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Invited Paper

Chemical Reaction Dynamics—The Study of Molecular Reactivity and Disequilibrium

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Recent progress in molecular reaction dynamics is discussed with special reference to the selectivity in the reactivity and the specificity in product formation. Topics considered in some detail include dynamical aspects of stereochemistry, rotational state distributions in reactive collisions and intramolecular dynamics of larger molecules. The conceptual foundations of the thermodynamic-like approach to molecular disequilibrium are considered.

1. Introduction

On the molecular level, a chemical reaction occurs when atoms or groups of atoms rearrange themselves so as to result in a new configuration. The process can be intramolecular as in a unimolecular isomerization in the gas phase. It can be intermolecular as in a bimolecular reaction. It can involve several species as in a reaction in a liquid which may require some reorganization of the solvent molecules or as in a reaction catalysed by some surface site. Chemical reaction dynamics[1-15] seeks to understand the motions which occur during the chemical reaction. It asks what are the primary factors which govern these motions. When some understanding has been achieved it seeks to apply the new concepts. The question then becomes which factors are under our experimental control and how can we best manipulate these factors so as to influence the outcome of the chemical reaction on the molecular level.

It is the study of reactions on the elementary level of the isolated chemical act which makes dynamics distinct from its older sister, chemical kinetics. An example will perhaps best serve to illustrate the point. Chemical kinetics studies reactions under bulk conditions. In general, we find that increasing the temperature of the reagents will often increase the reaction rate. This general observation is also correct for example for the reaction

$$H_2 + OH \rightarrow H_2O + H$$

which is of importance in combustion.[16,17] The very concept of 'the temperature of the reagents' is a macroscopic one valid under special bulk conditions when the rate of the chemical reactions is slow as compared to the rate of inelastic energy transfer, collisions. One can then assume that the rapid inelastic collisions maintain the system in a state of thermal (but not chemical) equilibrium. For rapid chemical reactions and particularly so for very exothermic reactions, one typically needs to add to the mixture an excess of buffer gas whose role is to rapidly dissipate any deviations from equilibrium. In a real combustion process, the reagents will often be in marked deviation from thermal equilibrium. We are then faced with the need for dynamics for the following reason. As long as the reagents are in thermal equilibrium there is only one way of changing their energy and that is by heating the system. Temperature is the only relevant factor. Increasing the temperature leads to an increase in the energy content of each degree of freedom of the reagents. At higher temperatures we have the classical 'equipartition' result that each degree of freedom has an energy of $(1/2)RT$ where R is the gas constant ($\simeq$2 cal deg^{-1} mol^{-1}). At low temperatures, the energy content of the vibrational degrees of freedom will be somewhat below the classical value but can be readily computed, if need be, from equilibrium statistical mechanics. The key point is that for chemical kinetics, temperature is the only relevant operational variable for governing the distribution of the reagents over their different energy states (which are electronic, vibrational, rotational, and translational). One cannot selectively increase, say, the vibrational energy content of the reagents. Thermal heating is a democratic process where every degree of freedom receives on equal footing.

Once we need to deal with reagents not in thermal equilibrium, the required understanding changes in an essential way. One will now have to consider different ways in which the energy of the reagents can be changed. Putting a given amount of energy into the relative motion of the reagents (so that they collide with a higher relative velocity) need not change the rate of the reaction to the same extent as putting the same amount of energy in the vibrational excitation. Indeed, there are two modes of vibrational motion, that of H_2 and that of OH. We now know that vibrational excitation of H_2 is much more conducive to reaction than that of OH[18] and we have an interpretation of that selectivity based on the nature of the forces that operate during the collision.[19] One can consider many other types of selectivity. Even for our simple example, recall that OH is a radical with a lone electron in a p orbital. This orbital can be

aligned in space. Equally, OH as a rotating diatomic molecule has a plane of rotation. The p orbital can lie within that plane (a, so called, Π^- state) or be perpendicular to it (a Π^+ state). Are the two states equally reactive? My guess is that the Π^+ state is much more reactive. Much more so than the slight energy difference between the two states (Π^- is lower in energy) would suggest. As far as I know, there is not yet a definite answer but I am fairly certain about my intuitive guess. Yet another selectivity concerns the angle of approach. What is the optimal orientation for the molecular axes of H_2 and OH for reaction to take place. Here too, chemical intuition would lead one to expect that not all orientations are equally reactive and such stereoselectivity[10] can again be related to the nature of the forces during the reactive collision,[20] Fig. 1.

Chemical reaction dynamics is concerned not only with reagents in selected states. Equally of interest is the probing of the state of the products. Of course, this need be done immediately after the reactive collision prior to any secondary collisions. Otherwise the subsequent collisions will rapidly equilibrate the products. In chemical kinetics we characterize the reaction as, say, exothermic. In chemical dynamics we need to know in which modes of motion the excess energy will be found in the receeding products of the reaction. Historically, it was often experimentally easier to probe the products than to select the reagents. Hence much of our initial evidence came from product's analysis.[4] It should however be stressed that the two are obverse to one another. This can be best seen by considering microscopic reversibility as in the following analogy: Imagine a movie showing the motion of the atoms during the collision of the reagents. Repeat the movie many times by using reagents in different energy states. Sometimes, the collision will end up in a reaction having taken place. Other times, the reagents will separate, the collision being nonreactive. Say most of the reactive collisions originated from vibrationally excited reagents. Now run all those movies backwards. Those reactive collisions are now seen to preferentially produce vibrationally excited products. (Recall that for a reactive collision, the roles of reagents and products is reversed when the movie is run in the opposite direction in time). Hence, if the reaction of $OH+H_2$ proceeds preferentially from vibrationally excited H_2 molecules, the reverse reaction, that of $H+H_2O$ will preferentially produce vibrationally excited H_2 products.

It is important to bear in mind that dynamics studies not only scalar quantities such as energy but also vectors such as momenta. Indeed, one of the earliest questions asked in molecular reaction dynamics is what is the disposal of the momentum of the

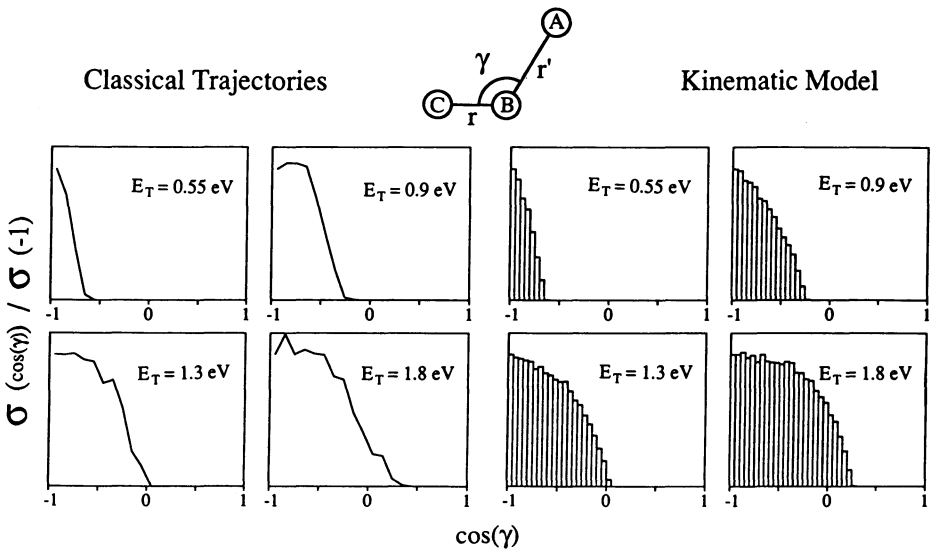

Fig. 1. An example of stereoselectivity. The reactivity in the $D+H_2 \rightarrow DH+H$ elementary reaction as a function of the angle of approach γ of the D atom to the axis of the H_2 molecule (see insert). Left panels: The reactivity computed using the method of classical trajectories[1] at a number of collision energies. Note how the 'cone of acceptance' for reaction opens up at higher collision energies. [For further details, see I. Schechter and R. D. Levine, *Int. J. Chem. Kinet.*, **18**, 1023 (1986)]. Right panels: The reactivity computed using a simple model where reaction takes place if the reactants can cross the barrier for reaction at the angle γ. [For further details, see I. Schechter, M. Prisant and R. D. Levine, *J. Phys. Chem.*, (1987)]. The success of the model shows that the cone of acceptance is governed primarily by the dependence of the height of the barrier to reaction on the angle of approach.

products. In particular, what is the direction of this momentum. To examine the question in detail we need to bear in mind that the motion of the systems' center of mass is unchanged during a chemical process in the gas phase. Hence it is the relative motion that we are really concerned with. So the issue is whether the (relative) momentum is distributed isotropically in space (suggesting that the collision has no memory of any preferred direction as would be the case for a long living collision complex), or not. One of the early indications of nonrandom dynamics was the observation that for many elementary reactions, the angular distribution of the products was strongly anisotropic indicating a very direct, brief process. It was indeed awhile before clear-cut examples of longer-duration reaction processes were discovered.[21] Nor is the study of products' angular distribution usful only for pure gas phase processes. Consider, for example, a beam of molecules incident on a surface at a given angle is the scattering mostly specular, with the angle of scattering about equal to the angle of incidence or is there a wide distribution in scattering angles? The latter is evidence for a trapping-desorption process where the scattered molecules spend some time at the surface prior to their 'evaporation' from the surface.

The study of the orientation dependence of chemical reactivity[10] also belongs to vector dynamics. More recently, the correlation amongst different vectors is also receiving much attention,[22,23] Fig. 2.

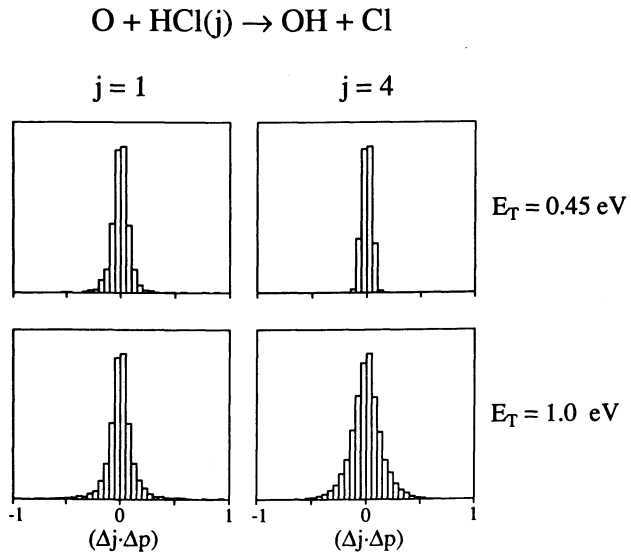

Fig. 2. Angular momentum correlations in the O+HCl→OH+Cl reaction. **Δj** is the change in the rotational angular momentum (**j** of OH minus **j** of HCl). **Δp** is the change in the linear momentum (momentum of the Cl–OH motion minus momentum of the O–HCl motion). The plot is vs. the scalar product of the unit vectors $\Delta\hat{\mathbf{j}}=\Delta\mathbf{j}/|\Delta j|$ and $\Delta\hat{\mathbf{p}}=\Delta\mathbf{p}/|\Delta p|$. The figure shows that for most collisions that result in reaction **Δj** is perpendicular to **Δp**. This need *not* be the case in general and can be shown due to the lighter mass of the exchanged H atom. (I. Schechter and R. D. Levine, to be published).

Experiments will typically select the reagents before the collision and/or probe the products after the collision. Theory is needed to bridge between these two ends. In their infancy are new experiments which use spectroscopic techniques to monitor the very process of the reactive collision.[24] Here, however, the need for theory is even more acute.

A generation ago, when I began work, the number of theorists actively interested in the field was so small that I could summarize everything I knew in one volume.[25] Less than ten years later two volumes were needed[26] and four volumes were required for a 1985 survey of the theory.[9] It is therefore no longer possible to overview the wide range of theoretical activity in the field. Instead, I have chosen to very briefly discuss one particular approach with which I have been closely associated.

2. The Distribution of Final States

Figure 3 shows the fraction of the total energy, E, carried by a CH_3 group as kinetic energy when an energy rich $Cd(CH_3)_2$ molecule dissociates.[27] The balance of the energy is in the other Cd–CH_3 bond and we have a distribution because a given total energy E can be partitioned in many different ways between the two bonds. Seemingly, the distribution is very asymmetic with the CH_3 group departing preferentially with either very little or with most of the available energy. Yet the theoretical analysis[27] suggested that

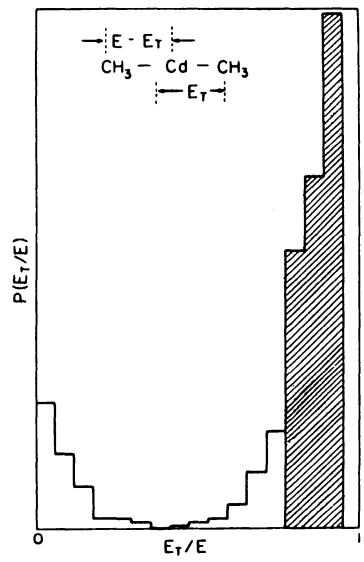

Fig. 3. The distribution of kinetic (E_T) and internal ($E-E_T$, see insert) energies in the dissociation of energy rich $Cd(CH_3)_2$.[27] The shaded region are those dissociating molecules where enough energy is taken by the dissociating CH_3 that $CdCH_3$ is stable.

this is *not* an example of specific energy disposal. Rather, this is what one should expect in the absence of specific effects. A uniform distribution, say, would have been much more surprising. It is not the shape of the distribution *per se* which one takes as evidence of specificity. What then is a disequilibrium distribution?

To answer this question we consider the complementary one: What is an equilibrium (or equipartition) distribution? The answer has been known in thermodynamics for a long time. At a given total energy, equilibrium is when all final quantum states are equally probable. It will take too much time to show that for the system of Fig. 3, the equilibrium distribution in kinetic energy E_T is [27]

$$P(E_T|E) \propto [E_T(E-E_T)]^{-1/2}, \tag{1}$$

which is indeed highly asymmetric. Instead, we consider a simpler case, say the products of the 'simplest' chemical exchange reaction

$$H + H_2 \rightarrow H_2(v=0,j) + H.$$

Here v and j are the vibrational and rotational quantum numbers of the product H_2 molecule. If the total energy is not too high only H_2 molecules in the ground vibrational state (i.e., $v=0$) can be formed. Of course, if reaction readily takes place then there need be enough energy to overcome the barrier along the reaction path.[28] In the products this energy is distributed between the rotation of H_2 about its center and the kinetic energy E_T of the motion of the H atom and the H_2 molecule. If we had to deal only with the H_2 molecule, the computation would be real simple: When H_2 is in the j'th rotational state it corresponds to $2j+1$ distinct quantum states. These correspond to the $2j+1$ distinct orientations in space of the angular momentum vector **j**. Another way of saying this is that a single rotational quantum state of a diatomic molecule is specified by two quantum numbers j and m_j and m_j can take up all integer values from $-j$ to $+j$ inclusive, i.e., $2j+1$ distinct values. When H_2 is in the rotational state j it has a rotational energy, E_j, which at lower j's is given by

$$E_j = Bj(j+1), \tag{2}$$

where B is the rotational constant. The energy which is then available for translation is $E_T=E-E_j$. The higher is the rotational energy of H_2, the less kinetic energy is available for the (relative) motion of H and H_2. Now the translational motion is also quantized. Just as for rotation, the larger the momentum **p**, the more quantum states are accessible. Since however the translational energy is, for all practical purposes, continuously varying, one typically speaks not of the number of such states but of their density, $\rho(E_T)$. It is defined so that there are $\rho(E_T)\delta E_T$ quantum states when the translational energy is confined to the short interval from E_T to $E_T+\delta E_T$. One shows that[1]

$$\rho(E_T) = A_T(E_T)^{1/2}, \tag{3}$$

where A_T depends on the mass. For the $H+H_2$ reaction we thus have that the density of final quantum states at the total energy E is

$$\begin{aligned}\rho(j,E) &= (2j+1)\rho(E_T) \\ &= A_T(2j+1)(E-E_j)^{1/2}\end{aligned} \tag{4}$$

At low j values, the dominant variation of $\rho(j,E)$ with j is the linear increase with j. As j increases, E_j increases even faster, (cf. (2)) and sooner or later E_j becomes a large fraction of E (Of course, $E_j \leq E$). When that happens, the square root term in (4) becomes rapidly variable and $\rho(j,E)$ decrease and becomes zero at $E_j=E$.

When the reaction is non-specific in its energy disposal we expect that the fraction $P^o(j)$ of H_2 product molecules in the state $(v=0,j)$ be proportional to $\rho(j,E)$

$$P^o(j) = (2j+1)(E-E_j)^{1/2}/\sum_j (2j+1)(E-E_j)^{1/2} \tag{5}$$

The denominator in (5) is simply there to insure normalization, i.e., that H_2 be found in some final j state

$$\sum_j P^o(j) = 1. \tag{6}$$

In both (5) and (6), the value of j is restricted by the

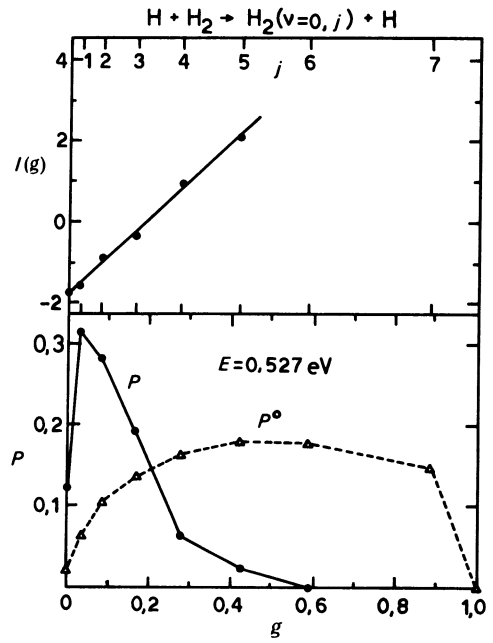

Fig. 4. Specificity of energy disposal. Bottom panel: Quantum mechanical computations (dots, from Ref. 29) and prior distribution (triangles, from Eq. 5) for the product H_2 rotational states vs. the reduced variable $g=E_j/E$. The two are quite different showing that lower rotational states are specifically populated by the reaction. Upper panel: The rotational surprisal, Eq. 7 vs. g. The line corresponds to $\theta_R=8$.

conservation of energy in a single collision, i.e., $E_j \leq E$.

How well does our equilibrium result (5) agree with the observed (or computed[29-32]) results? Not very well. Higher j values, as seen in Fig. 4 are far less probable than their fraction as given by (5). The reaction clearly selectively populates the final rotational states.

One can readily provide also an essentially quantitative characterization of the deviance from equilibrium. As in thermodynamics proper, a system can fail to reach complete equilibrium if it is subject to constraints. A simple example is compressed gas in a cylinder which is constrained from expansion by a piston which is firmly in place. If we free the piston, the gas will expand until its pressure equals the external pressure. A constraint can maintain a system in disequilibrium. This state of disequilibrium is really very simple to characterize: but for the constraint, the system is in equilibrium.

We find that precisely the same holds for disequilibrium in single collisions. The one difference is that the constraint(s), if any, is due to the preparation of the initial state and to the dynamics. The unexpected finding is that the dynamics gives rise to rather simple constraints. To see this, we shall return to the example of the $H+H_2$ reaction, and many others, in section 4.

As in thermodynamics proper we shall characterize the fraction of molecules in any given state by the chemical potential. This means that we regard the H_2 molecules in different quantum states as different and distinct chemical species. This give rise to no essential problem for it is known that a distinct chemical species is any molecule that can be distinguished from others and there are numerous spectroscopic and other methods whereby H_2 molecules in different rotational states can be sorted out. Even the $2j+1$ degenerate m_j states can be distinguished (e.g., by a Stern-Gerlach type experiment). Finally, the different orientations of the momentum $\mathbf{p}$ of the relative motion of H and H_2 can be studied by measuring the angular distribution of the products. Indeed, even in conventional, macroscopic thermodynamics it is sometimes useful to regard molecules in different states as distinct species.[33] Here however we are concerned with the nascent products of a single collision. We discuss the thermodynamics of a single collision in section 3 returning to our main theme in section 4. The reader willing to accept thermodynamic concepts can proceed directly to section 4.

3. Thermodynamics of Collision Processes

A single collision is a system of very finite number of degrees of freedom. Not only finite but often quite small (e.g., six for the three atom H_3 system, including the rotation). There is therefore a question of principle: Are we allowed to use thermodynamics for such a system? Is thermodynamics not a theory or systems of very many degrees of freedom? We have devoted considerable attention[33-38] to this question. Our starting point was information theory,[39] Thereby we have been able to extend the usual machinery of thermodynamics to small dynamical systems. Finally, we have been able to show[37,38] that exact quantum dynamics can be formulated as a thermodynamical theory. We shall return to this point in section 5 below.

The thermodynamical approach to dynamics that we have pioneered enables us to provide a dynamical justification to the procedures discussed section 4. One can wonder however, why do textbooks emphasize the 'large size' of thermodynamics systems. To clarify this point we need to discuss two conceps from probability theory. Since this is a point that many people are concerned about we would like to clarify it in some detail. We do this since the ideas are simple and the source of the confusion is semantic, that is the failure to properly distinguish between two, strictly distinct, concepts.

In the application of thermodynamics to finite, isolated systems it is essential to properly distinguish between the probability of an event (which is what is provided by the theory) and the frequency of an event (which is what is measured in an experiment). As an example we examine the most familiar example, that of tossing a coin. Take an honest coin. We assign a probability of 1/2 to each face. Let us call the two faces A and B. Now let us do an experiment-one tossing of the coin. Say the results is that face A is up. In our experiment the frequency of 'event A' is one and the frequency of 'event B' is zero. The frequency and the probability are quite distinct and both are well defined. Now consider another experiment: The coin is tossed twice. A possible outcome is that the coin fell 'face A up' in the first toss and 'face B up' in the second toss. In this experiment the frequency of 'event A' is 1/2 and so is the frequency of 'event B.' In this experiment the *numerical value* of the frequencies and the probabilities is the same. *However, an equally likely* outcome in our experiment is that the coin fell 'face A up' in both tosses. Then the numerical values of the frequencies and the probabilities would be quite different. Let us now toss the coin three times. A moment's reflection shows that whatever the outcome is, there is just no way for the *observed* frequency in such an experiment to be numerically equal to the *theoretical* probability. Indeed, it rapidly emerges that for any experiment where the coin is tossed an *odd* number of times, the frequency cannot equal the probability! The coin is but the simplest example. Take an honest die with six distinct but equivalent faces. The probability of each face coming up is 1/6. Unless we roll the die $6n$, n integer, times we will *never*

observe frequencies equal to the probabilities. Even if we do roll the die $6n$ times, there is no guarantee that all six faces will show up with exactly equal frequencies. In the great majority of all possible experiments with a die, the experimental frequency is not exactly equal to the probability.

Frequency and probability are thus two, quite distinct, concept which differ not only in their definition but also in their possible numerical values. What then gives rise to the confusion? The blame is on the law of large numbers. This theorem, very loosely stated, says that upon very many repetitions of an experiment, the observed frequencies will have numerical values very close to the theoretical probabilities. Hence the pragmatic result that the numerical value of the probability of an event can be determined as its frequency observed in a very large number of independent repetitions of the experiment. It must clearly however be understood that what the law of large numbers provides is a practical route to the assignment of a numerical value to the probability.

The purpose of the theory is to predict and explain observed results. What the law of large numbers tells us is that for the purpose of comparing observed frequencies with theoretical probabilities we require many repetitions. This is automatically insured if we carry an experiment on the distribution of H_2 rotational states on a macroscpic gaseous sample. Such a sample contains the order of Avogadro's number of molecules. We are thus assured that the observed frequency will be very close to the theoretical probability. The necessary conditions for the validity of the law of large numbers can also however be insured if the experiment is on the H_2 rotational state distribution after a single, isolated $H+H_2$ reactive collision. All that is necessary is that one observes many reactive collisions, each one isolated from the others. The experimenter knows this very well for if too few collisions are observed, the signal will not rise above the noise. The theorist is equally aware of this point on the pragmatic level. An instructive illustration is provided by the very common method — that of the study of the dynamics using classical trajectories.[40] Each one classical trajectory has a definite outcome. To simulate the inherent quantal uncertainty in the initial conditions and the resulting distribution of final states one needs to compute 'many' classical trajectories. How do we know how many is 'many'—by increasing the number of trajectories until the frequencies of the final states settles down to within the desired tolerance.

As a side comment we note the following implication. The method of classical trajectories is very extensively applied. However, as our experiments are reaching for higher and higher resolution we need to run more and more classical trajectories to achieve the corresponding computational resolution. We are already at a level where so many trajectories need be computed that fully quantal methods will soon become computationally more feasible!

4. Surprisal Analysis

As in thermodynamics, we characterize the observed distribution of products in terms of its deviance from a reference. Since we are typically dealing with collisions at a given value of the total energy, the typical reference is that of all final quantum states being equally probable. As discussed in section 2, one seldom fully resolves the final quantum states. Hence one needs to count the number of final states that correspond to the event of interest. For the $H+H_2 \rightarrow H_2(v=0,j)+H$ reaction we have performed the count in section 2 leading to Eq. (5) for $P^o(j)$, the reference or *prior* distribution of H_2 rotational states. We denote by $P(j)$ the actual, observed distribution. The corresponding thermodynamical potential known in this context as the *surprisal* is defined by

$$I_j = -\ln[P(j)/P^o(j)], \tag{7}$$

or

$$I_j = \ln[P^o(j)] - \ln[P(j)]. \tag{8}$$

Figure 4 shows a plot of I_j vs. the rotational energy of the H_2 molecule for a quantum mechanical computation of $P(j)$.[29-31] As is very clear, I_j is linearly dependent on E_j

$$I_j = \theta_o + \theta_R(E_j/E). \tag{9}$$

θ_o and θ_R are two constants, but θ_o is a function of θ_R as can be seen by combining (8) and (9)

$$P(j) = P^o(j) \exp(-\theta_o - \theta_R(E_j/E)). \tag{10}$$

Here $P^o(j)$ is given by (5) and since

$$\Sigma_j P(j) = 1, \tag{11}$$

it follows from (10) that θ_o can be computed from θ_R

$$\exp(\theta_o) = \sum_j P^o(j) \exp(-\theta_R(E_j/E)). \tag{12}$$

Hence the distribution of rotational states is fully characterized by the value of one (intensive) parameter, θ_R.

As in ordinary thermodynamics, one can use either θ_R or the corresponding (extensive) parameter, the mean value, $\langle E_j \rangle$,

$$\langle E_j \rangle = \sum_j E_j P(j), \tag{13}$$

of the rotational energy of the H_2 molecules. Since at a given total energy E, we have $E_j \leq E$, it is advantageous to work with the dimensionless reduced parameter $g \equiv E_j/E$ which spans the range from zero to

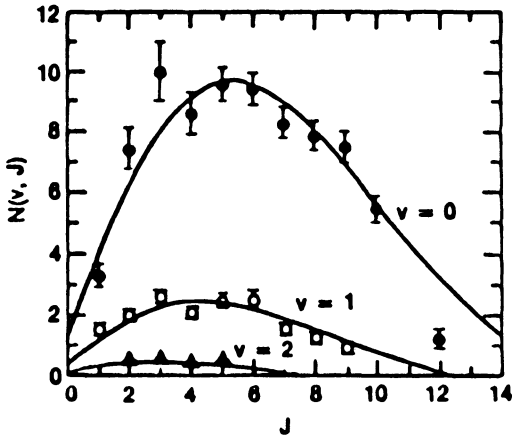

Fig. 5. The observed (points with error bars, from Ref. 41) HD vibrotational populations in the $H+D_2$ reaction using hot H atoms and the fit (curves) to the data using the functional forms (10) and (18) with a prior distribution given by (15). Note that the population scale is linear.

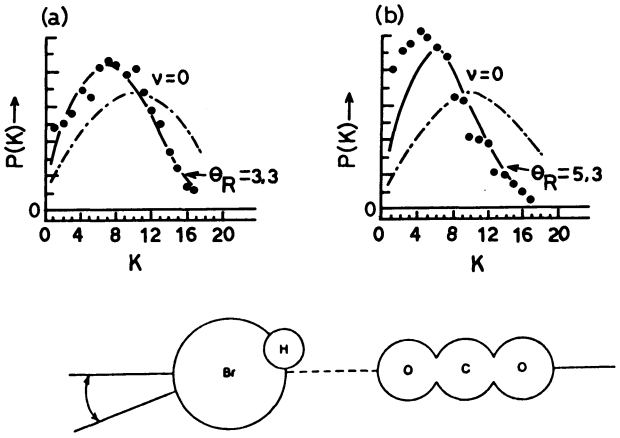

Fig. 6. The OH(v=0) rotational state distribution from the $H+CO_2 \rightarrow HO+CO$ reaction: (a) For a random approach; (b) For a geometry limited approach. Points are experimental data from Ref. 44. The line is Eq. 10 and the dashed line is the prior distribution. K is the OH rotational quantum number. The insert shows the principle of the geometry limited experiment. The $CO_2 \cdot HBr$ van der Waals adduct is photolyzed to yield hot H atoms. The angle of the HBr axis with respect to the CO_2 axis is largely confined to within the range indicated by a (weak, van der Waals) bending potential. Upon photolysis of HBr the H atom approaches CO_2 preferentially collinearly.

one. From (13) and (12) we see that there is a one-to-one relation between $\langle E_j \rangle / E$ and θ_R,

$$\langle (E_j/E) \rangle = \sum_j (E_j/E) P^o(j) \exp(-\theta_R(E_j/E)) / \sum_j P^o(j) \exp(-\theta_R(E_j/E)). \quad (14)$$

If $\theta_R > 0$ the population of the higher rotational states is below that expected on prior grounds and the value of $\langle E_j \rangle / E$ computed from (14) is below the value computed for $\theta_R = 0$ which is the prior limit. If $\theta_R < 0$, the higher rotational states are preferentially populated.

This distribution (10) provides an accurate fit for both quantal and classical computations[29-32] of product H_2 rotational distributions. More recently[41,42] using hot (i.e., fast) H atoms generated by laser-pulse photolysis of HBr, it was possible to experimentally resolve the H_2 product rotational states, Fig. 5. It is interesting to comment on the technique used to insure that the nascent products of a single collision are detected. This was achieved by using a second probe laser which is fired after the photolysis laser within a time short compared to the time between collisions. This second laser detects the H_2 products. The prior distribution used in Fig. 5 is not (5) but rather

$$P^o(j, v) \propto (2j+1)(E - E_v - E_j)^{1/2}. \quad (15)$$

The reason is that the hot H atoms carry sufficient energy for the H_2 products to be formed in excited vibrational states. When the H_2 molecule is in the vibrational state $v, v = 0, 1 \cdots$ with an energy E_v, the energy released as kinetic energy is not $E - E_j$ but rather $E - E_v - E_j$. Hence (cf. (4)) is the change between (5) and (15). Otherwise, a single value of θ_R suffices to reproduce the experimental distribution.†

It is only recently that using laser probing, reliable nascent products' rotational distribution became available. Such results have been extensively analyzed using (10). A particularly interesting case, shown in Fig. 6 is the

$$H + CO_2 \rightarrow CO + OH(v, j)$$

reaction. This has been studied both for H atoms approaching CO_2 from all possible directions[43] and for H atoms confined to approach with a cone along the (linear) CO_2 axis. The geometry-limited initial state is achieved[44] by photolyzing the HBr bond in the van der Waals adduct[1] $BrH \cdot CO_2$ formed via a supersonic expansion of an HBr/CO_2 mixture. As can be seen in Fig. 6, both initial states give rise to an OH final rotational distribution which is well described by (10). The value of θ_R is higher for the geometry-limited initial state indicating a stronger preference for rotationally unexcited OH molecules.

Highly exoergic reactions can populate several products vibrational states. Much of the earlier work (reviewed in Ref. 45) in surprisal analysis examined these vibrational distributions which are more readily

† Note that since now $E_j \leq E - E_v$, the reduced variable in (10) is not (E_j/E) but $E_j/(E - E_v)$.

available from experiment. The prior distribution of vibrational states $P^o(v)$ is obtained by summing over all final quantum states where the vibrational state is v. From (15)

$$P^o(v) = \sum_j P^o(v,j) \propto \sum_j (2j+1)(E-E_v-E_j)^{1/2} \quad (16)$$

where summation is over all those rotational states allowed by conservation of energy, i.e., such that $E_j \leq E-E_v$. When the rotational constant B defined (in (2)) is very small compared to $E-E_v$ so that many terms contribute to the sum in (16) we can replace summation over j by an integration over E_j to get

$$P^o(v) \propto \int_0^{E-E_v} dE_j (E-E_v-E_j)^{1/2} \propto (E-E_v)^{3/2}. \quad (16')$$

The observed vibrational state distribution $P(v)$ defines the vibrational surprisal by

$$I_v = -\ln [P(v)/P^o(v)]. \quad (17)$$

Here too it is often the case that the surprisal is a linear function of the vibrational energy so that $P(v)$ can be well represented as

$$P(v) = P^o(v) \exp(-\lambda_0 - \lambda_v (E_v/E)). \quad (18)$$

A recent example, that of the

$$D_2 + F \rightarrow D + DF(v),$$

exoergic reaction at a well defined energy[46] is shown in Fig. 7. Here, as in many other reactions λ_v is negative showing a preferential disposal of the reaction exoergicity into the products vibration.

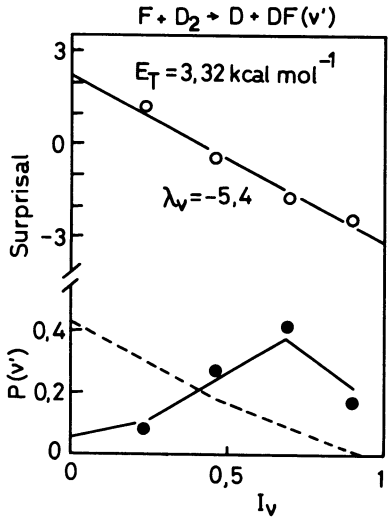

Fig. 7. Surprisal plot for the vibrational energy disposal in the F+D_2 reaction vs. $f_v \equiv E_v/E$. [Adapted from Y. M. Engel and R. D. Levine, *Chem. Phys. Lett.*, **123**, 42 (1986) using the experimental data (points) from Ref. 46]. The distribution (18) is shown as a solid line and the prior distribution (16) is the dashed line. $\lambda_v = -5.4$ as there is specific population of the higher vibrational states.

Microscopic reversibility, as discussed in section 1, can be used to show that the surprisal of the energy disposal equals the surprisal of the energy requirements in the reverse reaction.

Laser probing[7] of the states of molecules after a single collision has also provided much new information on inelastic, energy-transfer collisions. Typically, at energies in the chemical range such processes are constrained by the inefficient conversion of translational to internal energy.[47] Such an 'exponential gap'[1] behavior is illustrated in Fig. 8 for the

$$Xe + HgBr(v=52) \rightarrow Xe + HgBr(v')$$

process,[48] using thermal Xe atoms and HgBr in the $B^2\Sigma$ electronic state. The system 'resists' the change in the internal energy and the surprisal is linearly dependent on the magnitude of the 'gap' in vibrational energy $E_{v'}-E_v$ which is provided from the translation. Note that if $v'>v$, energy is taken out of the initial kinetic energy and the gap is positive, while if $v'<v$, energy is put into the final kinetic energy and the gap is negative. The surprisal which reflects the constraint on a change in energy is however a function of the absolute value of the gap, Fig. 8, and not on its sign.

We have centered attention on bimolecular, intermolecular processes. One can equally discuss intramolecular dynamics. Here we consider a particular aspect, that of optical excitation. When we excite the fundamental vibrational modes of a polyatomic molecule or the lower overtones, we have the limiting behavior familiar from spectroscopy. There are strong selection rules which limit the possible transitions and every spectral line can be assigned to a particular mode of excitation of the molecule. Newer experiments (e.g., Refs. 8 and 49) are preparing molecules with considerable excess energy.

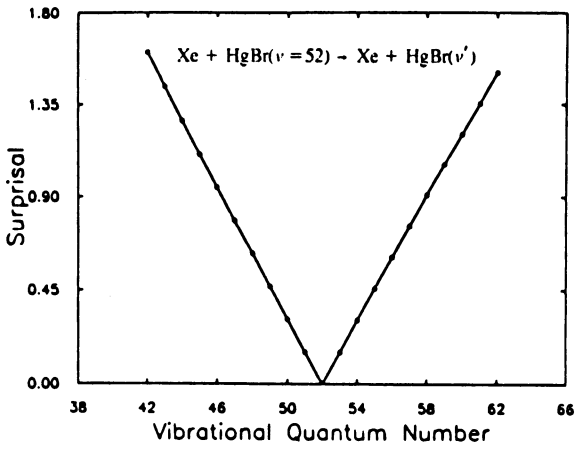

Fig. 8. Surprisal vs. the energy gap for the inelastic collision Xe+HgBr(v)→Xe+HgBr(v'). The surprisal is seen to be a function of the absolute value of the gap. From Ref. 48.

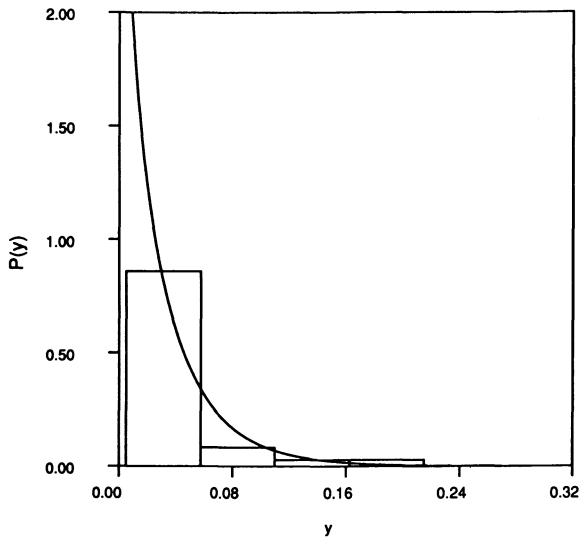

Fig. 9. The distribution of absorption intensities (data of Ref. 51) plottd as a histogram, for a fully resolved spectrum of pyrazine. The smooth curve is the corresponding prior distribution showing that the classical dynamics is chaotic.

There are numerous lines in the spectrum and it is by no means clear that the energy distribution in the optically excited molecule is very selective. It remains the case however that the intensity of lines in the spectrum gives the probabilities of the different transitions. Very recently[50] the thermodynamic approach has been applied to the distribution of intensities in optical spectra. Figure 9 shows the observed distribution[51] for pyrazine near the origin of the $^1Ag0_o^o \rightarrow {}^1B_{3u}$ transition. The coupling of the excited singlet $^1B_{3u}$ state to lower-lying triplet $^3B_{3u}$ states leads to vibrational energy redistribution, which, as shown by the analysis in Fig. 9 is totally non-selective (i.e., chaotic).

5. Thermodynamics

Surprisal analysis is used to quantitatively characterize the selectivity and specificity of chemical reactions and to identify the relevant variables. Can one however *predict* these variables and the parameters (e.g., θ_R, λ_v) directly from the forces that operate during the collision without computing the distributions first? It turns out[37,38] that this can be done if we center attention on the dynamics in phase space.[52,53] That is, we traceout the evolution of the distribution in phase space during the collision. The technical details will require too much space to be spelled out. The essential idea is that it proves possible to use the exponential forms as in (10) or (18) not only after the collision but also in the interaction region. The point of view we suggested earlier namely, that the state of a system is always one of equilibrium subject however to constraints is thereby shown to be equally valid for systems which evolve with time. It thus follows that thermodynamics is indeed also a theory of dynamics and not only of static equilibrium states.

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