P(E_{V-R})$ , are listed in Table 4, shown on the next page. The values are given for each populated vibrational level for each reaction.

A somewhat arbitrary choice must be made for the magnitude of the energy interval,  $\Delta$ ', which determines the number of approximately resonant states contributing to the distribution entropy. The value is chosen to correspond roughly to twice the full-width of the most narrow translational surprisal of each reaction. The most narrow surprisal is always found in the highest observed vibrational level which, according to the model, receives no entropy contribution from the energy redistribution process. The population in this level therefore results only from molecules initially selecting that vibrational manifold. Twice the width of this population is then centered on the surprisal peak energy and rotational levels are located within this range along the resonant diagonals, as illustrated before in Figure 13. The intervals chosen for reactions (I)-(III) and (V)-(VII) in units of cm<sup>-1</sup> are 1100, 1200, 1100, 1000, 1000, and 1000, respectively.

Using the data appropriate for each reaction and applying equation (36) produces the entropy predictions from the model shown in Table 5 and Figures 14 and 15. In the figures,

Rotational Distribution Maxima and Nascent Vibrational Populations Table 4.

<u>V-LEVEL</u> *	∞I			3/0.28				
	7			6/0.42	6/0.42			
	اں			7/1.00		7/0.05		
	νI			06.0/7		16/0.26	5/0.20	
	4		5/0.72	7/0.51	10/0.06	17/0.89	6/0.98	
	<b>س</b> ا	2/0.47	9/1.00	8/0.33	11/0.92	19/1.00	7/1.00	
	2	7/1.00	11/0.71	7/0.19	13/1.00	21/0.37	8/0.13	
	<u>N</u>	7/0.32	13/0.29	7/0.15	14/0.27		9/0.02	
	REACTIC	Ι	II	III	7	١٧	ΝIΙ	

\* For each reaction and vibrational level, the values of  $\hat{J}$  and  $P(E_{V-R})$  are denoted as  $\hat{J}/P(E_{V-R})$ .



Figure 14. Predicted (triangles) and experimental (circles) values of the translational entropy for reactions (V) and (VI).



Figure 15. Predicted (triangles) and experimental (circles) values of the translational entropy for reactions (III) and (VII).

the small circles represent experimental surprisal entropy values and the triangles are the predictions from equation (36). The convention of circles corresponding to observed data will be maintained throughout this work. The coefficient, C, in equation (36) is empirically determined by matching the largest observed and predicted translational entropy values, except for reaction (II) where the entropy values for v = 2 are equated. The exception is taken because the model predicts a maximum in entropy for v = 2 in reaction (II). This is the only case among the reactions studied where there is not accurate experimental data for the lower vibrational levels.

Table 5. Translational Surprisal Full-Widths,  $\Delta(f_T)$ , at I = ln2

V-LEVEL\*

#### REACTION

I 0.198/0.208 0.212/0.212 II 0.181/0.117 0.147/0.147 0.122/0.131 \* For each reaction and vibrational level, the values of  $\Delta_{obs}$  and  $\Delta_{pred}$  are denoted as  $\Delta_{obs}/\Delta_{pred}$ .

The normalization chosen results in relative predictions of translational entropy. The value of C is a constant for a given reaction. It should be noted that the model predicts translational entropy values for each vibrational level up to, but not including, the highest experimentally observed level. Therefore for reactions (I), (II), (III), and (VI) there is no comparison with the highest observed v-levels. For reactions (V) and (VII), a nominal value for  $P(E_{V-R})$  has been assigned to the vibrational level just above the highest one observed, in order to compare a reasonable number of data points. For reactions (I) and (II) this assignment is not justifiable since the v = 4 and v = 5levels, respectively, are not energetically accessible.

Each set of predicted data corresponds to the value of the adjustable parameter,  $\alpha$ , which generates entropies corresponding most closely to the observed values. This optimum value of  $\alpha$  was easily determined in each case except for reaction (II), and is identified for each reaction in Figures 14 and 15. Although an optimum for reaction (II) was not found, the value  $\alpha = 6$  identified for reaction (I) produces a maximum translational entropy for v = 2. This is a prediction of the model which remains to be experimentally verified since the data for the v = 1 distribution was only projected by extrapolation in reference 6.

In general, the optimum value of  $\alpha$  is determined by locating the minimum in the standard deviation function,  $\sigma = \sigma(\alpha)$ , where

$$\sigma^{2} = 1/N \sum_{v=1}^{\infty} \left[ \Delta(v, \alpha)_{\text{predicted}} - \Delta(v, \alpha)_{\text{observed}} \right]^{2} \quad (37)$$

Here the sum runs over the translational entropy data points corresponding to each v-level in a given reaction. In reaction (III), for example, calculation of equation (37) for the five lowest vibrational levels results in a pronounced minimum at  $\alpha$  = 14, as shown in Figure 16.

As described previously,  $\alpha$  is a measure of the



Figure 16. Standard deviation between predicted and experimental translational entropy values as a function of the parameter  $\alpha$  for reaction (III).
effectiveness of the reaction complex interaction in redistributing energy modes. Large values of  $\alpha$  will cause resonantly selected rotational states to contribute more to each distribution entropy. A large number of strongly contributing states will tend to make this statistical interaction dominant over miscellaneous dynamical effects. Therefore it is expected that reactions with many interacting vibrational modes will produce entropy values closely matching the results predicted by the model. This is indeed the case as a good correspondence between observed and predicted values is evident for reactions (V) and (VI) while excellent correspondence is noted for reactions (III) and (VII). The large energy separation in vibrational levels which tends to destroy a smooth statistical model is thus offset by a large number of v-levels mixing rapidly in the reaction complex.

The relationship between  $\alpha$  and C is shown in Figure 17 for reaction (III). The curve exhibits the necessary decrease in C in order to match the observed data, as  $\alpha$ increases. Large values of  $\alpha$  produce increasing contributions to the entropy from more distant vibrational levels. The smooth functional relationship exhibited coupled with the small but negative slope, dC/d $\alpha$ , for large  $\alpha$ , will be utilized in the next chapter for predicting unknown translational entropy values.

A significant observation can be made relating the  $\circ$ **P**timum value of  $\alpha$  to the total available energy of a



Figure 17. Relationship between the value of the reaction constant C and the parameter  $\alpha$  for reaction (III).

reaction. The values of  $E_{total}$  for those reactions in which an optimum value of  $\alpha$  could be determined are listed in Table 6.

Table 6. Total Available Energies Compared with Optimum Values of the Parameter  $\alpha$ 

REACTION	E <sub>total</sub> (kcal/mole)	a
I	34.7	6
VII	43.6	9
V	48.4	9
VI	49.6	8
III	102.0	14

A correspondence between  $E_{total}$  and  $\alpha$  is readily observed. Reactions exhibiting high available energy will have correspondingly strong secondary encounter effects in the reaction complex. These stronger interactions will facilitate greater interchange among the vibrational, rotational, and translational energy modes. Thus the value of  $\alpha$ , which measures the probability of interaction among distant energy levels, is anticipated to increase with increasing  $E_{total}$ .

As an aside, it should be noted that the energy intervals prescribed for the various reactions are arbitrary, although related to each reaction's minimum translational surprisal width. Contrary to the ease of determination of an optimum value of  $\alpha$ , there is usually no such optimum  $\Delta$ '. As long as  $\Delta$ ' is chosen large enough to select several rotational levels, but small enough to prevent interval overlap, various values will prove acceptable. As an example,

the predicted and observed entropy values for reaction (III) at  $\alpha$  = 14 are shown in Figure 18 for three different energy intervals. The quantity,  $\Delta E$ , is given simply by  $\Delta E = \Delta'/2$ . It is apparent for this case that only minor fluctuations in the results develop from variations in  $\Delta'$ .

A significant feature of the surprisals is their asymmetry toward the higher rotational levels. This asymmetry is particularly pronounced for reactions (III) and (VII) which exhibit significantly attractive potential energy surfaces, compared with reactions (V) and (VI) which are more repulsive in nature. The degree of asymmetry can be modeled using the ideas already developed.

The assumed energy path in the reaction complex is from vibration to rotation to translation. The transition or relaxation probability from rotation to translation is given by the exponential factor in equation (36). Suppose that the reaction complex is at some point along one of the resonant energy diagonals. Relaxation to the high rotational levels in the final distribution will be more probable than to lower J-levels. Specifically, the probabilities of transition to the half-width points are required. These are the two translational energies on either side of the surprisal maximum such that I = ln2. If the surprisal distribution is approximately triangular in shape, ie., given by the maximum and the two half-width points, then the ratio of the half-widths gives a measure of the ratio of the populations on either side of the maximum. This ratio should correspond, according to the model,



Figure 18. The effect of varying the energy interval which selects interacting energy levels within the reaction complex for reaction (III).

approximately to the ratio of transition probabilities to the half-width points.

The transition probability from a diagonal state of rotational energy  $E_0$  to a low rotational level of energy  $E_1$  is given by

$$P(E_0 \longrightarrow E_1) = \exp \left| -(E_0 - E_1) / \alpha kT \right|$$
(38)

where the value of  $\alpha$  is the optimum for a given reaction. Specifying the energy of a high rotational level in the same vibrational level as  $E_2$ , the ratio of transition probabilities to these levels is

$$\frac{P(E_0 \rightarrow E_1)}{P(E_0 \rightarrow E_2)} = \frac{\exp\left[-(E_0 - E_1)/kT\right]}{\exp\left[-(E_0 - E_2)/kT\right]} = \exp\left[-(E_2 - E_1)/\alpha kT\right] (39)$$

If  $E_1$  and  $E_2$  are the rotational energies of the half-width points, then  $E_2 - E_1 = \Delta$ , and the ratio of half-widths is predicted to be

$$\frac{\Delta_1}{\Delta 2} = e^{-\Delta/\alpha kT}$$
(40)

where the units of  $\Delta$  are chosen so as to make the exponent dimensionless. A further refinement to this simple model would take into account the difference in degeneracies between low and high J-levels. This would manifest itself by adding statistical weights to rotational levels within the final distribution in addition to those along the energy diagonals. This degree of complexity is unwarranted, however, since the purpose of this work is to develop a statistical model as simple as possible that adequately determines the product distributions.

A comparison of the predicted and actual ratio of half-widths for reaction (III) is shown in Figure 19, with  $\alpha$  = 14. The data corresponds reasonably well with this simple approach, although the best match occurs with  $\alpha$  = 11. The same technique was applied to reaction (VII) with less quantitative success, because the surprisals cannot be well approximated by simple triangular distributions. This destroys the simple correlation between the transition probabilities to the half-width points and the product population on either side of the surprisal maximum. The model does, however, qualitatively predict the reaction (VII) half-width ratios.

4.2 An Alternate Model to Predict Distribution Entropy Values

The model already described has been shown to accurately account for the entropy of translational product distributions. Assuming a reaction complex redistribution of energy, a more simple but reasonable path is directly from vibration to translation (V-T). After all, the final distributions are restricted to low fractions of available rotational energy. If a V-T interaction model could be made to account for distribution entropy values, there would be no need to postulate high intermediate rotational states along the resonant energy diagonals of Figure 13.

The same general approach as before is taken where the entropies are predicted by  $\Delta = C \ln \Omega'$ , where  $\Omega'$  represents the number of product states viewed from the initial



Figure 19. Predicted (triangles) and experimental (circles) values of the translational surprisal half-widths for reaction (III).

stages of the reaction complex. The energy intervals are chosen such that three rotational levels in each vibrational level are selected, specifically the rotational peak level with one on each side. This represents a uniformly broad nascent rotational population, as before, while the nascent vibrational population,  $P(E_{V-T})$ , weighted according to the values,  $P(E_{V-R})$  as given before in Table 4.

The significant difference in the V-T approach lies in the rotational level degeneracies. Since the interaction between the vibrational levels is restricted to very much the same rotational levels, there is no need to assign the 2J + 1 coefficient when summing selected product levels. Therefore the weighted number of product states is given by

$$\boldsymbol{\Omega}'(\mathbf{v}) = \sum_{\substack{\text{nascent} \\ J-\text{levels}}} P(E_{V-T}) e^{-\boldsymbol{\delta} E / \boldsymbol{\alpha} k T}$$
(41)

where the sum is over the rotational levels selected by the energy intervals in all vibrational levels above v. The energy difference between the peak rotational level in v and each selected rotational level above is denoted as  $\delta E$ . The values of  $\delta E$  are generally very close to those values in equation (33). Since  $P(E_{V-T}) = P(E_{V-R})$  in each case, the only essential difference between equations (41) and (33) is the degeneracy, 2J + 1. This difference is quite significant, however, as shown in Figure 20. The example taken is reaction (III) with  $\alpha = 25$ . For smaller values of  $\alpha$ , the predicted entropy values form even more narrow distributions. There is in fact no value of  $\alpha$  which



Figure 20. Vibration to translation reaction complex interaction model results for translational entropy values of reaction (III).

produces entropy predictions close to the observed values.

The low values of predicted entropy are due to the lack of contribution from states in distant vibrational levels. Here the exponential factor is dominant, thereby restricting interaction to nearby levels. In the vibration to rotation to translation (V-R-T) model, the more distant v-levels contribute significantly because of the resonant equivalence to high rotational levels, and a correspondingly high coefficient 2J + 1. It is observed that to bring the entropies for v = 6 and v = 7 in Figure 20 up to the observed values would require such a large value of  $\alpha$  that the data for the low v-levels would be random. Therefore the V-T approach is rejected in favor of the V-R-T model, which is not only dynamically reasonable, but also produces entropy values close to the empirically observed data.

## 5. PREDICTION OF REACTION RATE COEFFICIENTS

## 5.1 Development and Application of an Algorithm to Generate Rate Coefficients

In this section, an algorithm is developed to regenerate the reaction (III) rate coefficients based on the entropy and asymmetry predicted by the V-R-T model for each translational distribution. The purpose of this development is to provide a reliable method of prediction for isotopically related reactions for which there is no experimental data. In Section 5.2, this algorithm is applied to predict the full vibrotational distributions for reactions (IV) and (VIII) which are isotopic in hydrogen with respect to reactions (III) and (VII), respectively.

For most vibrational levels, the translational surprisals for reaction (III) can be approximated by a quadratic function for the low rotational levels,  $f_T > f_T(J)$ , and by a linear function for the high rotational levels,  $f_T < f_T(J)$ . This choice is of course somewhat arbitrary, and is taken simply as empirical information. Therefore, for large values of  $f_T$ , the coefficient m is determined such that

$$I - I(J) = m \left[ f_{T}(I = 1n2) - f_{T}(\hat{J}) \right]^{2}$$
(42)

where  $I(\hat{J})$  is the value of the surprisal maximum and the two values of  $f_T$  are taken at the half-width point and the surprisal maximum, respectively. The value for I is chosen to be ln2 to correspond to the half-width point for the low rotational levels.

The value of  $f_T(\hat{J})$  is taken empirically for reaction (III) and the value of  $f_T(I = \ln 2)$  is determined by knowing that

$$\Delta_1 + \Delta_2 = \Delta = C \ln \Omega'$$
(43)

and

$$\Delta_1 / \Delta_2 = e^{-\Delta/\alpha kT}$$
(44)

Combining equations (43) and (44) gives

$$\Delta_1 = \frac{\Delta}{1 + \exp(\Delta/\alpha kT)}$$
(45)

and

$$\Delta_2 = \frac{\Delta}{1 + \exp(-\Delta/\alpha kT)}$$
(46)

Thus for large  $f_T(small f_R)$ ,

$$f_{T}(I = 1n2) = f_{T}(\hat{J}) + \Delta_{1}$$
 (47)

The peak value of the surprisal,  $I(\hat{J})$ , must be predicted in order to make the technique as general as possible. It is observed that each product rotational distribution has a total population roughly proportional to the width times the height of the distribution. This is a reasonable approximation for distributions which are close to triangular in shape. Therefore the peak population can be expressed by

$$P(\hat{J}) = \frac{\gamma P(v)}{\Delta}$$
(48)

where  $\gamma$  is fixed to normalize the largest value of  $P(\hat{J})$ for the entire vibrotational distribution to unity.

From the definition of the surprisal,

$$P(f_T) = P^{O}(f_T)e^{-I(f_T)}$$
(49)

where the product distribution sums to unity for each vibrational level. To compare with experimental data, this normalized distribution must be multiplied by whatever factor was originally used as a normalizing divisor. Thus

$$P(f_T | v) = K(v)P^{o}(f_T | v)e^{-I(f_T | v)}$$
(50)

where

$$K(v) = \sum_{T} P'(J|v)$$
(51)

is the normalizing factor representing the sum of rotational level populations for each v-level, P'(J|v), as presented in the experimental literature. In effect the process in converting experimental distributions to surprisals has been reversed.

The result for the surprisal maximum is then

$$I(\hat{J}) = -\ln\left[\frac{P(\hat{J})}{KP^{0}(\hat{J})}\right] = -\ln\left[\frac{\gamma P(v)/\Delta}{KP^{0}(\hat{J})}\right]$$
(52)

For values  $f_T < f_T(\hat{J})$ , the distribution is simply approximated as a straight line through the points  $[f_T(\hat{J}), I(\hat{J})]$  and  $[f_T(\hat{J}) - \Delta_2, I = 1n2]$ . Using these linear and quadratic approximations to the translational surprisals, the predicted product distributions for reaction (III) can be generated. The quantized values of translational energy are identified with specific vibrational and rotational levels as shown in Figure 21. As before, the small circles represent the experimental data of reference 7. Note the especially accurate data prediction for the first five vibrational levels. From Figure 15, these are the levels for which the model predicts translational entropy most accurately.

The same technique was applied to reaction (VII) with somewhat less quantitative success due to the greater functional complexity of the translational surprisals.

5.2 Rate Coefficient Prediction for the Reactions D +  $F_2 \rightarrow DF$  + F and D +  $Br_2 \rightarrow DBr$  + Br

The technique developed in the previous section is now applied to reactions (IV) and (VIII) for which there is no experimental vibrotational product data. Several assumptions must be made and justified in applying the statistical model and algorithm to these reactions. The vibrational product distributions must be predicted, along with the location of the peak of each rotational distribution. The translational entropies can be predicted by equation (36) and used with the linear-quadratic surprisal form to generate the rate coefficients.

The vibrational distributions for isotopically similar reactions often exhibit the same form. The vibrational surprisals for reactions (I) and (II), for example, are nearly collinear, as reported in reference 29. The linearity of these surprisals indicate that the distribution



Figure 21a. Predicted (triangles) and experimental (circles) relative rate coefficients for reaction (III).



Figure 21b.

is characterized by just one constraint, namely the mean product vibrational energy. The similarity in surprisals is expected due to the similarity in reaction potential energy surfaces. The main difference lies in the quantization of vibrational energy, determined by the different masses of the hydrogen isotopes.

The vibrational surprisal for reaction (III) is shown in Figure 22, where the prior rates have been calculated by equation (25). The surprisal is not entirely linear but is assumed to be isotopically independent. Since Polanyi obtained the reaction (III) rate coefficients of reference 7, improvements in the values of the Einstein A coefficients have been cited by Herbelin and Emanuel in reference 30. Modifications to Polanyi's data would involve some decrease in the product v = 7 and v = 3 levels. This decrease would cause a smaller decrease in the corresponding surprisal values, and would not remove the non-linearity. The circles represent the HF product levels and the triangles are the predicted DF values. Note the closer vibrational level spacing for DF compared to HF. Using the predicted surprisal values, the DF vibrational distribution is generated by

$$P(v) = K'P^{o}e^{-I(f_V)}$$
(53)

where K' is determined such that the largest value of P(v) is unity. This normalization is the conventional one as given, for example, in reference 7.



Figure 22. Vibrational surprisal for reaction (III) (circles) with interpolated values for reaction (IV) (triangles).

The resulting DF product vibrational distribution (triangles) is compared with the HF data (circles) in Figure 23. The HF data represents v = 1-8 and the DF data represents v - 1-10.

The vibrational distribution predicted for reaction (IV) is then used as the weighting function,  $P(E_{V-R})$ , to predict the translational surprisal entropies. In generating  $\Delta$ (v) for reaction (III) the values for  $\alpha$  and C used in equation (36) were determined empirically. This of course cannot be done for reaction (IV). Since  $\alpha$  measures the strength of the secondary encounters in the reaction complex and has been shown to be related to the total available energy, it is assumed to be isotopically independent. This is reasonable for reactions (III) and (IV) since the potential energy surfaces must be similar in form and the values of  $E_{total}$ are approximately the same. Furthermore, the optimum values of  $\alpha$  for the isotopic reactions (V) and (VI) are nearly the same.

A smooth functional relationship exists between  $\alpha$  and C as shown earlier in Figure 17. It has also been observed that dC/d $\alpha$  is small and negative for large values of  $\alpha$ , particularly in the neighborhood of  $\alpha$  = 14, the optimum value for reaction (III). Therefore the parameter C, directly tied to  $\alpha$ , is also assumed to be isotopically independent. The values of the reaction (IV) translational entropies are presented as the triangles in Figure 24. Also shown are the reaction(III) entropies (circles). The squares represent



Figure 23. Experimental vibrational population for reaction (III) (circles) with predicted values for reaction (IV) (triangles).



Figure 24. Experimental entropy values for reaction (III) (circles) with predicted values for reaction (IV) (triangles and squares).

reaction (IV) entropies where the value of C is not assumed isotopically independent, but is fixed by normalization with respect to the reaction (III) data. This comparison illustrates the statistical differences between the HF and DF vibrational and rotational energy levels.

A significant prediction of the model, assuming isotopically independent values for C and  $\alpha$ , is larger translational entropies for the heavier isotope reactions, where the vibrational levels are more closely spaced. The closer spacing facilitates energy interchange among the modes present in the reaction complex. From the statistical point of view, the closer spacing produces a higher density of states leading to greater product entropies. Evidence for this prediction is observed in Figure 14, where the DC1 product entropies range significantly higher than the HC1 values.

The value of  $f_T(\hat{J})$  must also be predicted for reaction (IV). There has been shown in reference 31 an isotopic independence between reactions (I) and (II) for the function  $\hat{f}_R(f_V)$ . This independence is also assumed for reactions (III) and (IV) with results shown in Figure 25. The circles represent reaction (III) data where the simple curve is broken by one data point at v = 3. The open circle at v = 3 corresponds to J = 8. The solid circle at v = 3 corresponds to J = 7 and falls on the curve relating the rest of the data. The predicted DF data (triangles) are placed on the curve at the proper quantized values of vibrational energy. The significance of the curve in Figure 25 is in the increased



Figure 25. Maximum surprisal values for reaction (III) (circles) and interpolated values for reaction (IV) (triangles) as a function of fractional vibrational energy.

rotational energy of the most populated J-level as the available rotational energy,  $1 - f_v$ , increases.

In generating the rotational distributions, it is assumed that only one rotational level beyond each halfwidth point is significantly populated. This provides a reasonable cut-off in accordance with the surprisals based on experimental data. The full vibrotational distribution for reaction (IV) is shown in Figure 26.

It is assumed that the same arguments involving parameter isotopic independence can be applied to reactions (VII)-(VIII). The translational entropies for the DBr products are predicted in comparison with the predicted DF values in Figure 27. The DBr entropies are seen to be substantially larger than the HBr values in Figure 14. The predicted rotational distributions for reaction (VIII) generated by the technique developed in this chapter are shown in Figure 28. Less confidence should be attached to the reaction (VIII) data than to the reaction(IV) data because the simple linear-quadratic surprisal approximation does not work as well in the former case.

The model is also applied to the v = 1 rotational distribution of the reaction (II) which was not measured accurately according to the discussion in reference 6. The translational entropy was determined for this level using the optimum value,  $\alpha = 6$ , characteristic of reaction (I). The algorithm was applied as before, using the weighting factors and translational surprisal peaks taken from the experimental



Figure 26a. Predicted relative rate coefficients for reaction (IV).



Figure 26b.



f<sub>R</sub>

Figure 26c.



Figure 27. Predicted translational entropy values for reactions (IV) and (VIII).



Figure 28a. Predicted relative rate coefficients for reaction (VIII).



Figure 28b.

data for the product levels v = 2-4. The predicted rotational distribution is shown in Figure 29.



Figure 29. Predicted relative rate coefficients for v=1 of reaction (II).

## 6. APPLICATION TO NON-REACTIVE INELASTIC COLLISIONS

The information theory approach to reaction product distributions has been developed in detail for vibrationally and rotationally inelastic collisions, as in references 31 and 32. The general case of simultaneous vibrational and rotational relaxation is treated in reference 33. The reaction type of interest is given as

$$AB(v,J) + X \longrightarrow AB(v',J') + X$$
(XI)

The prior rate for this reaction is proportional to the total density of states of the system. The result derived in reference 33 may then be given as

$$P^{O}(E_{V}, E_{J}, E_{V}, E_{J})$$

$$= C' \exp \left[ f(\Delta E) / kT \right] (2J' + 1) \left( \left| \Delta E \right| / 2kT \right) e^{\left| \Delta E \right| / 2kT} K_{1} \left( \left| \Delta E \right| / 2kT \right) \right]$$
(54)

where  $K_1$  is the first order modified Bessel function of the second kind. The degeneracy of the initial rotational level is incorporated into the normalization constant C', since J remains unchanged for all final levels. The function  $f(\Delta E)$  is given by

$$f(\Delta E) = 0 \quad \text{if } E_{V} + E_{J} \ge E_{V}, + E_{J},$$
  
=  $\Delta E \quad \text{if } E_{V} + E_{J} < E_{V}, + E_{J},$  (55)

The total energy difference is

$$\Delta E = (E_V + E_J - E_V, - E_J,)$$
(56)

The usefulness of the analytical surprisal approach depends on the availability of experimental data. For example, in reference 33 linear surprisals of approximately equal slope are generated for collisions of I, with several monatomic species. This equivalence of surprisals leads to predictions of inelastic product distributions of  $I_2$  with atomic species for which there is no experimental data. In chemical laser modeling, inelastic product distributions for the HF molecule are necessary. Detailed relaxation data is available from trajectory calculations given in reference 34. The uncertainty in this data is quite large and the range of allowed product J' levels exhibits apparently arbitrary cutoff points. For example, in the case v = 3, J = 2, and v' = 2, the product rotational population lies in the range J' = 10-15. The energy resonance point,  $\Delta E = 0$ , lies between J' = 13 and J' = 14. The data points also exhibit no distribution symmetry for the various cases listed.

A characteristic feature of the inelastic surprisals in references 31-33 is their linearity as functions of the total energy difference. This has been reported for several different diatomic molecules and collision partners. Insight may be gained with respect to HF collisional relaxation if the corresponding surprisals are also assumed to be linear. The surprisal form is then given by

$$I = -\ln(P/P^{O}) = \lambda_{O} + \lambda \Delta E/kT$$
 (57)
Therefore

$$P = C'' P^{O} e^{-\lambda \Delta E / kT}$$
(58)

where the surprisal intercept,  $\lambda_0$ , is absorbed by the normalization constant C", which is determined to satisfy equation (11).

Results for the HF case where v = 3, J = 8, v' = 2, and J' = 0.17 are shown in Figures 30-33. Several positive and negative values of  $\lambda$  are selected and the data is presented in terms of both the total energy difference and the product rotational level. The initial level J = 8 is the most populated within the v = 3 manifold for reaction (III), as reported in reference 7. The energy resonance,  $\Delta E = 0$  lies between J' = 15 and J' = 16 in the v' = 2 level. The curves labeled  $\lambda = 0$  represent the prior distribution,  $P^{O}$ , given by equation (54). For the values of  $\lambda$  shown, the temperature is taken to be 300K. It is evident from equation (58) that varying the parameter  $\lambda$  is completely equivalent to varying the temperature in the inverse manner. Thus the condition

 $\lambda$  = 0.3 and T = 1800K is completely equivalent to the condition  $\lambda$  = 0.05 and T = 300K.

The parameter  $\lambda$  , formally given by

$$\lambda = kT \partial I / \partial (\Delta E)$$
 (59)

is described in reference 31 as a differential measure of the deviation of the actual rate from the prior rate. The magnitude of  $\lambda$  is a measure of the structure of the linear



Figure 30. V-R relaxation probability versus total energy difference.



Figure 31. V-R relaxation probability versus product J-level.

•



Figure 32. V-R relaxation probability versus total energy difference.



Figure 33. V-R relaxation probability versus product J-level.

Class 0 surprisal distribution, as described in Chapter 1. When  $\lambda = 0$ , all final states are equally probable and the prior distribution is the result. As  $\lambda$  becomes increasingly negative, as shown in Figure 30, the products populate increasingly distant energy levels. In this case the vibrational energy loss goes mostly into translation, at the expense of rotation. Negative values of  $\lambda$  are common to the highly exothermic reactions (I)-(VIII), as shown, for example, by the surprisal slope in Figure 22 for reaction (III).

Positive values of  $\lambda$  denote a tendency for the product population to cluster about  $\Delta E = 0$ , as shown in Figure 32. If Wilkins' data is accurate with respect to the allowed product rotational range, a positive value for  $\lambda$  of the order of 0.3 could be used to characterize the distributions. Recent experiments performed by J. J. Hinchen on the HF v = 1 to v = 0 transition, indicate a fairly fast relaxation by collision with other HF molecules, with a slight product excess population near  $\Delta E = 0$ . Although specific data is not available, indications from his experiments (reference 35) are favorable for the use of linear surprisals with positive slopes in modeling vibration to rotation relaxation mechanisms. The curves labeled  $\lambda = 0.05$  in Figures 32 and 33 might therefore be quite reasonable approximations to the product populations for the HF v = 3 to v' = 2 collisional transition at T = 300K. Verification of these proposals awaits accurate experimental data. The exact form of the experimental distributions is required if a statistical model, as described earlier, is to be employed.

## 7. SUMMARY AND CONCLUSIONS

The information theory approach to reaction product distributions develops correlations among large sets of experimental data points. The approach is used to discover and quantify similarities in the experimental results for several different reactions. The quantity of interest is the information content of a product distribution which is directly related to its entropy. The physical significance of the information is dependent on the symmetry of product distributions. Constraints must be identified which determine when the value of the information is useful as a measure of confidence in predicting the outcome of additional experiments. A proposed quantity termed the "structural information" is defined for use when product distributions of different classes are to be compared. This quantity is a function of the surprisal, which quantifies the difference between experimental and statistical product distributions. The structural information measures the absolute value of the derivative of the surprisal function, thereby quantifying structure in a distribution of arbitrary symmetry.

The transformation from experimental to surprisal distributions, subject to various constraints, produces distributions of like symmetry for the hydrogen halide exothermic

reactions. This circumstance allows analysis in terms of the entropy, rather than necessitating use of the structural information. A significant feature of the surprisal distributions as functions of translational energy is the approximate equality of the maxima for a given reaction. This feature, coupled with the identification of like symmetry, allows direct correspondence between the entropy and width of each translational surprisal distribution.

Other significant features of the surprisals include the variation of translational entropy as a function of product vibrational energy, and the degree to which the surprisals are asymmetric toward low translational (high rotational) energies. These features are related qualitatively to theoretical and experimental work done in reaction dynamics since 1966 by several researchers. The dynamical principles characteristic of the hydrogen halide reactions may be combined with the fundamental assumption of statistical collision theory to produce a model which predicts reaction product entropy values. These predictions compare favorably with the experimental values. The model predicts values most accurately for those reactions which involve the greatest number of product vibrational levels. It is proposed that the secondary encounters characteristic of these reactions, are directly responsible for the specific variation of the product translational entropies as functions of vibrational energy. The effects of the secondary encounters are most pronounced when a reaction is characterized by a large

value of total available energy,  $E_{total}$ . It is therefore not surprising that the model predicts results most accurately when the underlying mechanism, namely secondary encounters in the reaction complex, is most pronounced.

The model is quantified for comparision with experimental data by means of an adjustable paramter,  $\alpha$ . The value of  $\alpha$  is proposed to be related to the amount of interaction of product energy states within the reaction complex. This interaction via secondary encounters is dependent on the value of  $E_{total}$ . It is therefore expected that  $\alpha$  should increase as  $E_{total}$  increases. This correspondence has been demonstrated for those reactions where accurate data is available.

The asymmetry of the translational product distributions is proposed to be determined by the same dynamics, and to be most pronounced when the secondary encounters are substantially attractive in nature. This has been demonstrated quantitatively for the H +  $F_2 \rightarrow HF$  + F reaction which exhibits quite large attractive characteristics. The predicted asymmetries and distribution widths are incorporated into a simple algorithm which generates predicted relative rate coefficients for each vibrational level. The algorithm is applied to the H +  $F_2 \rightarrow HF$  + F reaction, and the predicted values compare favorably with the experimental data. The algorithm predicts the rate coefficients for the rotational levels most accurately when the predicted distribution widths are most accurate. Other differences between experimental and predicted values are due largely to the simplicity of the algorithm itself.

The model also predicts distribution widths for two reactions which have not been studied in detail experimentally. Several assumptions must be made in using these predictions in the algorithm to generate the full vibrotational distributions. It is significant that the model predicts greater distribution entropy values for the DF, DC1, and DBr products than for the HF, HC1 and HBr products, respectively. In the case of DC1 and HC1, this is also observed experimentally. According to the model, this is due to the close vibrational level spacing of the heavier isotope diatomics which results in more energy states contributing to the product entropy values. The larger translational entropies imply a greater range of rotational levels found in each product vibrational level. This prediction can be tested further only by future experiments.

The information theory approach has also been applied by several researchers to collisional relaxation processes. When relaxation surprisal functions assume simple forms, especially linear or quadratic functions, large sets of data can be reduced to a small set of parameters. This can be useful in chemical laser modeling. If no experimental data is available for a particular process, a surprisal function may be assumed based on results from similar processes. Assuming linear surprisals, several possible product distributions can be generated, simply by varying the slope of the surprisals. Trajectory calculations

by Wilkins and recent experiments by Hinchen on vibration to rotation relaxation processes in HF, indicate collisional transition primarily to near resonant energy levels. This type of distribution is easily modeled by linear surprisals with positive slopes. As before, these predictions await the results of future experiments.

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