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Exit-channel dynamics in barrierless unimolecular reactions: Criteria of vibrational adiabaticity

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Conversion of translational into vibrational energy during the last step of a unimolecular reaction is brought about by the curvature of the reaction path. The corresponding coupling is analyzed by an angle-action reaction path Hamiltonian (RPH). The accuracy of the vibrational adiabatic approximation is found to be completely independent of the shape of the potential energy $V(s)$. Vibrations are adiabatic when two independent dimensionless parameters are small. The first one, denoted as σ, controls the dynamic coupling. The physical significance of the condition $\sigma \ll 1$ is that the amplitude of the vibrations normal to the reaction path should be much smaller than the radius of curvature of the reaction path. The second parameter, denoted as μ, governs the static coupling. It results from the dependence of the vibrational frequency ω on the reaction coordinate s. The higher ω, the lower its derivative with respect to s and, more unexpectedly, the higher the translational energy ε, the lower μ is. A criterion for locating a particular dividing surface in barrierless reactions is proposed. This surface separates two regions of space: one where energy flows freely, and one where energy conversion between translation and vibration is hindered by adiabatic invariance. The nature of the dynamical constraint that prevents the product translational energy distribution from being fully statistical can be identified by a maximum entropy analysis. The constraint is found to bear on the translational momentum p_s, i.e., on the square root of the translational energy $\varepsilon^{1/2}$. This can be understood by applying Jacobi's form of the least action principle to the vibrationally adiabatic RPH. © *2005 American Institute of Physics*.
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I. INTRODUCTION

Substantial progress in the understanding of reaction dynamics is derived from measurements of product energy distributions, which are determined by the shape of the potential-energy surface at large values of the reaction coordinate (i.e., beyond the dividing surface postulated by transition state theory).[1,2] The analysis of these distributions reveals the existence of so-called "exit-channel effects," i.e., of interactions as the fragments separate in space.[3–13] Vibrational energy distributions have been especially studied and shown to be directly related to vibrational nonadiabaticity.

However, the present article concerns translational kinetic-energy release distributions (KERDs), which have been determined with good accuracy for a number of unimolecular dissociations taking place in ion beams, i.e., under collision-free conditions and with some selection of the internal energy of the reactant.[1,14–16] Very often, these reactions are characterized by the absence of any reverse activation energy barrier along the reaction path and special attention is paid here to such barrierless dissociations.

Efforts to improve on one-dimensional models of reaction dynamics have opened up to the concept of curvature of the reaction path. According to classical mechanics, a region of large curvature leads to a loss of vibrational adiabaticity, i.e., to a conversion of translational to vibrational energy that is vividly described as the bobsleigh effect.[3–7,17–19] The present article aims at relating exit-channel dynamics to that concept and at deriving information on the coupling between the reaction path coordinate and the bath of vibrational degrees of freedom from a study of KERDs. Regrettably, the study is limited to the case of rotationless molecules (zero total angular momentum).

Classical trajectories might be calculated by solving equations of motion in particular cases.[7,10,11,20–22] However, this is an approach that we want to avoid because what we are looking for is a better understanding of the tendencies that govern vibrational nonadiabaticity.

The article is structured as follows. Section II presents a model where the reaction path is partitioned into four dynamically different regions. In Sec. III, the reaction path Hamiltonian (RPH) analysis of vibrational adiabaticity is briefly reviewed. The two parameters that determine the accuracy of the adiabatic approximation are examined in Sec. IV, and a criterion for locating a dividing surface in barrierless reactions is proposed. Section V provides an extension to polyatomic molecules. Connection with experiment is made in Sec. VI. A maximum entropy analysis shows in Sec. VII that adiabatic invariance constrains the dynamics as a result of Jacobi's form of the least action principle, thereby providing an experimental confirmation of the RPH ap-

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proach. Section VIII concludes by showing that the range of validity of existing theories of unimolecular reactions should be extended by the present results.

II. PARTITIONING THE REACTION PATH

When the potential-energy curve increases monotonically along the reaction path, there is no clear indication about the position of the dividing surface postulated by transition state theory. The variational version of this theory[1,4,9,23–25] locates it at the minimum in the sum of states along the reaction path. However, for our purposes, it is expedient to divide the reaction path into no less than four dynamically different domains.

(1) The first one, to be denoted as the strong coupling region, is localized near the minimum of the potential-energy surface. In this domain, the dynamics is better understood in terms of a set of strongly coupled anharmonic oscillators among which energy is supposed to flow freely, as assumed in the Rice-Ramsperger-Kassel-Marcus (RRKM) theory.[1,2] The reaction path can be determined by solving Fukui's equation,[26] but its role is more formal than really physically meaningful.

(2) As the potential energy increases, the dynamics is restricted to a relatively local region of coordinate space. In the second domain, the reaction coordinate has to be singled out. If the internal energy is not too high, the dynamical motion in that region can be expected not to deviate too far from the minimum-energy path. The motion along the reaction path can be described as a translation, with the modes orthogonal to it treated as molecular vibrations. If so, the range of the potential-energy surface that influences the dynamics can be restricted to the description of a harmonic valley about the reaction path.[27] The interactions between translation and vibrations are nonadiabatic, i.e., they are strong enough to bring about changes in the vibrational quantum numbers (or in the actions in a classical treatment) of the vibrations perpendicular to the reaction path.[3–8] Therefore, this domain is denoted as the intermediate nonadiabatic range.

(3) Our contribution concentrates on the next region. The model of a harmonic valley about the reaction path is still appropriate, and the RPH model is the method of choice. However, the interactions between translation and vibrations are adiabatic in this domain, as shown by Miller *et al.*[27] This means that the actions or the vibrational quantum numbers remain conserved. This does not preclude some energy exchange between the reaction coordinate and the remaining vibrations, as will be seen later on. Therefore, this domain is denoted as the intermediate adiabatic range.

(4) In the outermost region, referred to as the asymptotic range, the RPH model ceases to be valid because the valley is now too flat. The appropriate description is now in terms of two moieties interacting via long-range forces. The distance between the centers of mass of the two fragments is strictly separable from the other Jacobi coordinates (i.e., the angles describing the rotations of the moieties about the line joining the centers of mass).[28,29] If one of the fragments is charged (in which case KERDs can be conveniently determined[1,14–16]), then the dynamics is determined by a well-defined long-range electrostatic potential, generated by the interaction between a point charge and either a permanent, or an induced dipole, or both. The orbiting transition state theory (OTST),[1,2,16,30,31] which is based on a partitioning between rotation and orbital motion, attempts to relate these interactions to KERDs. So does the statistical adiabatic channel model (SACM),[32–36] which usually focuses on the calculation of reaction rate constants, but which can also be used to study KERDs. The range of validity of methods based on a quantization scheme appropriate to the outermost region has been extended by Bonnet and co-workers.[12,13]

These four regions are certainly not separated by sharp borderlines but by fuzzy boundaries. A criterion will be proposed to specify the separation between the second and third domains. This provides a convenient reference position along the reaction coordinate, although not a dividing surface in the sense commonly used in statistical theories of chemical reactivity.

To summarize, the exit-channel effects that have been experimentally detected result from an energy exchange between the translational motion along the reaction coordinate and the vibrations perpendicular to it. This article concentrates on the third region where the experimentally determined KERD is generated. The reaction path and its curvature are preliminary pieces of information required to solve the dynamical problem in the intermediate region. Our aim is to determine the factors related to the curvature of the reaction path that govern the validity of the adiabatic approximation in classical mechanics and hence the conversion of translational energy.

III. VIBRATIONAL NONADIABATICITY IN CLASSICAL MECHANICS

In previous works, several attempts have been developed to characterize the quality of the adiabatic approximation.[3–6,18,33–35] In a quantum-mechanical framework,[17,18] the calculation of the elements of the S matrix has been attempted. However, what is required here is information about the validity of the adiabatic approximation at different points along the reaction path and, more generally, in different regions of the phase space. In other words, a more "local" approach to the problem must be developed.

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Since the analysis of exit-channel effects as the moieties separate requires simultaneous specification of position and momenta, a classical approach is called for.

Important developments in the field of reaction dynamics have resulted from the use of a RPH. Miller *et al.* have studied the intermediate regions and have analyzed the role played by Coriolis-type couplings in the energy transfer between translational and internal degrees of freedom.[27] First, a reaction coordinate s is defined as the arc length along the reaction path studied in a system of mass-weighted coordinates.[26] The reaction path is characterized by its curvature, which, for a collinear three-atom system, is a scalar having the dimensions of an inverse mass-weighted length. In polyatomic molecules, the curvature is a vector consisting of $3N-7$ components, each of which measures the coupling between the reaction coordinate and a particular normal mode orthogonal to it.[19,27,37] The RPH method is an extension to the case of polyatomic systems of the concept of natural collision coordinate introduced by Marcus.[3]

For a system restricted to two degrees of freedom (e.g., the dissociation of a collinear triatomic molecule when the total angular momentum is equal to zero), Miller *et al.*[27] derived the following action-angle Hamiltonian:

$$H(s,p_s,q,J)=\frac{[p_s+J\sin q\cos q\omega'(s)/\omega(s)]^2}{2[1+\sin q\sqrt{\sigma(s)}]^2}+V(s)+J\omega(s). \tag{3.1}$$

In this equation, s denotes the reaction path coordinate, $V(s)$ is the potential energy along it, and p_s is the corresponding momentum. The vibration normal to the reaction path is described by the angle-action variables q and J. The latter motion is supposed to be harmonic with the s-dependent frequency $\omega(s)$, whose first derivative with respect to s is denoted as $\omega'(s)$.

The dimensionless coupling parameter σ(s) is defined[27] as

$$\sigma(s)=2J\kappa(s)^2/\omega(s), \tag{3.2}$$

with $\kappa(s)$ denoting the curvature of the reaction path at point s.

Miller *et al.* then derive a vibrationally adiabatic Hamiltonian by averaging Eq. (3.1) with respect to q. The action J is now a constant of motion.[27]

$$H_{\mathrm{ad}}(s,p_s|J)=\left(\frac{1}{2\pi}\right)\int_0^{2\pi}H(s,p_s,q,J)dq=\frac{p_s^2}{2[1-\sigma(s)]^{3/2}}+V_{\mathrm{eff}}(s). \tag{3.3}$$

Let E denote the total internal energy of the system. The effective potential is defined as

$$V_{\mathrm{eff}}(s)=V(s)+J\omega(s)+16\varepsilon(s)\mu(s)\varphi[\sigma(s)], \tag{3.4}$$

where

$$\varphi(\sigma)=\left(\frac{\sigma}{4}-\frac{\sigma}{\sqrt{1-\sigma}}+\frac{3}{2\sqrt{1-\sigma}}-\frac{3}{2}\right)\Big/\sigma^2 \tag{3.5}$$

and

$$\varepsilon(s)=E-V(s)-J\omega(s)=\frac{p_s^2}{2(1-\sigma)^{3/2}[1-16\mu\varphi(s)]}. \tag{3.6}$$

The third term in the right-hand side of Eq. (3.4) has been recognized by Miller *et al.* as the diagonal part of the nonadiabatic coupling.[27] Therefore, the quantity $\varepsilon(s)$ defined in Eq. (3.6) represents the kinetic energy along the reaction coordinate. The dimensionless parameter

$$\mu(s)=[J\omega'(s)/\omega(s)]^2/[16\varepsilon(s)] \tag{3.7}$$

will shortly be seen to play a fundamental role in the conditions of validity of the adiabatic approximation.

To study the validity of the adiabatic approximation, we compare the two phase portraits of our system that arise from each of the two Hamiltonians H and H_{ad}. That of the latter is immediately derived from the equation $H_{\mathrm{ad}}=E$:

$$p_s^{\mathrm{ad}}=\{2[1-\sigma(s)]^{3/2}[E-V_{\mathrm{eff}}(s)]\}^{1/2}=\{2\varepsilon(s)[1-\sigma(s)]^{3/2}[1-16\mu(s)\varphi(\sigma(s))]\}^{1/2}. \tag{3.8}$$

To derive the phase portrait in subspace (s,p_s) from the full Hamiltonian in (3.1), the value of p_s is obtained by solving the equation $H(s,p_s,q,J)=E$. It is then averaged over the cyclic variable q. This procedure leads to

$$\langle p_s\rangle=\sqrt{2\varepsilon(s)}. \tag{3.9}$$

The smaller the dimensionless quantity

$$\Delta p_s=\frac{(\langle p_s\rangle-p_s^{\mathrm{ad}})}{\langle p_s\rangle}, \tag{3.10}$$

the more accurate the adiabatic approximation.

The two dimensionless parameters $\sigma(s)$ and $\mu(s)$ tend to zero as s increases. Therefore, they are expected to be small in the third, adiabatic intermediate region. A double series expansion of Eq. (3.10) leads to

$$\Delta p_s=(3/4)\sigma+(1/2)\mu+(3/32)\sigma^2+(3/8)\sigma\mu+(1/8)\mu^2+\cdots. \tag{3.11}$$

The same type of analysis has been repeated for other dynamical variables such as $\dot{s}$, p_s^2, and $\dot{s}^2$. The analogues of Eqs. (3.10) and (3.11)have been calculated. In all cases, the relative errors $\Delta\dot{s}$, Δp_s^2, and $\Delta\dot{s}^2$ are found to be expressed in terms of the two parameters σ and μ. Thus, although the numerical coefficients that appear in their double series expansion differ from those that appear in Eq. (3.11), the general conclusion is the same. Two independent conditions must be fulfilled for the adiabatic approximation to be fulfilled: $\sigma\ll 1$ and $\mu\ll 1$.

IV. DISCUSSION

A. Dynamic and static coupling

An important conclusion emerges from Eq. (3.11): The validity of the adiabatic approximation is completely independent of the function $V(s)$, i.e., of the profile of the potential energy along the reaction path (Morse function, inverse power law, etc).

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The accuracy of the adiabatic approximation is found to be determined by two independent parameters, $\sigma(s)$ and $\mu(s)$. Each one plays its specific role. The interaction between translation and vibration that results from the curvature of the reaction path (i.e., from a nonzero value of σ) has been termed the "dynamic coupling."[17,18] It subsists even when the vibrational potential does not depend on s, i.e., even when $\omega'(s)=0$. The "static coupling" between translation and vibration results from the dependence of the vibrational frequency ω on s, i.e., from the nonzero value of ω'.[17,18] This coupling subsists even when the curvature of the reaction path is equal to zero.

In the present work, both parameters σ and μ have been defined locally, i.e., have been expressed as a function of the reaction coordinate s. This is in clear contrast with the Massey parameters reported in the literature for the same process,[17,18] which are integral parameters, i.e., numbers. They result from S-matrix scattering calculations which aim at calculating the probability of transition resulting from a complete collision process.

The Hamiltonians $H(s,p_s,q,J)$ and $H_{\mathrm{ad}}(s,p_s|J)$ exist only provided that $\sigma \leqslant 1$.[19] The elementary requirement that p_s^{ad} calculated by Eq. (3.8) be real leads to a further condition on μ: $16\mu(s)\varphi[\sigma(s)] \leqslant 1$. This condition can be transformed further if the exact expression of $\varphi(\sigma)$ [Eq. (3.5)] is replaced by an excellent approximation,

$$\varphi(\sigma) \approx (1/16)[(1+\sigma/2)/(1-\sigma)], \tag{4.1}$$

which generates an explicit condition of the validity of the adiabatic approximation,

$$\mu \leqslant (1-\sigma)/(1+\sigma/2) = 1-(3/2)\sigma+(3/4)\sigma^2+\cdots. \tag{4.2}$$

The corrections to the translational energy with respect to its zero-order expression $p_s^2/2$ can be obtained by substituting Eq. (3.5) or (4.1) into Eq. (3.6):

$$\varepsilon(s) = (p_s^2/2)(1+3\sigma/2+\mu+3\sigma\mu+15\sigma^2/8+\mu^2+\cdots). \tag{4.3}$$

We now try to specify the physical meaning of parameters σ and μ.

B. Dynamic coupling and dividing surfaces

It is possible to give a clear and intuitive meaning to the adiabatic parameter σ. The vibrational energy E_{vib} can be expressed either as $J\omega$ or as $(1/2)\omega^2 x_m^2$, where x_m is the (mass weighted) amplitude of the harmonic vibration. Then, from Eq. (3.2),

$$\sigma(\mathrm{s,J}) = [x_m(s,J)/R(s)]^2, \tag{4.4}$$

where $R(s)=\kappa(s)^{-1}$ is the radius of curvature of the reaction path. Therefore, a necessary condition of validity of the adiabatic approximation for a particular value of J is that the amplitude of the vibrations normal to the reaction path should be much smaller than the radius of curvature of the reaction path (both being expressed in mass-weighted units). Now, in the inner region, close to the bottom of the potential well, the reaction path is strongly curved and R is very small. The internal energy is mostly kinetic. The coupling parameter σ is then very large and there is no restriction to energy flow, as should be the case in the statistical region. The opposite must be true in the third region of the reaction path where the adiabatic approximation is valid.

On this basis, a criterion for locating a particular dividing surface in barrierless reactions can be proposed. The criterion is based, not on the geometrical properties of the potential-energy surface, but on the validity of the adiabatic approximation. The value $\sigma=1$ indicates the onset of the range where the adiabatic approximation starts to be mathematically possible. However, this value is too large to restrict interaction between translation and vibration. A better choice to locate the onset of genuine adiabatic decoupling might be a value s^* at which, say, $\sigma=0.2$. Then, the onset of the domain where the reaction coordinate is decoupled would be characterized by the condition $x_m(s^*) \approx \sqrt{0.2}R(s^*)$.

Of course, this criterion does not generate the sharply defined dividing surface postulated by the conventional transition state theory. It should be best interpreted as defining a fuzzy region separating two regions of space: one where energy flows freely, and one where the adiabatic invariance hinders energy exchange between the reaction coordinate and the perpendicular vibrations.

Other theories[4–6,38] have been developed where transitional modes are assumed to be nonadiabatic in a certain range and adiabatic beyond a certain value of the reaction coordinate. The present treatment provides its own specification for choosing this value.

To illustrate further the difficulty in defining a sharp dividing surface, note that the proposed criterion is J dependent. This concurs with other statistical theories of unimolecular reactions, as the variational transition state theory[1,4,9,23–25] or SACM,[32–36] in pointing out that each dissociation channel is characterized by its own generalized transition state and is to be analyzed individually. This is true even when the overall rotational degree of freedom is disregarded.

C. Static coupling and influence of the internal energy

Parameter μ, defined in Eq. (3.7), controls the static coupling. Apart from a factor of 1/16, μ measures the ratio between the diagonal part of the nonadiabatic coupling[27] and the energy ε along the reaction coordinate.

Interestingly, the three quantities which make up the ratio $J\omega'/\omega$ often vary in a concerted way. At a given internal energy, a high-frequency stretching mode (large ω) has a low classical action J. Furthermore, its frequency often has a characteristic value which usually varies little along the reaction path (small ω'). Reversing the argument, translational energy is expected to flow preferentially into transitional modes.

However, the magnitude of μ also depends on the properties of the other subsystem. By definition, μ is a decreasing function of ε. This contrasts with the usual requirement that the translational motion be slow for the adiabatic approximation to hold.

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A simple expression obtains in a typical situation where, in the third region, the vibrational frequency ω varies exponentially as a function of the reaction coordinate s,

$$\omega(s) = \omega_0 \exp(s/s_r), \tag{4.5}$$

with s_r either positive or negative. A large value of s_r implies a stiff vibration. Conversely, s_r should be small for transitional modes. Then, Eq. (3.7) transforms into

$$\mu(s) = J^2/[16\ \varepsilon(s)s_r^2]. \tag{4.6}$$

In this expression, the properties of the two subsystems are mixed. However, μ is not a Massey parameter because it does not express the ratio between the range of a potential and the distance traveled during a vibrational period, or the ratio between two different time scales.

D. Conclusions

The appropriate way to discuss the validity of the adiabatic approximation in the study of exit-channel dynamics is not in terms of a decoupling between two subsystems, one fast and one slow, in spite of the fact that the derivation of Eq. (3.3) from Eq. (3.1) has been justified by the shortness of the vibrational period.

The ratio of the actual classical velocities of the translational and vibrational motions appears nowhere. Note that the latter concept is not very appropriate for the present purposes: during a vibrational period, the velocity varies between zero (at the turning point) and a maximum value (at the equilibrium position). The use of an averaged velocity $\bar{v}=(J\omega)^{1/2}$, which results from the equipartition theory, does not improve the analysis because what is involved in both parameters σ and μ is the ratio J/ω [Eqs. (3.2) and (3.7)]. This makes any attempt to relate them to the concept of vibrational velocity problematic.

V. THE MULTIDIMENSIONAL CASE

Miller *et al.* have derived the expression of the classical multidimensional Hamiltonian in terms of mass-weighted normal coordinates Q_k and conjugate momenta P_k [Eq. (2.17) of Ref. 27]. These coordinates can be replaced by harmonic action-angle coordinates J_k and q_k. The canonical transformation involves a F_2-type generating function and has been fully described by these authors. This leads to an action-angle Hamiltonian which generalizes Eq. (3.1). It now contains matrix elements $B_{k\ell}(s)$ that result from the Coriolis-type coupling among the different N vibrational modes induced by the motion along the curved reaction coordinate. The matrix elements $\kappa_k(s)$ describe the partitioning of the curvature among the N vibrational modes. Assuming small values of the different coupling elements $\kappa_k(s)$, $\omega_k'(s)$, and $B_{k\ell}(s)$, this Hamiltonian can be expressed as an awkward multidimensional series expansion. However, many terms vanish upon averaging over the angles q_k. This leads to the vibrationally adiabatic Hamiltonian for the s motion, which, when limited to its leading terms, reads

$$\begin{aligned} H_{\mathrm{ad}}(s,p_s|\{J_k\}) = {} & \frac{1}{2}p_s^2\left[1+\frac{3}{2}\sum_k^N \sigma_k(s)\right] \\ & + \frac{1}{16}\sum_k^N\left[\frac{J_k\omega_k'(s)}{\omega_k(s)}\right]^2 \\ & + \frac{1}{2}\sum_k^N\sum_\ell^N B_{k\ell}(s)^2 J_k J_\ell \frac{\omega_\ell(s)}{\omega_k(s)} \\ & + \sum_k^N J_k\omega_k(s) + V(s), \end{aligned} \tag{5.1}$$

where

$$\sigma_k(s) = 2\ J_k\kappa_k(s)^2/\omega_k(s). \tag{5.2}$$

Just as done previously in Sec. III, the value of p_s^{ad} is derived from the equation $H_{\mathrm{ad}}=E$, and is substituted in Eqs. (3.9) and (3.10). This leads to the accuracy index of the adiabatic approximation,

$$\begin{aligned} \Delta p_s = {} & \frac{3}{4}\sum_k^N \sigma_k(s) + \frac{1}{2}\sum_k^N \mu_k(s) \\ & + \frac{1}{4\varepsilon(s)}\sum_k^N\sum_\ell^N B_{k\ell}(s)^2 J_k J_\ell \frac{\omega_\ell(s)}{\omega_k(s)}, \end{aligned} \tag{5.3}$$

where

$$\mu_k(s) = \frac{1}{16\varepsilon(s)}\sum_k^N\left[\frac{J_k\omega_k'(s)}{\omega_k(s)}\right]^2 \tag{5.4}$$

and

$$\varepsilon(s) = E - V(s) - \sum_k^N J_k\omega_k(s). \tag{5.5}$$

VI. ADIABATIC APPROXIMATION IN POLYATOMIC MOLECULES

Oudejans *et al.*[8] have drawn a number of key observations from photodissociation experiments. We now select a few quotations from their article and show that one can draw a parallel between their analysis and Eq. (5.3).

Each term of the summation in (5.3) is positive: no fortuitous cancellation is to be expected. Each term decreases regularly as s increases, but at its own pace. Quoting from Ref. 8: "It is doubtful that the onset of adiabaticity will occur at the same region of the reaction path for all modes."

In a polyatomic system, the reaction coordinate is preferentially coupled to vibrational modes characterized by large values of the coupling parameters σ_k and μ_k. It follows from Eqs. (3.7), (4.4), and (5.4) that translational energy can be expected to flow preferentially into soft modes characterized by large amplitudes (dynamic coupling) and by a rapidly variable frequency along the reaction path (static coupling). This accounts for the preferential couplings to transitional modes. Stiff modes, on the other hand, tend to evolve adiabatically. Quoting again from Ref. 8, "The theory must allow a hierarchy of couplings and adiabaticities for the

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vibrational and rotational degrees of freedom." "It is clear that, as one might expect, the high-frequency modes of the system (high-energy vibrations and rotations) tend to evolve adiabatically, while the lower-frequency (transitional) modes display considerable nonadiabatic couplings."

Note finally that Eq. (5.3), seen as a criterion for the validity of the adiabatic approximation is based on the similarity between two phase portraits: that derived from the adiabatic Hamiltonian in (5.1) and that derived from the more general Hamiltonian after projection on the subspace (s,p_s). Therefore, a value $\Delta p_s \ll 1$ indicates separability between the reaction coordinate and the bath of orthogonal oscillators. However, it does not follow that each particular action J_k is individually conserved. No indication whatever on a possible energy redistribution among the N oscillators can be derived from the smallness of Δp_s.

VII. THE MAXIMUM ENTROPY METHOD

A very successful analysis of product energy distributions,[39–42] in particular of KERDs,[43–49] is provided by the maximum entropy method (MEM). The theory starts from the concept of prior distribution, which is defined as a limiting case where all available quantum states of the pair of fragments are populated with equal probability. Thus, the prior distribution represents the full statistical situation, i.e., the hypothetical KERD that would have been obtained in the case of totally unconstrained dynamics (excepting the obvious constraint resulting from energy conservation). The method then establishes that any discrepancy between an experimental KERD $P(\varepsilon|E)$ and the prior distribution $P^0(\varepsilon|E)$ can be expressed in the form

$$P(\varepsilon|E) = P^0(\varepsilon|E)\exp(-\lambda_0)\exp(-\lambda_1 A_1). \tag{7.1}$$

In this equation, E denotes the excess internal energy with respect to the dissociation asymptote, A_1 is an observable related to the dynamical constraint that prevents the reaction from being statistical, while λ_0 and λ_1 are Lagrange multipliers. Note that Eq. (7.1) is really a one-parameter expression, because λ_0 is determined by the condition that the distributions $P(\varepsilon|E)$ and $P^0(\varepsilon|E)$ should both be normalized.

The presence of dynamical constraints leads to incomplete phase-space sampling and reduces the information-theoretic entropy S. In the MEM language, this reduction is measured by a so-called entropy deficiency DS equal to[39–49]

$$\mathrm{DS} = -\lambda_0 - \lambda_1\langle A_1\rangle, \tag{7.2}$$

where $\langle A_1\rangle$ denotes the average value of A_1,

$$\langle A_1\rangle = \int_0^E A_1 P(\varepsilon|E)d\varepsilon. \tag{7.3}$$

When defined with a fine-grained description of the states, S is a constant of motion.[41] Hence, S and DS are determined by the initial conditions.[41]

In the present case, the MEM has to incorporate a dynamical constraint resulting from the adiabatic separation between the reaction path coordinate s and the orthogonal degrees of freedom within a one-dimensional model describing the motion along the reaction path. Now, introducing a constraint in the dynamics of a system can be done at the level of either the equations of motion or at the level of the initial conditions. In the first case, an invariance principle is introduced (e.g., conservation of energy or of angular momentum). In the second case, it may be specified, e.g., that the initial excitation obeys the Franck-Condon principle.[50]

In the matter in hand, the nature of the observable A_1 involved in the constraint can be understood by applying Jacobi's form of the least action principle[51] to $H_{\mathrm{ad}}(s,p_s)$ [Eq. (3.3)]. The actual trajectory is required to minimize the integral

$$\int_{s_1}^{s_2} [H_{\mathrm{ad}}(s,p_s) - V_{\mathrm{eff}}(s)]^{1/2} ds = \min. \tag{7.4}$$

If the quantity $(H_{\mathrm{ad}} - V_{\mathrm{eff}})^{1/2} = \varepsilon^{1/2}$ is considered to be proportional to an "index of refraction," then Jacobi's principle is seen to be formally identical with Fermat's principle of geometrical optics. A description of collision dynamics in terms of this generalized refractive index has been proposed by several authors.[52–54]

In principle, Eq. (7.4) can be used everywhere to study the dynamics. However, its application has particularly clear consequences in the third region where the dynamics is well described by a one-dimensional Hamiltonian $H_{\mathrm{ad}}(s,p_s|J)$. In this case, ε becomes a translational energy along the reaction path, directly derivable from experiment. The application of Jacobi's principle is then straightforward because the position of both points s_1 and s_2 is well defined: both are lying on the reaction path.

Note that a variational principle confines itself with selecting classical trajectories out of all virtual paths. It cannot discriminate among possible classical trajectories. What Eq. (7.4) indicates is that in order to obey the equations of motion, restrictions must be imposed on the possible values of $\varepsilon^{1/2}$. Note furthermore that a restriction on the average $\langle\varepsilon^{1/2}\rangle$ does not imply any restriction on higher-order moments of the distribution.[40,50]

Therefore, when the dynamics is analyzed in the intermediate range where the adiabatic RPH model is valid and where the conditions for vibrational adiabaticity are fulfilled, the MEM selects the square root of the translational energy, $\varepsilon^{1/2}$, as the appropriate variable in terms of which the major correction to the statistical estimate can be expressed via Eq. (7.1). (By contrast, the Lagrange multipliers λ_0 and λ_1 are determined by the initial conditions.[41]) This accounts for the fact that, for barrierless dissociations of molecular cations in an ion beam, decaying in an energy range where the lifetime is on the microsecond time scale, KERDs are found in nearly all cases[43–49] to be satisfactorily described by the MEM equation,

$$P(\varepsilon|E) = P^0(\varepsilon|E)\exp(-\lambda_0)\exp(-\lambda_1\varepsilon^{1/2}). \tag{7.5}$$

Note, however, that there are exceptions to this rule. A potential barrier along the reaction path is usually associated with a structural reorganization. In that case, a simple expansion of the form in (7.1) or (7.5) is no longer sufficient because the conversion of the barrier strongly influences the KERD.[49] Additional constraints and Lagrange multipliers are

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then required to relate the latter to the prior distribution. Also, the experimental evidence is inconclusive for some reactions conducted at too high internal energies (dissociation of the pyridine and benzene cations studied at $E \approx 1.3$ eV).[48] Presumably, the RPH model is then outside its range of validity.[27,55]

It is particularly gratifying to note that the result of this analysis does not depend on the number of vibrational degrees of freedom. More than that: the partitioning of the vibrational energy among $3N-7$ oscillators reduces the quantum number (or the classical action) of each mode and therefore reduces the coupling parameters σ_i, thereby favoring vibrational adiabaticity.

A MEM analysis of experimental KERDs can also determine the value and especially the sign of the Lagrange multiplier λ_1. As shown by Eq. (7.5), a positive sign ($\lambda_1 > 0$) implies that the average translational energy $\langle\varepsilon\rangle$ [i.e., the first moment of the distribution $P(\varepsilon|E)$] is smaller than the statistical estimate. This is found to be the case for nearly all of the barrierless reactions studied so far. The interpretation is clear. The energy partitioning in the inner region is determined by statistical mechanics. Immediately after leaving that region, all degrees of freedom are in a state of equilibrium. Loosely speaking, they have the same temperature. As the system proceeds in the intermediate region, the translational energy $\varepsilon=(p_s^2/2)[1-\sigma(s)]^{-3/2}$ must decrease along the reaction coordinate. The reason is that the potential energy increases steadily while the adiabatic regime prevents vibrational energy from flowing into the reaction coordinate. Hence, the s subsystem gets colder, which implies $\lambda_1 > 0$.

VIII. CONCLUDING REMARKS

Energy is not always fully randomized in an activated molecule because of the existence of dynamical constraints. Their presence can be discerned by a MEM analysis based on the comparison between the experimental KERD and the prior distribution $P^0(\varepsilon|E)$.[39–42] Only a single one can be detected in the barrierless dissociation of molecular cations decaying on the microsecond time scale. It has been identified with $\varepsilon^{1/2}$ in nearly all cases studied so far.[43–49] This leads to the conclusion that, beyond the dividing surface roughly characterized by the condition $\sigma \leqslant 0.2$, adiabatic invariance decouples the reaction coordinate from the perpendicular degrees of freedom. The dynamics can then be described as a one-dimensional motion governed by the RPH expressed by (5.1).

In a more general context, note that two well-established statistical theories of unimolecular reactions (RRKM[1,2] and OTST[1,2,16,30,31]) were each formulated for a particular model. The former assumes short-range forces and strong intermode couplings whereas the validity of the latter is limited to long-range interactions and asymptotic values of the reaction coordinate. The RPH method analyzes the situation from a third vantage ground and the connection with the SACM is particularly fruitful.

When the basic assumptions of the RPH model[27,55] are fulfilled, the effective adiabatic channel energy curves postulated in the SACM can be constructed in a range where the reaction coordinate is moderately curved. This range is followed by the asymptotic region 4 where SACM assumes adiabatic behavior for the orbital and rotational states. Necessary conditions of validity of this assumption have been derived by Gridelet *et al.*[31] for an ion-induced dipole interaction and by Nikitin and co-workers[33–35] for an anisotropic long-range electrostatic interaction. During the transition between regions 3 and 4, the transitional modes transform from bending vibrations to rotations and orbital motion. Each region is thus characterized by its own degrees of freedom and its own set of quantum numbers. The correlation between both sets has been studied by Quack and Troe[56] and by Nikitin and Troe.[57]

However, the RPH theory is based on the simplest possible model. The vibrations are assumed to be harmonic and to be coupled by a Coriolis-type interaction. Certainly, more complicated situations exist where the potential energy requires the inclusion of anharmonic and of additional coupling terms. In such a case, the calculation of adiabatic channel potentials would require a more elaborate determination of the appropriate action-angle variables, which is not a trivial problem.

Nevertheless, the RPH model is thought to be sufficiently realistic to deduce at least the most important features that govern the adiabatic separation of translation and vibrations. Moreover, some parts of our analysis may be transferable to more elaborate models.

Some connection with quantum mechanics can be found in the work of Hose and Taylor.[58] These authors have given theoretical and experimental arguments for the existence of so-called extreme-motion states, which can be thought of as consisting of a highly excited anharmonic oscillator (in our case the reaction coordinate) accompanied by a set of harmonic oscillators in their ground vibrational state. These states are generally not strongly coupled to other zero-order states characterized by a more uniform distribution of the internal energy, especially if the excitation is localized in a high-frequency stiff mode. They are found to exist even in the continuum above dissociation. Furthermore, Hose and Taylor have shown that, as a result of a quantum version of the Kolmogorov-Arnold-Moser theorem,[51] such a situation implies the existence of a set of action variables J_k. The available experimental evidence[59,60] supports the validity of an adiabatic separation very similar to the one that has been presented here.

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