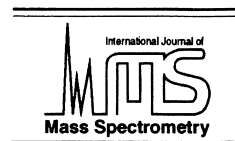




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International Journal of Mass Spectrometry 200 (2000) 43–56



Landmarks in the theory of mass spectra

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Received 8 June 2000; accepted 2 August 2000

Abstract

Statistical theories of mass spectra are based on two assumptions. The first one, which postulates efficient phase space sampling, is substantiated by various experimentation and is now theoretically much better understood. The efficiency of phase space sampling can be estimated and is found to be quite good. Much effort remains to be done concerning the second assumption. A new impetus should be given to the concept of transition state. A better understanding of the role played by the conservation of angular momentum, the exact significance of transition state switching, and the incorporation of quantum effects are set as goals for the future. (Int J Mass Spectrom 200 (2000) 43–56) © 2000 Elsevier Science B.V.

Keywords: Intramolecular vibrational redistribution (IVR); Maximum entropy method; Phase space; Statistical theory; Transition state

1. Prologue

In 1938, the Faraday Society organized a general discussion [1] entitled “On the theoretical methods of treating activation energy and reaction velocity.” The meeting was mainly devoted to the examination of the newly developed absolute rate theory. Such celebrities as Eyring, Polanyi, Wigner, and others were invited to present their views. Defend themselves might be a more appropriate term. The President opened the conference with the following address: “After making a certain amount of progress in the study of chemical kinetics, we have arrived virtually at an impasse. There are certain obstacles to further progress, and with a view to overcoming them new methods of exploration are suggested. As to whether these methods are fundamentally sound or unsound is

a question the consideration of which belongs rather to the domain of philosophy than to that of chemistry.” To give a feeling of the prevailing tone of the discussion period, let us quote, as an example, a comment by Guggenheim: “I am pleased to note in Eyring’s paper an admission that ‘we very frequently do not know’ the reduced mass normal to the barrier. This seems to be a confession that we do not know what the reaction co-ordinate is and in such a case I do not believe the treatment described can be of any use.” Earlier, in his own contribution [2], Guggenheim had declared: “When . . . simplifying assumptions concerning the nature of the reacting complex . . . are not made, Eyring’s formulae are at present sterile.”

Twenty years later, the atmosphere was slightly more cheerful. However, in opening the first international conference of mass spectrometry, organized in London by the Petroleum Institute in 1958 [3], Sir Cyril Hinshelwood, then President of the Royal So-

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ciety, declared in his opening address that the fundamental processes by which the ions fragment was “one aspect of mass spectrometry where the cleavage into laymen and experts does not yet apply.” Wahrhaftig was in the room, ready to report on the six-year-old quasiequilibrium theory (QET). Presumably, he did not feel particularly flattered.

Great strides have been made since that time. Over the years, endless efforts of many individuals have induced distinguished members of the Royal Society to revise their judgement. There is no doubt that Henry M. Rosenstock was the leading exponent of the theoretical modeling of ionic fragmentation. The present article is dedicated to his memory, in recognition of his impressive insight.

2. Building up a statistical theory: the starting point

A statistical treatment is possible if all the properties of a conservative isolated system (e.g. the unimolecular dissociation rate constants of an isolated molecular ion) are completely determined by a single parameter only: its total internal energy E , irrespective of the way the ion is excited. This theoretical criterion is eminently suitable for experimental probation.

The verdict is clear. A considerable number of scientists have devoted enormous efforts to devise mode-specific enhancement of chemical reactions, especially, of course, for neutral systems. For that purpose, they used, e.g. selective excitation with a carefully chosen monochromatic laser light. The question is: at a given value of the internal energy, do different preparations of the initial state lead to different reaction yields? Except in the case of van der Waals complexes (in which there is frequency mismatch between a very weak bond and a reservoir of high frequency modes), examples of mode-specificity are rare. On the contrary, the photoelectron-photoion coincidence spectroscopy (PEPICO) [4–6] (and, before it, cruder charge-exchange experiments [7,8]) have revealed that, for most molecular ions, the

breakdown graphs are smooth functions of the internal energy E alone.

Other experiments confirm these views. The dissociation rate constant is observed to increase smoothly and monotonously with E , irrespective of the way energy is delivered to the molecule [4,9,10]. The determination of time-resolved breakdown graphs by ion-trapping devices led to a systematic study of the kinetic shift (i.e., the amount of energy in excess of the thermodynamic threshold or activation energy that is necessary to bring the lifetime in the time scale of the measurement) [11,12].

The results of all of these experiments justify the use of a statistical model [4,12–18]. The condition of validity of a statistical treatment can be expressed in many equivalent ways, depending on individual tastes and background: the internal energy is completely randomized; all regions of phase space are equally a priori probable; phase space is sampled in an ergodic way; all of the quantum states characterized by a given total energy E are equally probable; the molecular ion has reached a state of microcanonical equilibrium; isolated molecules with a definite internal energy E can be described in terms of averages over a microcanonical ensemble. All of these are equivalent statements.

However, molecular ions are not born as members of a microcanonical ensemble. They are initially formed by a set of Franck-Condon transitions and relax to that equilibrium state. As time goes on, energy progressively randomizes, i.e. delocalizes in an increasing number of degrees of freedom. During the last meeting which he attended (a NATO conference organized in Portugal in 1982), Rosenstock, as a comment to a talk that the present author had just delivered, reminded the audience of an analogy that dates back to Gibbs [19] and that he thought very appropriate. Phase space exploration, he said, can be compared to progressive diffusion in the entire available volume, in exactly the same way as a drop of ink that has been gently deposited in a glass of water.

But what is the mechanism of this relaxation? Special emphasis has been put on strong anharmonicity leading to efficient intramolecular vibrational redistribution (IVR). However, the evolution to equilib-

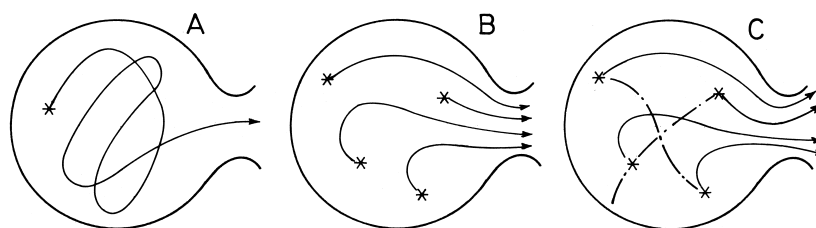


Fig. 1. Schematic view of phase-space sampling. (A) Selective excitation giving rise to an ergodic trajectory (efficient IVR). (B) Nonselective excitation (as in thermally excited systems) generating a swarm of nonergodic trajectories. (C) Initial conditions are located on a network of surface-crossing seams (represented by the dashed-dotted lines).

rium is greatly facilitated if the preparation is nonselective, i.e. if the system is prepared by a set of very different initial conditions, corresponding to widely scattered points in phase space. Coming back to the analogy, if now, instead of gently depositing a single, well localized drop, ink is sprayed on the surface of the water, then the final mixed state will be more rapidly attained. In other words, the initial preparation of the system matters just as much as (if not even more than) the intrinsic tendency to IVR brought about by anharmonicity. The difference between efficient IVR consecutive to a selective excitation and a global effect resulting from thermal excitation is schematically represented in Fig. 1(A) and (B). As noted by Lifshitz [13], in thermal systems, “it is never clear whether one is testing the statistical nature of the activation process or the statistical nature of the intramolecular energy flow.” But does an analogous purely intramolecular mechanism of generating very different initial conditions exist in the case of isolated molecular ions? It will be seen in Sec. 8.2 that, as anticipated by the founders of QET [20], a cascade of radiationless transitions plays a leading role in the process of energy randomization.

3. Transition state assumption

In essence, as expected in a statistical treatment, the Rice-Ramsperger-Kassel-Marcus (RRKM) and QET theories simply state that the rate constant is proportional to the fraction of molecules having an internal energy E that are apt to react. Even more simply, it is proportional to the ratio of favourable

events divided by the total number of events. But how can one define the favourable circumstances leading to capacity for reacting? At this juncture, the RRKM-QET theory introduces a second basic assumption: reaching the transition state ensures that dissociation will take place.

Stated in this way, the transition state is a mysterious and ill-defined concept. The simplest assumption, proposed by Eyring and Polanyi, consists of identifying it with a saddle point of the potential energy surface. However, the analysis of this problem has generated an enormous literature [21–23], making the task of complete coverage impossible. A recent review [23] of modern developments included 843 references! Developments that can be found in many textbooks [18,24–28] lead to the fundamental equation

$$k_{\text{RRKM}}(E) = \sigma \frac{N^\ddagger(E - E_0)}{h\rho(E)} \quad (1)$$

where $N^\ddagger(E)$ is the number of states of the transition state, E_0 is the energy of the reaction threshold, $\rho(E)$ is the density of states of the reactant, and σ is the number of equivalent reaction paths. Thus, k_{RRKM} depends only on E , irrespective of the way the molecular ion has been activated to that energy.

The vibrational and rotational energy-level densities that appear in Eq. (1) should be calculated either by inverting the partition function combined with the method of steepest descents [24] or by an exact state counting algorithm [18,27]. The development of simple, yet efficient methods to calculate densities of states stopped endless discussions that plagued many

of the early papers. The arbitrary reduction (sometimes by a factor of 5) of the number of oscillators down to an effective number was shown to result from an incorrect calculation of the vibrational density of states [20]. The use of the so-called classical approximation for the calculation of energy-level densities can, when applied to low internal energies, lead to enormous errors.

The transition state assumption amounts to replacing a dynamical criterion for reactivity by a structural assumption. Improvements on the theory can only result from the reintroduction of intramolecular dynamics. Over the years, several attempts to do this appeared in the literature.

4. Refinements

4.1. Variational transition state theory

What is the criterion for reactivity if no barrier is encountered along the reaction path, as often happens in simple bond fission reactions? Marcelin [29], as early as in 1915, and then Wigner [30] proposed to define a dividing surface in phase space separating reactant and products, such that the crossing of the dividing surface is irreversible: dissociating trajectories are expected not to return to the reactant region of phase space.

Under these circumstances, a variational criterion becomes essential for the application of transition state theory [12,13,15–17,22,23,25,31]. The minimum flux criterion locates the position of the transition state at the position where the numerator of the RRKM formula reaches its minimum. This position, which minimizes the reactive flux and thus provides an upper bound on the rate constant, is usually referred to as the “dynamical bottleneck of the reaction.” It is found to be energy-dependent and to occur at much shorter interfragment separations than those characterizing rotational barriers [22,23,25,31,32].

4.2. Phase space theories

A major advance occurred with the development of several related theories, often referred to as phase-

space theory [16–18,21,33–40]. They all have several characteristics in common. (1) The principle of microscopic reversibility (also termed detailed balance theorem) [19] establishes a connection between the unimolecular dissociation rate constant and the cross section for the reverse association reaction. Therefore, the theory is built on the properties of the fragments. Attention is focused on the energy levels of the separated fragments with completely free overall rotation and no longer on those of an often ill-defined transition state. Association cross sections are related to the long-range forces between fragments. The simplest case, studied by Langevin [41], results from a charge-induced dipole interaction. (2) As a result of strict conservation laws derived from classical mechanics, the microcanonical rate constant $k(E,J)$ is known to depend on the total angular momentum J as well as on the energy E . Therefore, each reaction product is assumed to be formed with a probability that is proportional to the volume of phase space available to the product divided by the total phase space volume under conservation of total energy and angular momentum. In other words, equal weight is assigned to any state consistent with these restrictions. (3) The long-range potential is assumed to be isotropic, as in the case of a charge-induced dipole interaction. Reaction can only take place when the relative translational energy of the pair of fragments exceeds the rotational barrier. Stated in other words, the orbital angular momentum of the pair of fragments must be small enough to allow dissociation. Alternatively, the transition state can be reintroduced and is placed at the centrifugal barrier (orbiting transition state). Thus, the looser the actual transition state, the better the model. Restriction to central forces is obviously unsatisfactory and noncentral field effects have also been discussed by Chesnavich and Bowers [17]. On the other hand, Klots has developed the point that central-field potentials are especially suited to loose systems, such as clusters [42].

In practice, the calculated rate constant is often overestimated. However, phase space theory turns out to be much more successful for the calculation of product energy partitioning, especially in the case of

ionic systems which are characterized by a long-range interaction potential.

4.3. Transition state switching

In the two previous models, attention is concentrated on different regions of the potential energy surface: short range for variational transition state theory and long range for phase-space theory. To overcome this dichotomy, a model is suggested [12,15,17,22,23,40,43] in which a series of flux minima (i.e. of transition states) is encountered along the reaction path. At low energies, the dynamics is dominated by the loose orbiting transition state, which is found at very large values of the reaction coordinate. At higher energies, a switching to a tighter transition state at shorter internuclear distances is expected. However, the development of this interesting idea has to be set as a goal for the future: further progress requires a realistic parametrization of the potential energy surface, including its anisotropic properties in order to examine more reliably the behaviour of the transitional modes along the reaction path. Further, more attention should be paid to regions of strong curvature of the reaction path which are known to throttle the reactive flux and to generate bottlenecks. In more fundamental terms, it should be realized that the genuine dividing surface in phase space is not necessarily a plane; it might even be discontinuous, piecemeal scattered, and even lacunar.

4.4. Classical trajectory calculations

Numerous nuclear trajectories have been calculated by integrating the classical equations of motion [18] on a previously calculated- or assumed-potential energy surface. By and large, they confirm the assumption of rapid IVR. The higher the internal energy, the more ergodic the dynamics, although long-lived vibrational states are found to persist even at high energies [18,44].

The dynamics of ion collision theory and of ion-molecule capture reactions has been extensively studied [17,45]. Classical trajectory calculations have been used to study unimolecular reaction mechanisms

[46,47]. They proved to be particularly useful in the analysis of large translational energy releases resulting from a high reverse activation energy barrier [48–51].

A very surprising result, which has a direct incidence on the concept of transition state is provided by classical trajectory calculations showing how a delocalized distribution of vibrational energy suddenly accumulates in the reaction coordinate as a very large amplitude localized motion that leads to reaction [52].

4.5. Concept of effective temperature

Klots has developed a model where canonical equilibrium is postulated among translational, rotational and vibrational degrees of freedom of an isolated molecular ion [18,53,54]. The translational energy is assumed to be in thermal equilibrium with a heat bath formed by the rotational and vibrational degrees of freedom. Under these circumstances, the usual equations of statistical thermodynamics can be used to define an effective temperature. This model seems reasonable and leads to interesting considerations. When applied to the study of translational energy releases, its results are in excellent agreement with the so-called prior (i.e. most statistical) distribution, to be discussed later on in Sect. 8.1. What is much less clear, however, and what deserves further scrutiny is the additional assumption that the number of translational and rotational degrees of freedom should be reduced in order to simulate the constraints imposed by the conservation of angular momentum.

4.6. Statistical adiabatic channel model

This theory, developed by Troe and Quack [25,55–58], implies a separation (somewhat similar to the Born-Oppenheimer separation between electronic and nuclear degrees of freedom) of the reaction coordinate from the remaining degrees of freedom. As a result, the complicated multidimensional motion of a reactive trajectory is reduced to a one-dimensional motion along the reaction coordinate in an effective channel potential. Each channel corresponds to a particular rovibrational state of the degrees of freedom other

than the reaction coordinate as they evolve from reactant to products in a continuous way. The potential energy curve of each individual reaction channel is plotted as a function of the reaction coordinate. In practice, each curve is obtained by interpolating between the rovibrational energy levels of reactant and products in a way that preserves conservation of angular momentum. The resulting channel energy curves are characterized by maxima and each channel is declared open or closed depending on whether its maximum is below or above the available internal energy E . This procedure has been used to study the kinetic energy release distributions by Ruttink [59]. More recently, a canonical version has been developed by Schröder et al.[60].

5. Quantum chemistry to the rescue

The development of computer programs that were able to calculate reliable potential energy surfaces gave a new impetus to the theory. As a remarkable recent advance in *ab initio* calculations, the DFT method has to be singled out because it provides the best compromise between simplicity and accuracy [61].

The vibrational frequencies required in the evaluation of energy-level densities occurring in Eq. (1) now can be calculated in a nearly routine way, not only for stable species but also for saddle points [62].

Modern *ab initio* programs also allow the routine calculation of the minimum energy path, which is called the “intrinsic reaction coordinate” when defined as the path of steepest descent in mass-scaled coordinates [61]. It can be viewed as a classical trajectory starting at a saddle point (but extending on both sides of it) if the kinetic energy of the representative point is continuously damped.

5.1. Fluxionality

Numerous *ab initio* calculations of potential energy surfaces have confirmed a well-known experimental fact: ionic systems are often highly fluxional. As a rule, the potential energy surface of an ionized mol-

ecule is characterized by the presence of many minima. In particular, classical and bridged structures often coexist. Isomerization barriers are generally small and, further, are often erased (or at least substantially reduced) when the zero-point energy is added to the *ab initio* calculated potential energy curve. When the internal energy exceeds these barriers, a large-amplitude nuclear motion results. The potential energy surface is thus very anharmonic and this considerably complicates the calculation of reliable energy-level densities $\rho(E)$ and $N(E)$ by the rigid-rotor-harmonic-oscillator approximation. Examples of this behaviour abound [63,64]. For instance, the $C_3H_7^+$ ion undergoes hydrogen scrambling above $E \geq 7$ kcal/mol (0.3 eV) and carbon atom scrambling above about 19 kcal/mol (0.8 eV) [65,66]. Another example is provided by the $C_2H_3^+$ ion: as the internal energy increases, several vibrational modes successively thaw out in turn so that, at high values of E , the hydrogen atoms are no longer localized to regions near an equilibrium configuration but undergo exceedingly large-amplitude motions along the three directions of space [67]. The concept of molecular structure then entirely breaks down and has to be replaced by that of a bag of marbles.

In a similar way, reaction mechanisms calculated by *ab initio* methods are often found to be complicated multistep sequential processes implying a tortuous reaction path involving numerous isomerizations. It has long been realized that the chemistry of ionic systems is characterized by the complicated nature of its reaction mechanisms. The last step often involves the dissociation of a weakly bonded species (hydrogen-bridged or ion-neutral complex). Fluxionality, complicated reaction paths, hidden isomerization processes, back and forth nuclear motions before dissociation, outward stretches of some nuclear coordinate followed by a return to another equilibrium position, spectacular Longevialle-Botter rearrangements, etc., are the rule rather than the exception. Recent examples are readily found [68–70]. However, it must be realized that what is lost on one side is recovered on the other. This complicated chemistry is in a sense a blessing in disguise, because all of these processes favour the exploration of phase space.

The tortuous character of the reaction path can often be accounted for by the presence of many conical intersections that, as explained in Sec. 6.2, lower the activation energy.

5.2. Bond orders

When looking for shortcuts to simplify the problem, the use of bond indices derived from molecular orbital theory has often been suggested, at least in the past. This is to be discouraged because the bonding or antibonding character of a particular molecular orbital cannot be expected to describe the main features of an entire potential energy surface. Bond indices are essentially a static concept, i.e. information derived from the calculation of a particular molecular geometry and thus valid for one point of the potential energy surface only. They satisfactorily correlate with equilibrium bond lengths but not with dissociation energies. The electronic wave function calculated at an equilibrium position cannot be expected to remain valid at the dissociation asymptote. These indices cannot predict the complicated mechanisms described in the previous paragraph. Therefore, no correlation can in general exist between breakdown graphs and a set of bond orders.

5.3 Charge distributions

However, reliable calculations of charge distributions in ionized molecules are possible. This analysis has compelled us to revise completely the mental schemes associated with the conventional formal charges derived from valence rules. An ionization process is found to remove electron density from the hydrogen atoms (especially from those at the periphery of the ion because this minimizes the electrostatic repulsion) and, surprising as it may seem, is found to increase the electron density at the carbon atoms [71]. For example, removing a π electron from ethylene increases the electron density near the carbons; thus, more than an electronic charge is removed from the hydrogens. Another example is provided by the methyl, isopropyl, and *t*-butyl cations in which the central carbon atom is found to be negatively charged.

Let us also mention that the charge distribution also depends on the surrounding medium. In the gas phase, the charge is as delocalized as possible. In a polar solvent, the charge distribution results from a compromise between stabilization via electronic delocalization (which is the only factor that operates in the gas phase) and stabilization via solvation (which reaches its maximum when the positive charge is fully localized). This casts doubt on alleged mechanisms often presented by some organic chemists as a consequence of resonance theory. For the same reason, it is the opinion of the present writer that no fundamental significance should be attached to the separation between charge and radical site in a distonic ion.

6. Nonadiabatic interactions and crossing potential energy surfaces

All of the efforts to rationalize chemical reactivity are based on the use of potential energy surfaces. However, the latter concept relies [61] on the validity of the Born-Oppenheimer approximation, which is known to break down when the density of electronic states is large, i.e. when the potential energy surfaces cross or get too close in energy. This is frequently the case for ionized molecules, much more so than for neutral systems.

6.1. Mechanisms

The importance of non-adiabatic reactions at each stage of gas-phase ion chemistry can hardly be over-emphasized [72]. Let us mention a few examples. Vibrational autoionization requires a breakdown of the Born-Oppenheimer approximation. The relaxation of the population of electronically excited states to the ground state of the ion takes place via a cascade of radiationless transitions. A nonadiabatic step is necessarily involved in the reaction mechanism of charge-transfer processes. It also often operates in ion-molecule reactions. Unsuspected spin-forbidden processes may control reaction mechanisms [73,74]. Energy deposition in collisionally induced dissociations is adequately rationalized by the Massey param-

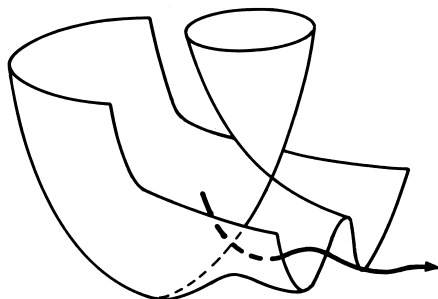


Fig. 2. Conical intersection between two crossing potential energy surfaces. Thick line: low-energy adiabatic nuclear trajectory around the cone.

eter, which measures the degree of nonadiabaticity in a collision process [75,76].

6.2. Conical intersections

The most important concept derives from a particular kind of surface crossings, denoted conical intersections, and represented in Fig. 2. They are important for the following reasons. (1) They occur much more frequently than commonly thought [77]. (2) They lead to ultrafast relaxation mechanisms since they bring about radiationless transitions with lifetimes of the order of 10^{-14} s [78,79]. (3) They generate tortuous reaction paths that lower the energy of activation [28,80,81]. Conical intersections between two potential energy surfaces lead to a decrease of the activation energy at the cost of a curvature of the reaction path. One needs not supply a large amount of energy to bring about dissociation. A low-energy reaction path exists as a circular motion around the lower cone. Further, this path is adiabatic, i.e. requires no electronic coupling. Moreover, the reaction path is curved, and this curvature brings about a bottleneck in the reactive flux, i.e. generates a transition state. (4) Finally, the strong vibronic coupling that results from conical intersections is known to generate chaotic dynamics and thus to greatly assist in the randomization of the internal energy [82–85], as already early anticipated [20] and as further discussed in Sec. 8.2. Thus, here again, as typical in a statistical theory, complications can be turned to simplification: the

advantages that are lost on one side are recovered on the other.

6.3. Isolated state decay

Since its initial observation by Lifshitz and Long [13,14,86] this (relatively rare) situation has been interpreted as indicating a possible failure of the assumption of fast radiationless conversion to the ground electronic state of the ion. Further, it has often been related to the bonding character of a particular molecular orbital. However, *ab initio* calculations provide a more detailed picture [28,72,80,81]. Isolated state decays are examples of bimodal dissociation mechanisms in which a branching of the reaction path takes place. This branching is brought about by an avoided crossing between two potential energy surfaces. The major fraction of the reactive flux is converted to the lowest potential energy surface and undergoes statistical dissociation. However, some nuclear trajectories remain in the upper electronic state and generate fragments by a fast, diatomiclike, non-statistical mechanism. Thus, for example, production of CH_3^+ ions from CH_3OH^+ [87] or of C_2H_3^+ fragments from $\text{C}_2\text{H}_3\text{F}^+$ [88] corresponds to the dissociation of the nonrandomized fraction of the population. This branching can only be brought about by avoided crossings, which are relatively rare. The much more frequently encountered conical intersections [77], on the other hand, are very efficient processes that do not lead to branching, but to ultrafast relaxation processes [78,79] and to ergodic nuclear motion [82–85].

Analogous situations have been studied by Shukla and Futrell [76]. The presence of long-lived excited states has been detected in their collision-induced experiments on the acetone and nitromethane ions.

7. Checking the ergodic assumption

Great insight into the relaxation process that leads to energy randomization can be obtained via a very general theorem of mathematical physics which says that a Fourier transformation converts spectroscopic

information obtained in the energy domain to dynamic information expressed in the time domain [89]. From a practical point of view, the better the energy resolution, the longer the period of time during which the dynamical process can be followed. The method has been applied to photoelectron spectra and produces evidence in favour of the sequential nature of IVR. As already said, as time goes on, energy progressively delocalizes in an increasing number of degrees of freedom. However, the process cannot at all be compared to a random walk in phase space, as often stated. It is found to obey interesting regularities [90–93]. The first step consists in a fast energy exchange among the optically active vibrational modes in which energy is initially deposited (i.e. the few, usually limited to two or three, modes that make up the vibrational progressions detected in the spectrum). The second step of IVR consists in a slower energy transfer from symmetric to antisymmetric modes via anharmonic coupling. The two steps take place on different time scales. For molecular ions like $C_2H_4^+$, $HCOOH^+$, and CH_2CHF^+ (which receive only a modest amount of internal energy when excited from the neutral by a Franck-Condon transition), the first step is over after about 10^{-13} s [90,92,93]. It has been shown that, by that time, the fraction of phase space that has been sampled represents a few percent of the available volume [92]. Unfortunately, the second step, which is the most interesting one from the point of view of chemical kinetics, cannot be studied on currently available photoelectron spectra, because the latter are notoriously poorly resolved by spectroscopic standards.

8. Rating the efficiency of phase space sampling

The RRKM-QET equation (1) provides a reasonably good estimate of the rate constant. In addition, other statistical treatments, described in Sec. 4, lead to a satisfactory, yet not perfect rationalization of translational kinetic energy release distributions (KERDs). How can one improve on these results? One would like to think of a method that would start from a simple statistical estimate and would upgrade it to the exact solution or at least up to a point where the

difference between experiment and theory is of the same magnitude as the experimental errors. Fortunately, this method exists and is called the maximum entropy method. It can be credited with impressive success in the analysis of product energy distributions observed in the dissociation of neutral molecules [94–97]. It can also be viewed as an interpolation between the RRKM model (characterized by free energy flow among all modes, without any constraint) and the Slater model (which is highly constrained because the assumed harmonic nature of the vibrations prevents any energy exchange) [95]. Although it requires a fit to experimental data, it has solid theoretical foundations and can be shown to converge to an exact solution of the Schrödinger equation [98]. Note especially that the origin of the method is the desire to derive the least biased inference from a given situation. Its very aim is precisely to avoid pushing the data analysis a bit too far.

8.1. Kinetic energy release distributions

A great deal of information can be derived from a comparison between the experimentally determined KERD and the so-called prior distribution, obtained by assuming that all of the quantum states of the pair of fragments are populated with equal probability. Thus, the prior distribution represents the most statistical situation, i.e. the hypothetical KERD that would have been measured in the case of totally unconstrained dynamics [18,94–97,99]. Note that it represents a reference and not a crude and mediocre first approximation. Any discrepancy between the actual and the prior distributions indicates the operation of dynamical factors, denoted constraints, that lead to a situation of lesser entropy, i.e. to incomplete phase space sampling [94–97]. Lifshitz was the first to recognize the power of this method [100].

Three precious pieces of information can be obtained from this analysis. First, a so-called entropy deficiency, denoted DS, can be derived. It can be shown that the quantity $\exp(-DS)$ measures the fraction of phase space effectively sampled during the dissociation process and thus the degree of energy randomization [95]. The quantity $\exp(-DS)$ can

properly be termed an “ergodicity index.” Second, a maximum entropy analysis (e.g. in the form of a surprisal graph [94–97]) leads to the identification of the dynamical constraint (or constraints) that prevent(s) the reaction from being purely statistical. Thirdly, it is also possible to derive information on the way the efficiency of phase space sampling varies with the internal energy.

Application of this method to the molecular ions of chloro-, bromo-, and iodobenzene [101,102], of pyridine [103], vinylbromide [67], ethyliodide [104], and iodopropane [105] leads to the conclusion that, in most cases, about 75%–80% of the available phase space is effectively sampled prior to dissociation. This ought to be sufficient to make a statistical treatment meaningful.

What are the missing 20%–25% due to? The maximum entropy method identifies the constraint as related to the linear momentum associated with the relative translational motion (i.e. to the square root of the energy) of the separating fragments. In other words, there exists a systematic discrimination effect that prevents the energy partitioning between the reaction coordinate and the subset of internal modes from being fully statistical [67,101–105]. Large translational energy releases are disfavoured, while energy channeling into the rotational and vibrational degrees of freedom of the pair of fragments is favoured with respect to a pure statistical partitioning. This reluctance to modify nuclear momenta, which has been detected in vibrational predissociations, is known as the momentum gap law [106].

Excellent agreement with experimental data can be achieved upon imposing this single constraint while assuming complete randomization within the subset of internal degrees of freedom of the fragments. For the rest, there exists at the present stage no compelling reason to question the assumption of complete randomization among the subset. The role of constraints linked to the conservation of angular momentum could, so far, not be detected by the maximum entropy method.

8.2. *How does the efficiency of phase space sampling vary with internal energy?*

The way the degree of randomization varies with internal energy is also quite interesting. Right at

threshold, it must be equal to 100%, simply because the system has no choice when only a single reaction channel is available. (Phase space is necessarily completely sampled when it is reduced to a single cell.) Therefore, the efficiency of phase space sampling [measured by the quantity $\exp(-DS)$] can only decrease as the number of reaction channels increases. Most remarkably, however, the quantity $\exp(-DS)$ is found to increase again as the internal energy increases [67,104]. This is very strange because, as E increases, the lifetime of the ion rapidly decreases, leaving less time to explore an extremely rapidly increasing volume of phase space! This amazing paradox can be solved by noting that energy randomization does not exclusively depend on anharmonic coupling among vibrational modes. As already said in Sec. 2 [see Fig. 1(B)], a system can behave ergodically if its preparation leads to widely scattered initial points in phase space as, for example, in thermal reactions where the preparation involves collisions. Now, a vertical Franck-Condon transition leads to a very restricted region of phase space. However, it is immediately followed by a cascade of extremely rapid radiationless transitions brought about by a complicated network of surface crossings extending all over a wide range of molecular geometries [Fig. 1(C)]. Therefore, the initial conditions are dispersed all over phase space and a wide range of initial conditions results. The great complications observed in the electronic spectra of open-shell systems like NO_2 or C_2H_4^+ are described as resulting from a state of molecular chaos and are ascribed to the presence of conical intersections [82–85]. In a different context, nearly perfectly statistical vibrational energy distributions have been experimentally observed in crossed-beam experiments involving metal atoms [96]. Here again, the statistical behaviour has been ascribed to “a maze of curve crossings.”

These observations were already present (if not elaborated upon) in the 1963 article by Rosenstock and Krauss [20]: “a considerable part of the energy localized in excited electronic levels will find its way into vibrational excitation of the ground state more or less randomly.” The modern version of this statement involves the presence of seams resulting from conical

intersections. The missing link in Rosenstock's argumentation was the realization that a seam extends over a large range of molecular geometries and that each point of it corresponds to a set of possible initial conditions [Fig. 1(C)].

8.3. Validity of the RRKM equation

Information theory teaches us that when phase space is not completely or not uniformly sampled before dissociation, then the statistical theory should be developed in terms of effective densities of states that, invariably, have a lower value than those that are calculated by usual state-counting algorithm [28,107]. Note, however, that this is true for both the reactant and the transition state. Hence, Eq. (1) remains valid, but both its numerator and denominator should be reduced. In other words, the errors cancel, at least to some extent.

Hence, the RRKM-QET formula is a very robust equation [28,107,108]. It cannot fail miserably. Conversely, however, its success does not allow a claim that its basic assumptions are exact.

8.4. Summary

In summary, the maximum entropy method has shown that for most molecular ions created in a conventional way (i.e. by electron impact, photoionization, or chemical ionization), the assumption of rapid energy randomization leading to nearly complete phase space sampling seems to be a good approximation paving the way for the application of a statistical theory ($e^{-DS} \approx 75\%–80\%$). This success probably results from the nonspecific nature of the conventional ionization, which involves a sequence of initial points, just as in the case of thermal reactions (Fig. 1).

KERDs, on the other hand, are more sensitive (i.e. less robust) than rate constants. This dichotomy has been known for a long time [13,16,17,37,109].

9. Conclusions

Combining its two main assumptions, the statistical theory of mass spectra should be, more appropri-

ately, denoted the microcanonical transition state theory [12,22,23].

Typical of mass spectrometric research is a clever blend of careful experimentation, *ab initio* calculations of reaction paths and of vibrational frequencies, and statistical modeling. "Theory and experiment in concert" have led to the elucidation of interesting dissociation mechanisms. With apologies to unmentioned authors, let us single out the case studies of acetone [14,110], pentanol [69,111–113], tropylium [114,115], and the still controversial case of methylnitrite ions [72,116–118]. The feedback between experiment and theory is the hallmark of a mature field.

It has been seen in the previous sections that the assumption of efficient energy randomization provides a very satisfactory starting point. However, obscure problems remain. (1) What is a transition state? How can one define it when there exists no barrier along the reaction path? In principle, a transition state is a structural assumption that is meant to bypass a dynamical calculation. Obviously, improving upon this considerable simplification requires reintroducing the dynamics in a hopefully simple way. Ensuing problems will not be easily solved. (2) The role of angular momentum has to be better understood. This topic would require an entire review of its own [12,15–17,37,119,120]. (3) Interplay with quantum mechanics.

The marriage of unimolecular reaction theory and fundamental quantum mechanics is, so far, not a happy one, or rather, is until now fairly tumultuous. For example, the basic assumption of transition state theory involves simultaneous specification of momentum and position along the reaction coordinate, resulting in incompatibility with quantum mechanics [30].

It is important to realize that statistical theories of dissociation processes that go far beyond the RRKM or VTST equations are currently the subject of active research. In the quantum mechanical approach, a unimolecular fragmentation channel is viewed as a resonance. It has been recently demonstrated [121] that the RRKM equation is valid only when these resonances overlap, i.e. when their widths exceed the energy spacings. The reader is referred to recent

articles [23,121] to get some idea of the complexity involved in the discussion of these ideas.

If, as predicted by quantum mechanics, the unimolecular law of decay is not necessarily exponential, then reaction criteria derived from macroscopic classical kinetics, such as the criterion of equal rates for competitive reactions, are not necessarily valid for microcanonical systems [122].

10. In memoriam

The original theory, developed in 1952, was termed “the statistical theory of mass spectra” and was presented as an outgrowth of the absolute rate theory. Three years later, its authors adopted a more restricted denomination: “the quasiequilibrium theory” to indicate concern about the assumption of microcanonical equilibrium. Rosenstock wrote [20]: “We recognize that the assumption of a microcanonical distribution to represent our system is purely heuristic and does not signify any deep understanding of the problem. . . . The extent of nonequilibrium is debatable. . . . It must be emphasized that the use of the microcanonical ensemble is not secure.” Obviously, he was worried, in spite of the fact that, on many occasions, he displayed considerable shrewdness and put his finger on the right consideration that, later on, turned out to provide the answer to the question. But at that time the necessary experimental information and theoretical tools were simply not available to take full advantage of his insight.

Rest in peace, Henry. Problems subsist and we miss you very much, but the starting point is now on much firmer grounds. A better acronym than QET could have been chosen, but your memory and your achievements will survive.

Acknowledgements

The author is indebted to Professor B. Leyh for many interesting discussions. This work has been supported by a research grant from the “Actions de Recherche Concertées, Direction de la Recherche

Scientifique de la Communauté française de Belgique.”

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