Roaming: A Phase Space Perspective

1. INTRODUCTION

The topic of roaming reactions has caused a re-examination of chemists' traditional ideas concerning the transformation from reactants to products in chemical reactions. This is clear from the provocative title of the review paper of Bowman & Suits (1): "Roaming reactions: the third way."

The notion of a roaming reaction was born after the spectacular success of Townsend et al. (2) in explaining some puzzling features of formaldehyde photodissociation (3). This work was made possible by the timely development of experimental and computational methods that could be employed in tandem, leading to significantly deeper understanding of the details of the reac-tion mechanism than had previously been possible. Since this pioneering work, there have been numerous review papers dealing with different aspects of roaming (4–9).

The focus and goals of this review are different from those of previous reviews. Although advances in experimental and computational methods have certainly played a significant role in our recognition of roaming phenomena, this recognition has in turn firmly pointed to a need for advances in the fundamental theory of reaction dynamics. When considering roaming dynamics, several questions commonly arise, such as: Is the dynamics statistical? Can transition state (TS) theory (TST) be applied to estimate roaming reaction rates? What role do saddle points on the potential energy surface (PES) play in explaining the behavior of roaming trajectories? How do we construct a dividing surface that is appropriate for describing the transformation from reactants to products for roaming trajectories? Can we define the roaming region of phase space associated with a transient roaming species?

In this review we outline the necessary theory required to provide answers to these questions, as well as tools for quantitative understanding and prediction in the context of roaming. We strongly advocate a phase space, as opposed to a configuration space, point of view for framing these questions. Consequently, we rely on recent advances in the theory of phase space structure in multimode systems and associated developments in reaction-rate theory from the dynamical systems point of view. A recent general review of this approach is given in Reference 10.

The present review is organized as follows: In Section 2, following a brief discussion of certain precursors to the roaming concept, we review the seminal work on roaming in formaldehyde (Section 2.2), which has served as a model for the description of roaming. A brief survey of some key experimental and theoretical works that have identified the roaming phenomenon (Section 2.3) is followed by an attempt to identify general characteristics of roaming (Section 2.4). In Section 3, we discuss some aspects of the energy landscape paradigm that play an important role in the description of roaming. This discussion leads naturally to a survey of the issues and concepts surrounding the phase space approach to reaction dynamics in Section 3.2. The review and discussion up to this point culminates in a formulation of a phase space characterization of the roaming region in Section 4.1. In Section 4.2, we highlight some important work of Chesnavich on ion–molecule reactions and Miller's "unified statistical theory." In Section 5, we return to formaldehyde and provide a phase space analysis of the reaction dynamics for a model with two degrees of freedom (DOFs). We show that, in phase space, roaming can be precisely characterized via a new dynamical mechanism, which we term shepherding (11). We compare and contrast our results with the recent work of Houston et al. (12) in Section 5.3. In Section 6, we consider some additional case studies of the roaming phenomenon, again drawn from our own work (13–15); these examples again force a consideration of the configuration space point of view versus the phase space point of view. In Section 7, we address the vexing question of the significance of so-called roaming saddles. The issue of the roaming saddle leads naturally to consideration of several important questions already raised: the dynamical significance of flat regions of the PES, statistical versus nonstatistical dynamics, the

validity of TST, and configuration space versus phase space descriptions of the dynamics. Section 8 summarizes and concludes with a discussion of some worthwhile future directions for research on roaming.

2. ROAMING, PAST AND PRESENT

2.1. Roaming Before "Roaming": An Example

With the benefit of hindsight, certain theoretical developments can be seen as precursors to the roaming concept: specifically, the phenomenon of transition-state switching (or competition) in ion–molecule reactions and Miller's unified statistical theory of reaction rates (see Section 4). It is also important to recall that reactions involving dynamics that avoids the minimum energy path (MEP), so-called non-MEP reactions, were extensively studied before the term "roaming" was coined (16–20).

As pointed out by Klippenstein et al. (21), an interesting example of the identification of a reaction mechanism that we would now recognize as roaming is found in the work of Audier & Morton (22) on the reaction

$$CH_3CH_2CH_2NH_3^+ \rightarrow CH_2CH_2CH_2 + NH_4^+. \quad 1.$$

Isotopic labeling experiments established that H-atom transfer to the NH^+_3 moiety takes place from all positions on the alkyl chain. On the basis of these experiments and of self-consistent field (SCF) electronic structure calculations, Audier & Morton concluded that Reaction 1 occurs via the complex

$$[CH_3CHCH_3^+ \ldots NH_3], \quad 2.$$

where the NH_3 fragment undergoes large-amplitude excursions and internal rotations (i.e, roams) in the presence of the $CH_3CHCH^+_3$ ion. Rice–Ramsperger–Kassel–Marcus (RRKM) theory calculations suggested that the lifetime of such a complex was ~100 ps (22).

The proposed intermediate complex is held together by ion–dipole and/or ion–induced dipole attraction. According to Audier & Morton, such complexes are "transient species in which charged and neutral fragments sojourn in the vicinity of one another even though they are not covalently bonded" (22, p. 1218).

2.2. Formaldehyde

The term "roaming" was first applied to chemical reactions in a 2004 study of the photodissoci-ation of formaldehyde by Townsend et al. (2). When excited by photons of sufficient energy, the formaldehyde molecule can dissociate via two channels: $H_2CO \rightarrow H + HCO$ (radical channel) or $H_2CO \rightarrow H_2 + CO$ (molecular channel). In earlier work, van Zee et al. (3) found that, above the energy threshold for the H + HCO dissociation channel, the CO rotational state distribu-tion exhibited an intriguing shoulder at lower rotational levels correlated with a hot vibrational distribution of H_2 coproduct. This observed product state distribution did not fit well with the traditional picture of the dissociation of formaldehyde via the well-characterized saddle point transition state for the molecular channel.

Using high-resolution state-resolved imaging measurements of the CO velocity distributions, Townsend et al. were able to distinguish two dissociation pathways to molecular products. The first proceeded through a standard transition state indicated by an index-one saddle point on the PES to produce rotationally excited CO and vibrationally cold H_2. The second pathway to dissociation to molecular products yielded rotationally cold CO and a highly vibrationally

excited H_2. The second pathway was explored with quasiclassical trajectory (QCT) calculations performed on a global PES for H_2CO. The trajectory results suggested that the second pathway to molecular products was characterized by a hydrogen atom exploring a large region of the PES before encountering the other hydrogen atom and undergoing a hydrogen abstraction mechanism, while never approaching the standard transition-state saddle point structure. This second pathway was termed roaming.

Since the seminal work on roaming by Townsend et al., a great deal of further work on the photodissociation of formaldehyde has been carried out (see Section 2.3), culminating in the recent tour de force of QCT analysis by Houston et al. (12) (see Section 5.3).

2.3. Other Examples of Roaming

Following the work of Townsend et al., the second example of roaming was identified in the photodissociation of acetaldehyde, CH_3CHO. This molecule was observed to dissociate to molecular products along the pathway $CH_3 + HCO \rightarrow CH_4 + CO$ in a manner sharing many of the characteristics of formaldehyde dissociation via roaming, where the hydrogen atom in formaldehyde roaming is replaced by a methyl group. However, whereas the standard transition-state pathway is the dominant pathway to molecular products for formaldehyde, the roaming pathway is dominant in acetaldehyde (23).

Following the formaldehyde and acetaldehyde work, there has been a flood of observations of roaming in chemical reactions. Rather than provide a comprehensive survey of the literature, in the **Supplemental Material** we provide a table summarizing this work, with references classified according to the following attributes:

Supplement

the reacting molecule;

whether the reaction is unimolecular or bimolecular;
whether the reaction is adiabatic or non-adiabatic;

the reaction initiation mechanism, e.g., photodissociation or collision;
gas phase or condensed phase;

the nature of the roaming entity, i.e., what detaches and reattaches to the core; for a theoretical paper, classical or quantum treatment.

There have also been a relatively large number of papers reviewing different aspects of roaming reactions in recent years (1, 4–6).

With such a large body of work on roaming in reactions, it is possible to identify the common molecular characteristics that are responsible for, or define, roaming dynamics. We consider this in Section 2.4.

2.4. Molecular Characteristics Associated with Roaming

As noted above, in the work of Townsend et al., molecular products created as a result of passage via the standard transition state (saddle point) are characterized by rotationally excited CO and vibrationally cold H_2. Contrastingly, molecular products created as a result of following the roaming pathway are characterized by rotationally cold CO and highly vibrationally excited H_2. Hence, for formaldehyde, roaming was originally distinguished by an energy partitioning criterion. This is a phase space criterion.

In recent years, however, a consensus has developed that the key molecular characteristic responsible for roaming is a flat region (or plateau) on the PES. (For formaldehyde, see 12; for

molecules in general, see 21.) Flat (slowly varying) regions of the PES are typical of long-range interactions between molecular fragments, and this idea has played a central role in the study of ion–molecule reactions. (See the work of Chesnavich described in detail in Section 4.2.) Flat regions of the PES also play an important role in the understanding of the reaction dynamics of certain organic molecules (see Section 3.2).

The manifestation of flat regions of the PES in phase space provides a natural dynamical definition of the roaming region, as discussed in more detail in Section 4.1 and explicitly for a 2-DOF model of formaldehyde in Section 5.2.

Describing reaction mechanisms in terms of features of the PES constitutes a configuration-space approach. Nevertheless, the concept of a chemical reaction is concerned with transformation or dynamics. An index-one saddle point on the PES results in a constriction or bottleneck in phase space [over a (problem-dependent) range of energies] that constrains trajectories in a way that can often be related directly to the reaction mechanism, e.g., by projecting reacting trajectories onto configuration space. However, in flat regions of the PES where forces are weak, there may not be any obvious potential energy signatures that influence the dynamics. Full understanding of dynamics then requires a phase space analysis, e.g., a consideration of how phase space structure constrains the motion of trajectories whose configuration space projections spend time in the flat regions of the PES.

In Section 3, we briefly review the energy landscape paradigm for chemical dynamics, one which is firmly based in configuration space rather than phase space (24, 25).

3. REACTION RATE THEORY: THE POTENTIAL LANDSCAPE PARADIGM AND PHASE SPACE APPROACHES

The concept of the PES (24, 25) remains the foundation of current theories of chemical dynamics and molecular physics in general. Even after decades of research, global potentials defined over the entire molecular configuration space are still available mainly only for triatomic and tetratomic molecules. For larger polyatomic species, the computational effort of quantum chemistry is mainly focused in locating critical (stationary) points (minima and saddles) and MEPs or on computing forces on the fly for QCT analysis (26).

The landscape paradigm asserts that knowledge of critical points provides a qualitative description of molecular dynamics, at least in the neighborhood of the potential extrema.

The standard picture in reaction dynamics is firmly based on the concept of the reaction coordinate (27), for example, the intrinsic reaction coordinate (IRC) (28). According to conventional wisdom, the IRC is the path a system follows (possibly modified by small fluctuations about this path) as reaction occurs. However, a 1976 paper by Pechukas (29) presaged some of the points that we make in this review. Pechukas (29, p. 1516) wrote: “There is no dynamical significance to a path of steepest descent. It is a convenient mathematical device to get from high ground, around the transition state, to low ground where the stable molecules are.”

3.1. The Potential Energy Landscape and Reaction Rate Theory

A comprehensive description of the so-called energy landscape paradigm is given in Reference 25. Here we note that energy refers to potential energy, in contrast to total (kinetic plus potential) energy, whose consideration is essential for a phase space analysis. The energy landscape approach is an attempt to understand dynamics in the context of the geometrical features of the PES, i.e., a configuration space model. In such a model, reaction rates are deduced by making some assumptions about the (classical) dynamics of the system.

In the most commonly used theories of this class, TST (30–32) and RRKM theory (33–36), one begins by searching for a hypothetical dividing surface (DS) separating reactant(s) from product(s). The key feature of the DS is that reactive trajectories—those making their way from reactants to products—cross it only once. By specifying the DS in terms of trajectory behavior, one is defining it to be an object in phase space (see Section 3.2), but the most common implementations of TST and RRKM theory characterize the DS in configuration space. The two theories compute the reaction rate constant in terms of the one-way flux through the DS.

The widespread adoption of the configuration space approach to reaction-rate theory is perhaps surprising, as two of the seminal papers responsible for the development of TST formulate the DS and the theory in phase space (32, 37). A central theme of this review is the importance of the phase space point of view in understanding the roaming phenomenon. This point is also emphasized by the statement of Shepler et al. (38, p. 9344) that "a more general definition of the TS is a minimum flux, phase space dividing surface, depending on both coordinates and momenta, and not simply a TS with a coordinate definition, as is usually done in the literature, separating reactants." With respect to roaming in particular, they further state (38, p. 9344): "It is an especially useful concept for reactions without a prominent saddle point and associated IRC." In Section 5.2, we describe how this approach is useful for understanding what makes trajectories roam in formaldehyde. It is important to note that the TS is the DS and not the saddle point. Some confusion on this point exists in the literature, and Harding et al. (39) emphasize the importance of being clear on this distinction in the context of the roaming phenomenon.

In order to compute reaction rates using the flux through the DS, RRKM theory explicitly invokes (and TST implicitly invokes) the statistical approximation (40–43). The statistical approximation assumes that the intramolecular vibration energy redistribution (IVR) in reacting molecules occurs very much faster than the time required for their conversion to products. It is this approximation that allows one to sidestep the calculation of explicit dynamics in RRKM and TST theories and that guarantees a single exponential decay for the reaction (the random lifetime assumption for the reactant part of the phase space; see 44). As a corollary, the claim that TST is an exact theory, given the correct DS (45), is valid only to the extent that the statistical approximation is also valid. If the random lifetime assumption fails, then TST also fails, even for a perfect DS.

As we have pointed out, the DS is fundamentally dynamical in nature: a surface in the phase space of the reacting system satisfying the local nonrecrossing condition (32). Locating such a surface in the high-dimensional phase space of a chemical system is not an easy task. Indeed, the DS is a $2(n-1)$-dimensional surface embedded within a $2n$-dimensional phase space for a system with n DOFs. The normally hyperbolic invariant manifold (NHIM) approach to TST provides a conceptual solution to this problem, and we discuss this in more detail in Section 3.2.

In the simplest versions of TST and RRKM theory, the DS is associated with a first-order saddle point on the PES, but in the variational versions of these theories (46–49), the location is chosen to minimize $k(E)$ (for variational RRKM theory) or $k(T)$ (for canonical variational TST). In the latter case, the optimal location will always turn out to be a first-order saddle point on the standard free-energy surface. One can also investigate the flux through surfaces specified by sets of parameters to determine optimal DSs in a given family of such surfaces. (Such surfaces have been applied to the roaming phenomenon; see 21.)

3.2. Periodic Orbit Dividing Surfaces, Normally Hyperbolic Invariant Manifolds, and Reaction-Rate Theory in Phase Space

As noted in Section 2.4, of key relevance to roaming is the fact that, for polyatomic molecules, one commonly encounters regions that are energetically rather flat. Technically, they are identified

as regions for which $\nabla V(\mathbf{q}) \approx 0$. The forces acting on the reacting system in such regions are often very weak and ineffective in changing the motion of the reacting system. These PES regions typically occur when there are hypo-coordinate atoms—for example, for molecular configurations corresponding to the homolysis of a bond.

If, when intact, the bond formed part of a ring, its cleavage would create a chain with hypo-coordinate atoms at the ends. In such cases, the ends of the chain often become capable of large-amplitude relative motions with little associated change in potential energy. Hoffmann et al. (50) were the first to suggest the generality of such phenomena, and, in recognition that the associated PES regions possessed characteristics somewhere between those of minima and saddle points, coined the term twixtyl for the molecular species so generated. The flat PES regions themselves have been likened to geological features: a caldera (51, 52) if access to the plateau is protected by barriers, or a mesa (53) if it is not.

If the bond suffering homolysis was not originally part of a ring, its cleavage would create two radical fragments, whose motions would now become relative translations and rotations, again typically with small associated changes in potential. This latter situation is exactly what happens in reactions exhibiting roaming.

In extended regions of a PES for which $\nabla V(\mathbf{q}) \approx 0$, where the forces are near zero, the dynamics will be heavily influenced by the momenta that the atoms possessed when they entered the plateau region. Inclusion of the momenta requires a phase space model.

Critical points on the PES do have significance in phase space: They are the equilibrium points for zero momentum. They continue to have influence for nonzero momentum, however, for a range of energies above the energy of the equilibrium point. In particular, there has been a great deal of recent work describing phase space signatures of index-one saddles on the PES. These are relevant to reaction dynamics (see, for example, 10, 54–56). More recently, index-two (57–59) and higher-index (60) saddles have also been studied (see 61–63).

The construction of a DS separating the phase space into two parts, reactants and prod-ucts, has been the subject of many studies. As we have emphasized, the DS is in general a sur-face in phase space, and the lack of a firm theoretical basis for construction of such surfaces for systems with ≥ 3 DOFs has until recently been a major obstacle in the development of the theory.

In phase space, the role of the saddle point is played by an invariant manifold of saddle sta-bility type, the NHIM (64–66). In order to fully understand the NHIM and its role in reaction rate theory, it is useful to begin with a precursor concept: the periodic orbit dividing surface or (PODS).

For systems with 2 DOFs described by a natural Hamiltonian, kinetic plus potential energy, the problem of constructing the DS in phase space was solved during the 1970s by Pechukas and colleagues (45, 67–69). They showed that the DS at a specific energy is intimately related to an invariant phase space object, an unstable periodic orbit (PO). The PO defines (i.e., is the boundary of) the bottleneck in phase space through which the reaction occurs, and the DS that intersects trajectories evolving from reactants to products can be shown to have the topology of a hemisphere in phase space whose boundary is the PO (55, 70). The same construction can be carried out for a DS intersecting trajectories traveling from products to reactants, and these two hemispheres form a sphere of which the PO is the equator.

Generalization of the above construction to higher-dimensional systems has been a major question in TST and has only rather recently received a satisfactory answer (55, 70). The key difficulty concerns the higher-dimensional analog of the unstable PO used in the 2-DOF problem for the construction of the DS. In his 1981 review of TST, Pechukas (48, p. 161) wrote: “It is easy to guess that generalized transition states in problems with more degrees of freedom must be

unstable invariant classical manifolds of the appropriate dimension, . . . but to our knowledge no calculations have been done."

This conjecture of Pechukas has indeed turned out to be correct (provided we interpret "transition state" as the DS associated with such invariant objects). Results from dynamical systems theory show that transport in phase space is controlled by various high-dimensional manifolds, NHIMs, that are the natural generalization of the unstable PO of the 2-DOF case (10). Normal hyperbolicity of these invariant manifolds means that they are, in a precise sense, structurally stable, and they possess stable and unstable invariant manifolds that govern the transport in phase space (71). Existence theorems for NHIMs are well established (71).

For 2-DOF systems, the NHIM is simply an unstable PO. For a fixed-energy system with $n > 2$ DOFs, the NHIM has the topology of a $(2n - 3)$-dimensional sphere. This $(2n - 3)$-dimensional sphere is the equator of a $(2n - 2)$-dimensional sphere that constitutes the DS. The DS divides the $(2n - 1)$-dimensional energy surface into two parts, reactants and products, and one can show that it is a surface of minimal flux (70).

The NHIM approach to TST consists of constructing DSs for the reaction studied built from NHIMs, and ensures a rigorous realization of the local non-recrossing property. Once these geometrical objects (NHIM and DS) are computed the reactive flux from reactant to products through the DS can easily be expressed as the integral of a flux form over the DS. Furthermore, it is possible to sample the DS and use this knowledge to propagate classical trajectories initiated at the TS (DS).

One route to the computation of NHIMs and their associated DSs for systems with ≥3 DOFs involves application of normal-form theory to the Hamiltonian (10, 72). The idea is to find a set of canonical coordinates by means of canonical transformations that put the Hamiltonian of the system into a simple form in a neighborhood of an equilibrium point of saddle–center–$\cdots$–center type (an equilibrium point at which the linearized vector field has one pair of real eigenvalues and $n - 1$ pairs of imaginary eigenvalues for a system of n DOFs). The simplicity comes from the fact that, under generic nonresonance conditions among the imaginary frequencies at the saddle point, one can construct an integrable system valid in the neighborhood of the equilibrium point and thereby describe the dynamics in this neighborhood very simply. The geometrical structures that govern reaction dynamics are thus revealed (10).

Fundamental theorems assure the existence of these phase space structures and invariant manifolds for a range of energies above that of the saddle (66). However, the precise extent of this range, as well as the nature and consequences of any bifurcations of the phase space structures and invariant manifolds that might occur as energy is increased, is not known and is a topic of continuing research (73–76).

Although work relating phase space structures and invariant manifolds to saddle points on the PES has provided new insights and techniques for studying reaction dynamics (10, 54–56), it by no means exhausts all of the rich possibilities of dynamical phenomena associated with reactions. In fact, the roaming phenomenon calls into question the utility of concepts such as the conventional reaction path and/or transition state (1, 2, 4–6, 16, 17, 23, 38, 77) and provides further motivation for phase space approaches. There are important classes of chemical reactions, such as ion–molecule reactions and association reactions in barrierless systems, for which the TS (DS) is not necessarily directly associated with the presence of a saddle point on the PES. Such TSs might be generated dynamically, and so are associated with critical points of the amended or effective potential, which includes centrifugal contributions to the energy (78–80).

The phenomenon of TS switching in ion–molecule reactions (81–83) provides a good example of the dynamical complexity possible in such systems, and we address this question in Section 4.

4. PHASE SPACE PERSPECTIVE ON ROAMING

4.1. The Roaming Region: Generalities

Audier & Morton's (22) characterization quoted above captures the essential nature of many intermediates in which roaming putatively occurs. This picture of a roaming intermediate naturally invites the question: How can we characterize the associated roaming region? Such a characterization should be based on inherent features of the system dynamics, i.e., phase space structure, rather than on arbitrary boundaries drawn in configuration space. Strictly speaking, such a roaming re-gion should be defined as a $(2n - 1)$-dimensional constant-energy subregion of the $2n$-dimensional molecular phase space. This roaming region will then, presumably, have boundaries, which are $(2n - 2)$-dimensional surfaces in phase space: These boundaries are DSs, or phase space portals, through which activated molecules enter and leave the roaming region. In other words, they are TSs for the reactions where the roaming species is a reactant or product. [Kinetic models invoking rates of passage in and out of the roaming region have been developed by Harding et al. (39) and Houston et al. (12); see Section 5.3.]

Roughly speaking (for more details, see Section 4.2), for dissociation reactions involving roaming, there are two types of DS. One type of DS is located at the generalized centrifugal barrier (48) associated with relative rotation of the separating fragments; this is called the loose or outer transition state (OTS). Dynamically defined DSs such as the OTS arise whenever one molecular fragment rotates relatively freely with respect to the other (80). The other type of DS is associated with passage into and out of the roaming region at smaller interfragment distances than the OTS; this is an example of a so-called tight transition state (TTS).

In our view, then, the roaming region of phase space is by definition demarcated by the OTS and the TTSs (there may be several). Given this conceptual model, it is possible to discuss the kinetics of, for example, formation and decay of roaming species (see also 12, 21).

Kinetic models for such situations have been discussed by Miller (46) in his unified statistical theory of reaction rates. This theory is a general framework for considering reactions where several DSs are relevant for determining the overall rate of capture, for example. As discussed in Section 4.2, this theory is applicable to the case of TS switching in ion–molecule reactions, which is in our view a prototypical case of roaming (82).

4.2. Ion–Molecule Reactions and the Unified Statistical Theory

As we have noted, a common characteristic of systems exhibiting roaming reactions studied so far is the presence of long-range attractive interactions between the dissociating fragments. This characteristic is typical of ion–molecule reactions, and roaming is thus expected to be at play in these reactions.

The theory of ion–molecule reactions has a long history going back to Langevin (84), who investigated the interaction between an ion and a neutral molecule in the gas phase and derived an expression for ion–molecule collisional capture rates. Assuming an isotropic long-range attraction (for example, r^{-4}), the capture cross section can be computed for 2-body systems as the flux through the DS associated with the OTS, which is bounded by an orbiting trajectory (PO) located at the centrifugal barrier. Further developments along these lines are discussed in References 45, 80, 82, 85, and 86.

Note that capture theories, by definition, only compute the rate of passage through the DS associated with the OTS. The subsequent fate of captured species is not treated; it is often assumed that reaction follows with probability unity.

There has been much debate in the literature concerning the interpretation of experimental results on ion–molecule reactions. Some results support a model for reactions taking place via the OTS, whereas others suggest that the reaction operates through a TTS (for a review, see 82). In order to explain this puzzling situation, the concept of transition state switching was developed (82), in which both kinds of TS (TTS and OTS) are present and the relative fluxes determine the overall reaction rate. This is precisely the kind of dynamical situation treated by Miller's (46) unified statistical theory, where it is assumed that the dynamics in the phase space regions bounded by the relevant set of DSs is entirely statistical, so a kinetic scheme can be formulated for the overall rate of reaction.

The minimal flux requirement for a DS in TST can be cast as the condition of a minimum in the sum of states at the DS. As we move along some reaction coordinate from reactants to products, two effects determine the sum of states in the DS (46). First, as we move to the dissociation products, the potential energy rises monotonically (for a barrierless dissociation), and hence the available kinetic energy decreases, which has the effect of lowering the sum of states. Second, there is a lowering of the vibrational frequencies at the DS that tends to increase the sum of states. Competition between these two effects can result in a minimum in the sum of states located at some value of the reaction coordinate. This minimum has been called an entropic barrier for the reaction, or a TTS.

By contrast, in the orbiting model of complex formation, the DS is located at the centrifugal barrier induced by the effective potential (the orbiting TS) (46, 80, 82). In general, the TTS and OTS are not located at the same position along the reaction coordinate, so one might ask which of these two DSs should be used to compute the rate of the reaction. This problem gives rise to the theory of multiple TSs; in the Chesnavich (81–83) model, both TSs (DSs) exist simultaneously and the actual TS (DS) for the computation of the reaction rate in a naive TST calculation is the one giving the minimal flux or, equivalently, the minimal sum of states. As already noted, Miller's (46) approach provides a unified theory appropriate when the fluxes associated with each DS are of comparable magnitude.

Chesnavich (83) presented a simple model to illustrate the concept of TS switching in the reaction $CH^+_4 \rightarrow CH^+_3 + H$. (For related work in the context of variational TST, see 87.) This relatively simple model has all the ingredients required to manifest essential aspects of the roaming effect.

In our own work (88, 89), we have revisited the Chesnavich model in light of recent developments in TST. For barrierless systems such as ion–molecule reactions, the concepts of OTS and TTS can be clearly formulated in terms of well-defined phase space geometrical objects (for recent work on the phase space description of OTSs, see 80). We demonstrated how OTSs and TTSs can be identified with well-defined phase space DSs attached to NHIMs.

5. ROAMING IN FORMALDEHYDE

In the previous section, we discussed the notions of OTS and TTS in the context of a reaction occurring without a potential barrier. We also discussed how the NHIM approach to TST pro-vides a rigorous way of constructing a DS that satisfies the local no-recrossing requirement of TST. In this section, we show how the approach can be explicitly implemented for formaldehyde and used to answer the question: What is the mechanism that distinguishes between trajectories that roam and trajectories that dissociate to radical products? We show that the phase space ap-proach provides an answer that could not be deduced from configuration space considerations alone.

5.1. A Model Hamiltonian

We begin by describing a model 2-DOF Hamiltonian derived by Chesnavich (83) that contains the essential features of this problem:

$$H = \frac{p_R^2}{2\mu} + \frac{p_\theta^2}{2}\left(\frac{1}{I} + \frac{1}{\mu R^2}\right) + V(R, \theta). \quad (3)$$

The Hamiltonian in Equation 3 describes the motion of a hydrogen atom in the vicinity of a rigid core. Here, R is the distance between the center of mass of the rigid fragment and the hydrogen atom. The coordinate θ describes the relative orientation of the two fragments in a plane. The momenta conjugate to these coordinates are p_R and p_θ, respectively, and μ is the reduced mass of the system and I is the moment of inertia of the rigid fragment. The potential $V(R, \theta)$ describes the so-called transitional or bending mode.

This Hamiltonian describes both the Chesnavich (83) model and our two-dimensional planar model for roaming in formaldehyde (11).

5.2. Formaldehyde Revisited: Why Do Trajectories Roam?

We now turn to the prototypical roaming system, formaldehyde (2), and consider hydrogen atom roaming in formaldehyde decomposition from a phase space perspective (11).

The reduced 2-DOF model in Equation 3 describes the dynamics of a hydrogen atom moving with respect to a rigid HCO fragment. The reduced potential energy function $V(R, \theta)$ is computed from the full six-dimensional PES produced by Bowman and coworkers (90). The PES and the coordinate system used are shown in **Figure 1**. This model describes the long-range part of the potential and is appropriate for investigating the dissociation of formaldehyde into the radical products H + HCO (indicated by the R coordinate becoming large) as well as the molecular product channel $H_2 \ldots CO$.

The roaming phenomenon is manifested as follows. Trajectories initiated in the formaldehyde well leave the well and are apparently on a path to dissociate to the radical products H + HCO. In the course of their evolution, however, the roaming trajectories deviate from this path and the hydrogen atom rotates around the HCO fragment before binding with the other hydrogen atom and finally dissociating to H_2 + CO.

To analyze the questions raised above, we first identify the relevant reactive events and then determine the unstable POs (NHIMs for 2-DOF systems). Using these POs we construct DSs, the crossing of which defines these reactive events. In one relevant reactive event, the formalde-hyde molecule breaks into the radical products H + HCO. The PO identified with this event (which we denote by PO_{OTS}) is associated with the centrifugal barrier. PO_{OTS} is at a large value of R, with R essentially constant and with θ making a full cycle from 0 to 2π. In other words, the roaming hydrogen atom rotates around the HCO fragment at a large value of R. Another reactive event occurs when the system escapes from the formaldehyde well and reaches the flat region of the PES, i.e., the roaming region. In our model, this occurs for $R \approx 6$–8 au and $\theta \approx 0$–2 rad. We have located an unstable PO (denoted by PO_{TTS1}) that defines the DS for passage from formaldehyde to the complex HCO · · · H. The final reactive event that we con-sider consists in the binding of the two hydrogen atoms just before the molecule breaks into the molecular products, H_2 + CO. The PO defining the DS for this event (denoted by PO_{TTS2}) is similar to the one just described and is located in approximately the same range of the R coordi-nate, with $\theta \approx 4.5$–6 rad. **Figure 2** shows the projections of PO_{OTS}, PO_{TTS1}, and PO_{TTS2} onto configuration space, as well as the contours of the PES and a PO called PO_{ROT} that we discuss below.

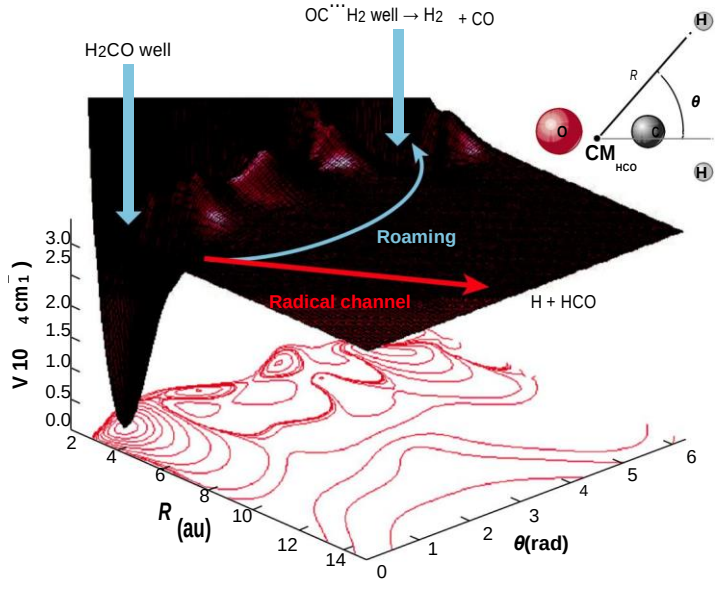

Figure 1

Potential energy surface with two degrees of freedom and coordinates employed in the reduced-dimensional model of formaldehyde.

Each of the POs is 1D and defines a 2D DS; these DSs serve to partition the 3D constant-energy surface. Each of the three POs we have identified belongs to a family of POs that exists for a range of energies. For our study, we have located the POs at an energy just above the threshold for the dissociation to radical products H + HCO.

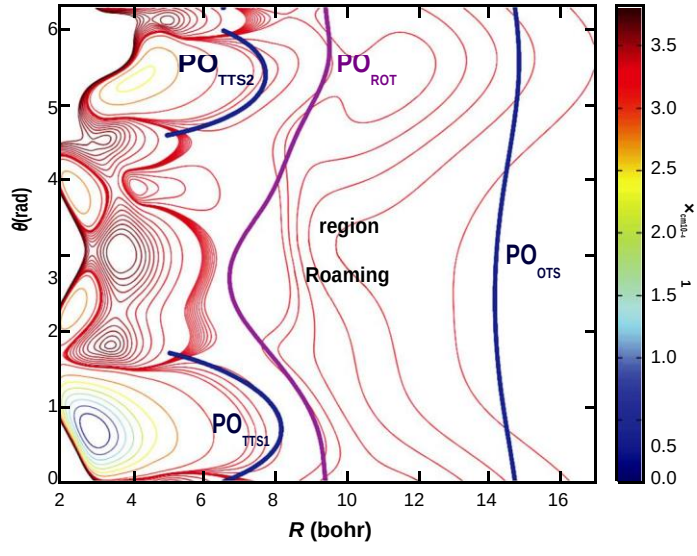

Figure 2

POs associated with DSs that describe different reactive events in formaldehyde decomposition. A resonant PO in the roaming region is also shown. Abbreviations: DS, dividing surface; PO, periodic orbit.

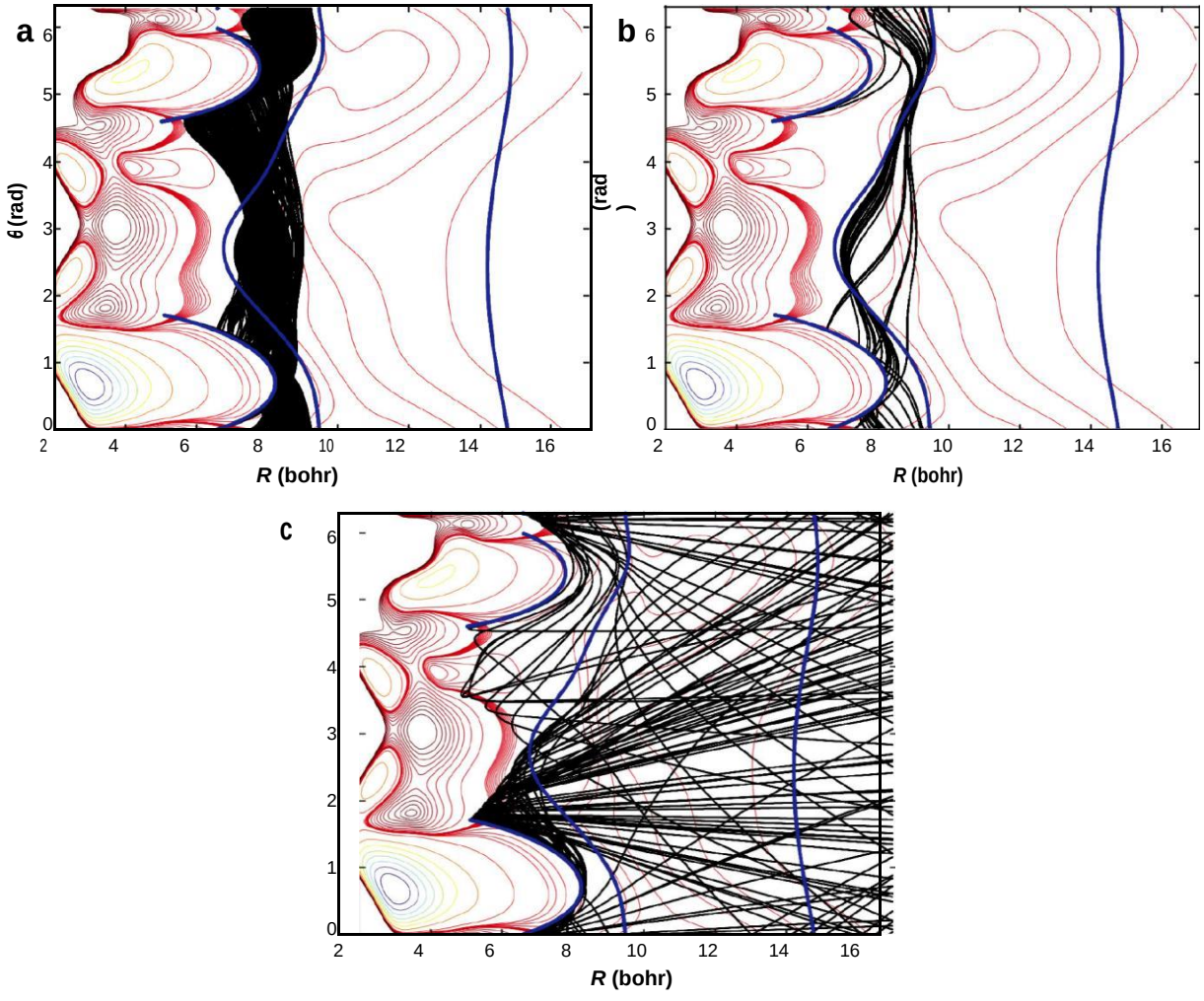

Figure 3

Trajectory propagation from the dividing surface. (*a*) Roaming trajectories. (*b*) Trajectories returning to the formaldehyde well. (*c*) H **+** HCO trajectories.

To investigate the dynamics of formaldehyde dissociation, we sampled the DS attached to PO_{TTS1} (the PO associated with the reactive event $H_2CO \rightarrow HCO \cdot\cdot\cdot H$). We then propagated the trajectories until they crossed the DSs associated with the other POs (or the same PO). Roaming trajectories are those initiated on the DS controlling the escape from the formaldehyde well and ending up in the $H_2 \cdot\cdot\cdot CO$ well by crossing the DS associated with PO_{TTS2} (**Figure 3*a***). Similarly, the system has completed the reaction $HCO \cdot\cdot\cdot H \rightarrow H_2CO$ when the trajectories cross the backward DS associated with PO_{TTS1} (**Figure 3*b***). Finally, the reaction $HCO \cdot\cdot\cdot H \rightarrow H$ **+** HCO occurs when the system crosses the DS associated with PO_{OTS} at a large value of *R* (**Figure 3*c***).

For trajectories initiated on the DS controlling the escape from the formaldehyde well, there are therefore three possible outcomes: the roaming behavior just described, a return to the formaldehyde well by recrossing the other hemisphere of the DS from which the trajectories

were initiated, and dissociation to the radical product by crossing the DS at a large value of *R*. Those trajectories that end up dissociating to H + HCO can exhibit several turning points in *R* with an extended range in angle θ before crossing the DS at large *R*; such trajectories orbit around HCO before producing the radical products.

To identify the dynamical mechanism that causes roaming trajectories to turn in the θ direction instead of evolving directly to the radical products, we must consider the dynamics in the region where a trajectory has the three possible fates. This is the roaming region bounded by the three DSs associated with the PO_{TTS1}, PO_{TTS2}, and PO_{OTS} discussed in Section 4.1. The roaming region is associated with the flat region of the PES where the dynamical complex HCO · · · H is defined (88, 89). In this region, the molecule is not yet dissociated, and couplings between the two DOFs are still present which enable the system to transfer energy between these DOFs. Note that there is no arbitrariness in our definition of the roaming region once we have identified the relevant DSs.

Figure 3*a* shows a relatively small spread of roaming trajectories in configuration space, in the range $R \approx 6.5$–9.5 au. The roaming trajectories appear to approximately follow a nearby orbiting PO that we call PO_{ROT} (see **Figure 2**). From PO_{ROT}, which passes directly through the roaming region, emerge the phase space structures that cause the hydrogen atom to roam.

Computation of the (2D) stable and unstable manifolds associated with PO_{ROT} shows that these surfaces intersect to form a phase space conduit that envelops the roaming trajectories and leads them to particular regions of phase space. This phase space shepherding is the mechanism for transferring energy from the radial to the angular mode. The series of 2D surfaces of section at different values of θ shown in **Figure 4** strikingly reveal the influence of these manifolds on the roaming trajectories: They are trapped in a region bounded by the stable and unstable manifolds of the PO and extending to the intersection point of the stable and unstable manifolds of PO_{ROT}, which is referred to as a homoclinic point. The area confined by the stable and unstable manifolds of PO_{ROT} is conserved, but it does change shape as θ varies. In fact, **Figure 4** shows that, as θ increases, this region deforms and moves toward the DS controlling access to the H_2 · · · CO well. This is the phase space mechanism for energy to be transferred between the two DOFs and for trajectories to be shepherded from the formaldehyde well, through the roaming region, and into the H_2 · · · CO well.

Such a mechanism could not have been discovered through a purely configuration space analysis. It is intrinsic to phase space. Such pictures of phase space transport involving turnstiles and lobes have a long history in studies of phase space transport (91). In a series of important pa-pers, Davis, Gray, Skodje, and Rice applied these ideas to a variety of 2-DOF models of chemical reaction dynamics (for a review, see 92).

Roaming in formaldehyde has been treated by statistical theories (21, 93). Our findings indicate that the dynamics in the roaming region in our model is nonstatistical. As the basic assumptions of TST are not fulfilled in the roaming region, resorting to a dynamical approach to predict rates for this system may be required.

5.3. Roaming Under the Microscope

Houston et al. (12) recently carried out classical trajectory calculations for formaldehyde in the full-dimensional space and presented a detailed analysis of the roaming trajectories. In this work, the motion of the remote hydrogen with respect to the CO diatom is studied by projecting the trajectories onto spherical coordinate configuration space (R, θ , φ). *R* is the distance from the center of mass of CO to the furthest hydrogen atom and φ and θ are azimuthal and polar angles, respectively.

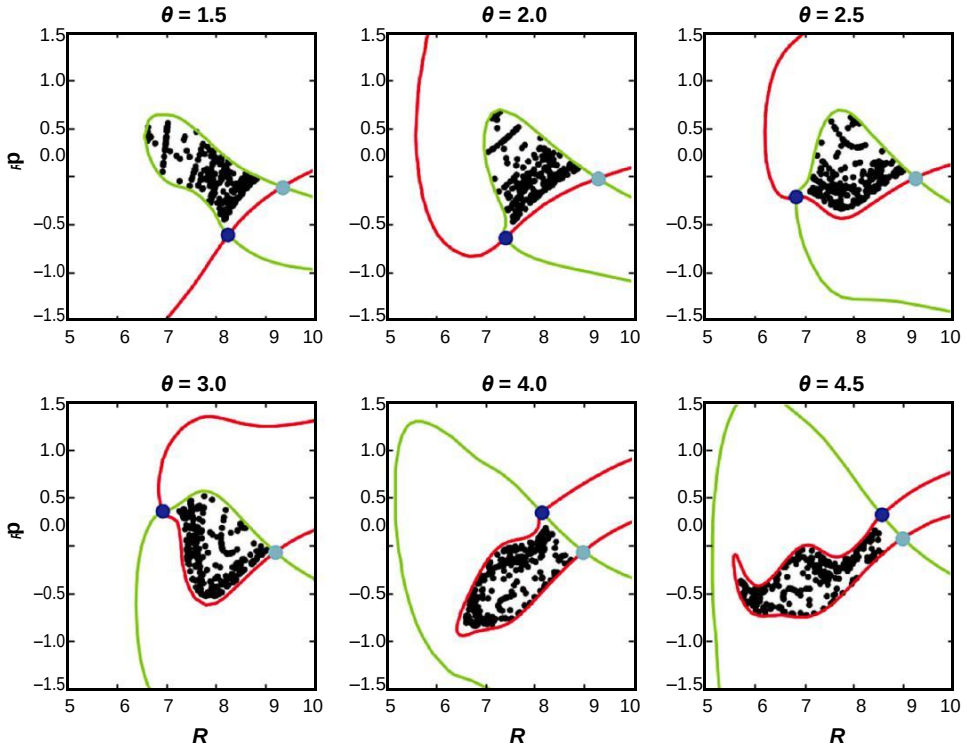

Figure 4

Stable and unstable invariant manifolds of the periodic orbit PO_{ROT} in the roaming region on different surfaces of section located at various values of θ. The stable manifold is shown in green and the unstable manifold in red. The blue (resp. cyan) bullet is the intersection of the orbiting periodic orbit (resp. homoclinic orbit) with the plane of section. Black dots represent crossings of the different surfaces of section by the roaming trajectories.

After analyzing hundreds of trajectories, these investigators concluded that roaming is associ-ated with the hydrogen rotating around the CO axis described by the azimuthal angle φ. According to them (12, p. 5112), "long roaming periods are characterized by unstable periodic orbits that involve, mostly, rotation of the distant H atom around the CO axis (φ) or, less commonly, end-to-end rotation (θ)." However, they do find that the roaming reaction takes place after the H atom enters the HCO plane ($\varphi \approx 0$).

The 3D analysis of Houston et al. (12) not only reveals the important role of the azimuthal angle in the roaming mechanism for the full-dimensional problem, but also demonstrates that orbiting POs, now in both φ and θ (see 12, figure 3), act as the mechanism for transferring energy from the radial DOF to the angular DOF. Moreover, their findings are not inconsistent with our 2D model study (11). The free rotation in the φ coordinate, which takes place in a region of phase space where the associated angular momentum p_φ is approximately conserved, acts as a clock measuring the time taken between significant dynamical events involving coupling between the R and θ coordinates occurring in a planar or near-planar configuration.

Houston et al. have also formulated a kinetic model involving a roaming entity as one of the species, and rate constants were extracted from trajectory data. Nevertheless, no explicit definition of the roaming region as a subset of phase space was given.

6. ROAMING: FURTHER CASE STUDIES

We now briefly discuss several other examples of roaming that we have recently studied that provide further motivation for the phase space point of view.

6.1. Ketene

The photodissociation of ketene, CH_2CO, to yield product fragments CO and CH_2 has been the subject of many studies (94–96). Isotopic substitution shows that isomerization (carbon exchange) in ketene takes place prior to dissociation. The postulated mechanism involved in the isomerization of ketene is the Wolff rearrangement mechanism (97). Ab initio calculations (94, 98) have shown that the relevant portion of the PES for ketene isomerization has three different minima associated with two symmetrically related formylmethylene species and an oxirene structure situated midway between these structures, respectively (96). On each side, a high barrier leads to the two isomers of ketene.

Recently, Ulusoy et al. (99, 100) studied the effect of roaming trajectories on the reaction rates for the isomerization of ketene. For ketene isomerization, there are no long-range interactions at play, and this raises the question of the broader relevance of the roaming mechanism. Ulusoy et al. (99, 100), in their effort to find trajectories that avoid the MEP on the PES, carried out isomerization rate constant calculations at very high energies, accessible neither to experiments (94–96) nor to the quantum-mechanical calculations of Gezelter & Miller (101).

We have used a reduced-dimensional model initially proposed by Gezelter & Miller to study the isomerization dynamics of ketene (13). The study of Ulusoy et al. (99, 100) discussed the connection between ketene isomerization and the roaming reactions mechanism. The question of how our previous interpretation of the roaming phenomenon (11, 89) fits the ketene isomerization situation naturally arose.

It was found that our general interpretation of the roaming mechanism in terms of a trap-ping mechanism of trajectories between two DSs enhanced by nonlinear resonances also fits the dynamics observed in the ketene isomerization reaction at experimentally relevant energies (13). We were able to classify classical trajectories into qualitatively different types of trajectories and compute fractions of different types of trajectories. The question of statistical dynamics was in-vestigated by gap time analysis (102), and significant deviation from the statistical assumption of TST was found. In addition, evidence of the trapping mechanism of the trajectories by resonant POs was found.

These studies of ketene isomerization have therefore led to two distinct kinds of dynamics being labeled as roaming: the non-MEP dynamics found by Ulusoy et al. (99, 100) and the trapping dynamics found in our study. In the work of Ulusoy et al. (99, 100), the non-MEP trajectories are able to access flat regions of the potential, albeit at very high total energies.

6.2. Recombination of the Ozone Molecule

We have examined the phase space structures that govern reaction dynamics in the absence of critical points on the PES (14). This work is significant because we showed how phase space NHIMs could be located in the neighborhood of a hyperbolic torus (a phase space signature) as opposed to the neighborhood of an index-one saddle (a configuration space signature). In particular, it was shown that, in the vicinity of hyperbolic invariant tori, it is possible to define phase space DSs that are analogous to the DSs governing transition from reactants to products near a critical point of the PES.

We showed the power of this phase space approach by investigating the problem of capture of an atom by a diatomic molecule and showed that a NHIM exists at large atom–diatom distances, away from any critical points on the potential. Exploiting adiabatic separability of the diatomic vibrational mode in the phase space region of interest, we presented an algorithm for sampling an approximate capture DS.

As an illustration of our methods, we applied the algorithm to the recombination of the ozone molecule: $O + O_2 \rightarrow O_3$, a reaction known to exhibit an unconventional isotope effect (103). We treated both 2- and 3-DOF models with zero total angular momentum and found the coexistence of the OTS and TTS in ozone recombination. Roaming dynamics may therefore have important consequences for the unconventional isotope effect in ozone formation. Further work along these lines may be fruitful.

6.3. Quantum Roaming: MgH_2

A recently studied molecule exhibiting roaming is magnesium hydride (39, 104, 105), a promising storage medium for hydrogen molecules (106, 107). Li et al. (108) have carried out both quantum and classical trajectory calculations on an improved ab initio ground electronic state PES (104) to study the reactions

$$H + MgH \rightarrow Mg + HH \quad \text{(reactive: direct and roaming)} \qquad 4.$$

$$\rightarrow H + MgH \quad \text{(nonreactive: direct and roaming)} \qquad 5.$$

$$\rightarrow H + MgH \quad \text{(exchange).} \qquad 6.$$

Direct and roaming abstraction (Reaction 4) and nonreactive (Reaction 5) reaction channels as well as an exchange reaction (Reaction 6) were identified for the three elementary reactions. It was found that Reaction 4 is dominated at low collision energies by the direct abstraction channel, whereas the exchange reaction, which involves a highly energetic intermediate complex, $[MgH_2]^*$, plays almost no role at the collision energies studied. As in the formaldehyde dissociation, the two dominant channels (direct and roaming) produce similar highly excited vibrational distributions for the H_2 product. However, it should be noted that the energetic complex is prepared here by collision rather than by photoabsorption.

On the basis of classical trajectory studies, Li et al. (108) have concluded that it is difficult to define roaming trajectories unambiguously solely on the criterion of their passage near the geom-etry of any putative roaming TS and so defined roaming trajectories as those reactive trajectories in which the H–H distance extends beyond a certain distance (8.5 a_0) after the first turning point in the R coordinate.

Furthermore, on the basis of their quantum calculations, Li et al. (108) have argued that, for a rotationless MgH_2, roaming is quantum mechanically manifested as a large-amplitude vibrational progression that emerges below the radical reaction threshold and continues into the energy continuum, leading to roaming resonances.

We have investigated the mechanisms of $H + MgH \leftrightarrow [MgH_2]^* \leftrightarrow Mg + HH$ using classi-cal trajectories. A 4D DS associated with the OTS PO (see **Figure 5**) that separates the radical reactants from the complex $[MgH_2]^*$ was rigorously defined and partially sampled in order to run trajectories that result in all possible reactive or nonreactive events, according to the theory described in Reference 14. Classification of the trajectories into different reactive events demon-strates nonstatistical dynamical behavior of the highly energetic MgH_2.

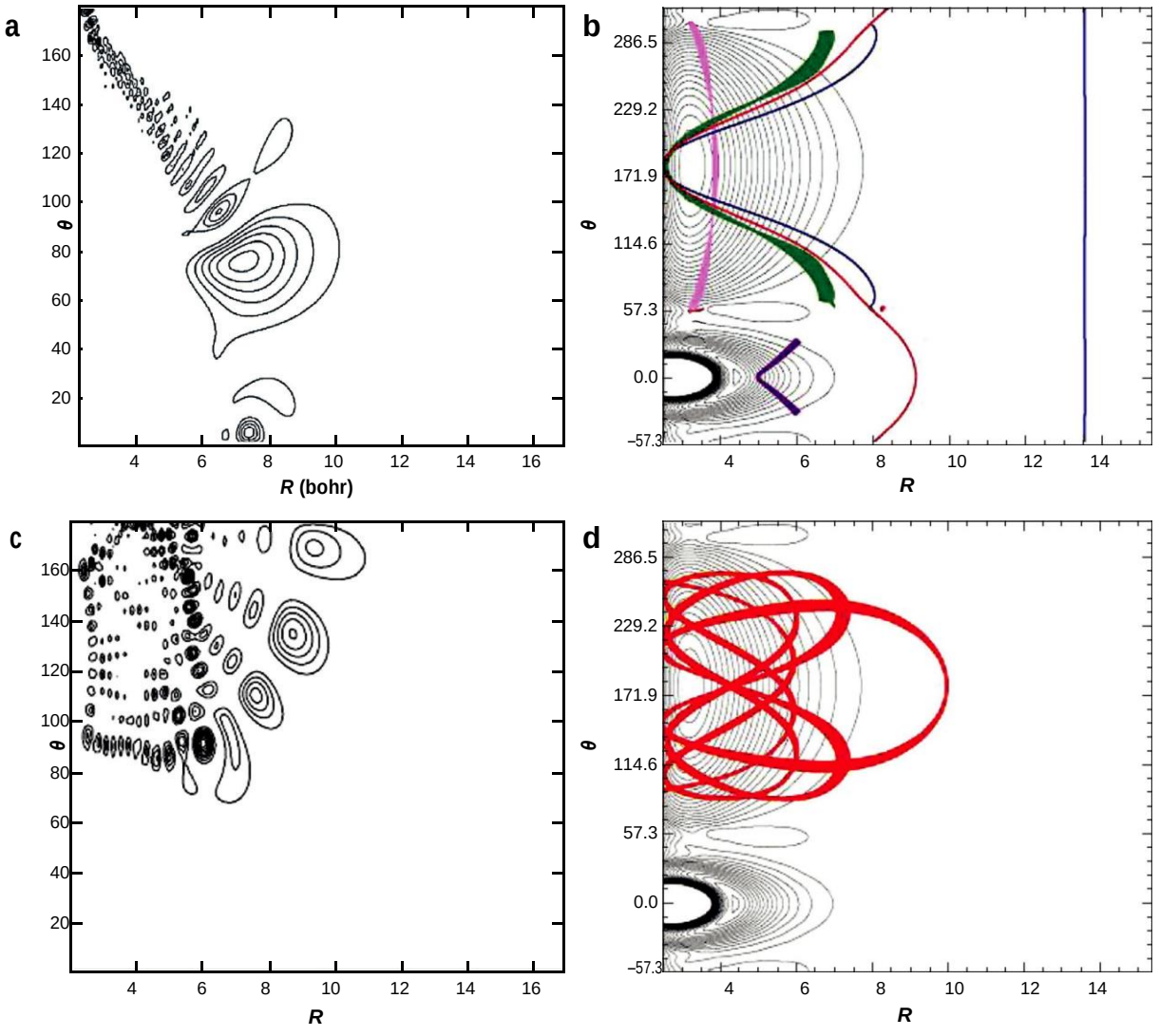

Figure 5

(*a*) Quantum density (wave function squared) for the bound eigenstate at energy −0.02 kcal/mol relative to the asymptotic potential in the radical channel. (*b*) Potential energy contours and simple periodic orbits (POs) originated from center-center-saddle bifurcations and projected in the (R, θ) plane. (*c*) Quantum density for the resonance eigenstate at energy +0.05 kcal/mol relative to the asymptotic potential in the radical channel. (*d*) Family of symmetric POs extending along the $\theta = \pi$ axis corresponding to the eigenfunction shown in the left at energy +0.05 kcal/mol. For details, see Reference 15.

Calculations of quantum bound and resonance wavefunctions for the eigenstates of MgH_2 reveal localization in configuration space with characteristic patterns identified by POs, in accord with previous studies (109, 110). **Figure 5** depicts two typical eigenstates with corresponding POs.

The roaming mechanism is attributed to trapping of trajectories in specific regions of phase space associated with POs (11, 13, 88, 89), wherein energy can be transferred from R to θ. For

MgH_2, however, there is no unique roaming reaction path but rather several different pathways according to which region of phase space the trajectories visit (15).

7. THE ROAMING SADDLE AND ITS ROLE IN ROAMING

There has been an interesting discussion in the literature concerning the possible existence of saddles in the PES that are, in some fashion, responsible or necessary for the roaming mechanism, often referred to as roaming saddles (21, 111–113). For example, in the case of the Chesnavich model, there exists a saddle point on the PES (labeled EP3 in Reference 89, table I) that could be considered a candidate to be a roaming saddle, but it appears to play no immediate role in the roaming dynamics that we have described in this model. Moreover, as we have emphasized, in general phase space TSs need not be associated with particular potential saddle points on the PES (14).

Several putative index-one roaming saddles have been found to be characterized by very low potential curvatures (vibrational frequencies) transverse to the direction of negative curvature; this property means that the associated DS is unlikely to be a dynamically significant bottleneck for any aspect of the roaming reaction (39).

A broader issue concerns energetic (i.e., relative energetics of saddle points) versus dynamical separability of DSs associated with different mechanisms. By dynamical separability we mean separation in phase space. According to Harding et al. (39), a key question is whether there is some separation in phase space between trajectories that follow one mechanism (conventional dissociation) as opposed to the other (roaming). In Section 5.2, this question has been definitely answered for a 2-DOF model of formaldehyde in terms of the shepherding mechanism in phase space.

Nevertheless, the potential landscape paradigm continues to motivate the search for configuration space explanations for the dynamical phenomena of roaming. Harding et al. (39) have proposed that index-two (second-order) saddles (as well as conical intersections) might be of key significance in distinguishing between different dissociation mechanisms, because, according to the Murrell–Laidler theorem (57, 114, 115), an index-two saddle can be found between two index-one saddles defining nominally distinct DS. (We note that use of the term "theorem" in relation to the Murrell–Laidler work has no strict mathematical justification and that the notion of "between two points" in high dimensions requires a careful explanation.)

Nonetheless, examples show that an index-two saddle may be naturally considered to be a component of a global DS that divides reactants from products and that is crossed by trajectories associated with either mechanism (molecular versus roaming). A challenge is then to further define a mechanism DS, within the global DS, that separates reactive trajectories corresponding to different mechanisms.

As noted above, the role of higher-index saddles in chemical dynamics has been extensively explored (see 61 and references therein). For a model 2-DOF isomerization problem, we have studied the role of the index-two saddle in defining phase space criteria for distinguishing between synchronous (concerted) and asynchronous (sequential) isomerizing trajectories (61). In this way, we were able to define a global DS together with the associated mechanism DS.

Such global DSs have been studied in the context of bifurcations of NHIMs and associated DSs (61–63; see also 116, 117). These concepts have yet to be applied to the case of roaming.

A recent paper of Maronsson et al. (118) provides an algorithm for finding an index-two saddle point on a (1D) ridge connecting two index-one saddle points. Note that this algorithm does not prove that the existence of two index-one saddles implies that there is a ridge connecting them

that contains an index-two saddle. Moreover, such a ridge is a configuration space notion. Careful consideration of related phase space structures, and the associated energetics of the saddle points, is essential for understanding its dynamical significance for roaming and, indeed, for reaction dynamics in general.

8. CONCLUSIONS AND FUTURE OUTLOOK

In this review we have considered the roaming phenomenon and, in the context of the currently known results, presented an answer to the question: Why do molecular fragments roam? Up to now, the general consensus (from experiment and theory) is that the roaming phenomenon is manifested as a frustrated dissociation of the molecule, with the fragments initially sampling the long-range part of the PES and then returning to the strong interaction region to react by avoiding conventional MEPs. With respect to the PES, the key role in this mechanism is played by flat regions of the PES, and we have discussed the dynamical significance of such flat regions in some detail.

We have argued that the precise definition of such alternative reaction paths (roaming), as well as a dynamical understanding of the mechanism of energy transfer among the internal coordinates, requires a phase space structure analysis. We have described recently developed techniques in nonlinear dynamical systems theory (most notably the NHIM) and how they can be used to develop the skeleton of a phase space landscape paradigm. The fruitfulness of such an approach was established in a study of a 2-DOF model of formaldehyde. In this example, NHIMs were used to identify the roaming region and reactive events, all in phase space. Unprecedented insight into the roaming process was gained, and a new phase space mechanism, shepherding, was identified, enabling a precise characterization of the initial conditions of trajectories that evolve to each reactive event. Our results definitively show that the dynamics in this model is nonstatistical, and thus that TST is not applicable. This phase space approach can in principle be extended to higher-dimensional examples (O_3, MgH_2).

The phase space interpretation allows one to extend the definition of roaming not necessarily to reaction paths involving dynamics in the long-range part of the PES, but to other regions of the PES, where nonlinear dynamics play a significant role, for example by generating new types of motion (bifurcations).

Topics in dynamical systems theory, such as NHIMs, as well as other general results in the geometry of phase space transport theory, are relatively unfamiliar to chemists, which is perhaps one reason why the phase space approach is not more widely applied. Another factor is the dearth of computational tools for such geometrical phase space analyses. Whereas there exist many methods for locating saddle points and saddle point connections on PESs (configuration space methods), computational phase space methods are less familiar. POMULT is a widely used software package for locating POs in Hamiltonian systems (119); unstable POs are the simplest phase space NHIMs. As noted in Section 3.2, software has been developed to find NHIMs and DSs near index-*k* saddles in Hamiltonian systems (available at **https://github.com/Peter-Collins/NormalForm**).

The method of Lagrangian descriptors (LD), originally from fluid mechanics (120–123), is a new numerical approach for exploring and discovering phase space structures that has been applied to several fundamental problems in chemical reaction dynamics by Hernandez and coworkers: chemical reactions under external time-dependent driving (124), phase space structure and reaction dynamics for a class of barrierless reactions (125), and the isomerization dynamics of ketene (126).

The LD method provides a completely new point of view for visualizing phase space structures in high dimensions by realizing the geometric structures in terms of the initial conditions of

trajectories, rather than the asymptotic-in-time behavior of trajectories, and has great potential for advancing our understanding of chemical reaction dynamics in general and roaming in particular.

SUMMARY POINTS

1. Invariant geometrical structures govern phase space reaction dynamics.
2. The roaming region is defined in phase space.
3. The roaming region is a dynamical complex.
4. The phase space shepherding mechanism shows why trajectories roam.

FUTURE ISSUES

1. The roles of, and relationships between, roaming saddles, higher-index saddles, and global DSs should be studied.
2. Higher-dimensional generalizations of the shepherding mechanism need to be identified.
3. Use of Lagrangian descriptors in analysis of roaming in multimode systems should be developed.
4. Phase space analysis of quantum mechanical roaming needs to be explored further.
5. The phase space approach to roaming dynamics in nonadiabatic systems and in the liquid phase needs to be developed.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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