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Multiple transition states and roaming in ion–molecule reactions: A phase space perspective

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ABSTRACT

We provide a dynamical interpretation of the recently identified 'roaming' mechanism for molecular dissociation reactions in terms of geometrical structures in phase space. These are NHIMs (Normally Hyperbolic Invariant Manifolds) and their stable/unstable manifolds that define transition states for ion–molecule association or dissociation reactions. The associated dividing surfaces rigorously define a roaming region of phase space, in which both reactive and non reactive trajectories can be trapped for arbitrarily long times.

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1. Introduction

Until recently, it was believed that unimolecular dissociations [1] can occur in either of two ways: (i) passage over a potential energy barrier or (ii) barrierless dissociation (e.g., bond fission) [2,3]. However, recently a variety of so-called 'non-MEP' (Minimum Energy Path) reactions have been recognized [4–9]; for non-MEP reactions a 'reaction coordinate' cannot be defined in the usual way [10], and statistical theories such as transition state theory (TST) are not necessarily applicable (see below).

Of particular interest here is the class of 'roaming reactions' [3]. The roaming phenomenon was discovered in the photodissociation of the formaldehyde molecule, H_2CO [11]. In this process, H_2CO can dissociate via two channels: $H_2CO \rightarrow H + HCO$ (radical channel) and $H_2CO \rightarrow H_2 + CO$ (molecular channel). Above the threshold for the H + HCO dissociation channel, the CO rotational state distribution was found to exhibit an intriguing 'shoulder' at lower rotational levels correlated with a hot vibrational distribution of H_2 coproduct [12]. The observed product state distribution did not fit well with the traditional picture of the dissociation of formaldehyde via a well characterized saddle point transition state for the molecular channel. The roaming mechanism, which explains the observations of Ref. [12], was demonstrated both experimentally

and in trajectory simulations in Ref. [11]. Following this work, roaming has been identified in the unimolecular dissociation of a number of molecules, and is now recognized as a general phenomenon in unimolecular decomposition (see [13–15] and references therein). See also Refs. [16–19]. A quantum mechanical investigation of the roaming effect for the $H + MgH \rightarrow Mg + H_2$ reaction at low collision energies has recently been published [20].

These studies have highlighted some general characteristics which a dissociating molecule should have in order to manifest roaming: the existence of competing dissociation channels, such as molecular and radical products; the existence of a saddle on the potential energy surface (PES) just below the dissociation threshold for radical production; long range attraction between fragments.

Reactions exhibiting roaming do not fit into conventional reaction mechanistic schemes, which are based on the concept of the reaction coordinate [10], for example, the *intrinsic reaction coordinate* (IRC). The IRC is a MEP in configuration space that smoothly connects reactants to products, and according to conventional wisdom it is the path a system follows as reaction occurs. Roaming reactions, instead, avoid the IRC and involve more complicated dynamical behavior. The roaming phenomenon seems to arise in the presence of long range interactions between dissociating fragments, where the possibility of orientational dynamics of the two fragments can lead to a different set of products and/or energy distribution than the one expected from MEP intuition. However, despite much work, it is still unclear how general the roaming phenomenon is and, specifically, which classes of reaction might show similar behaviors. The unusual nature of roaming reactions is a challenge for TST, where the aim is to compute reaction rates for a specific (given) reaction pathway.

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TST can take various forms, such as RRKM (for Rice, Ramsperger, Kassel, and Marcus) theory [21] or variational transition state theory (VTST) [22]. The central ingredient of TST is the concept of a *dividing surface* (DS), which is a surface the system must cross in order to pass from reactants to products (or the reverse). Association of transition states with saddle points on PES (and their vicinity) has a long history of successful applications in chemistry, and has provided great insight into reaction dynamics [1,23,24]. Accordingly, much effort has been devoted to connecting roaming reaction pathways with the existence of particular saddle points on the PES, as is evidenced by continued discussion of the role of the so-called "roaming saddle" [25,26].

Klippenstein et al. [27] have produced a statistical theory for the effect of roaming pathways on product branching fractions in both unimolecular and bimolecular reactions. This theory uses approximate dividing surfaces in configuration space, which do not in general satisfy any rigorous non-recrossing property [28–30] (unlike the dividing surfaces investigated in the present Letter). Discrepancies noted in Ref. [27] between this statistical theory and the results of trajectory simulations can be attributed either to recrossing effects or to nonstatistical dynamics in the roaming region.

Generally, reactions proceeding without a clear correlation to features on the potential energy surface are likely mediated by transition states that are dynamical in nature, i.e., *phase space structures*. The phase space formulation of TST has been known since the beginning of the theory [28]. Only in recent years, however, has the phase space formulation of TST reached conceptual and computational maturity [31]. Fundamental to this development is the recognition of the role of phase space objects, namely *normally hyperbolic invariant manifolds* (NHIMs) [32], in the construction of relevant DS for chemical reactions. While the NHIM approach to TST has enabled a deeper understanding of reaction dynamics for systems with many ($\geqslant 3$) degrees of freedom (DoF) [31,33], its practical implementation has relied strongly on mathematical techniques to compute NHIMs such as normal form theory [34]. Normal form theory, as applied to reaction rate theory, requires the existence of a saddle of index $\geqslant 1$ [31] on the PES to construct NHIMs and their attached DSs. For dynamical systems with 2 DoF the NHIMs are just unstable periodic orbits, which have long been known in this context as Periodic Orbit Dividing Surfaces (PODS) (for a review, see Ref. [29]). As we shall see, these particular hyperbolic invariant phase space structures (POs/PODS) are appropriate for describing reaction dynamics in situations where there is no critical point of the potential energy surface in the relevant region of configuration space.

As noted, the roaming effect manifests itself in systems having long range interactions between the two fragments of a unimolecular decomposition, thus allowing mutual reorientation dynamics. Ion–molecule reactions are good candidates to exhibit the roaming effect, as it is well known that long range interactions determine the dynamics of this type of reactions in the absence of saddle points on the PES along the MEP [1,13].

There has been much debate concerning the interpretation of experimental results on ion–molecule reactions [35]. Some results support a model for reactions taking place via the so-called loose or *orbiting transition states* (OTS), while others suggest that the reaction operates through a *tight transition state* (TTS) (for a review, see Ref. [35]). To account for this puzzling situation the concept of *transition state switching* was developed [35], where both kinds of DS (TTS and OTS) are present and determine the overall reaction rate (see also Ref. [36]). Chesnavich presented a simple model Hamiltonian to illustrate these ideas [37].

In this Letter we revisit the Chesnavich model Hamiltonian [37] in the 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 work on the phase space description of OTS, see Refs. [38–40].) The first goal of the present article is the identification of these notions with well defined *phase space dividing surfaces* attached to NHIMs. The second and main goal is an elucidation of the roaming phenomenon in the context of the Chesnavich model Hamiltonian. The associated potential function, possessing many features associated with a realistic molecular PES, leads to dynamics which clearly reveal the origins of the roaming effect. Based on our trajectory simulations, we show how the identification of the TTS and OTS DSs with periodic orbit dividing surfaces (PODS) provides the natural framework for analysis of the roaming mechanism.

2. Chesnavich model Hamiltonian

The transition state switching model was proposed to account for the competition between multiple transition states in ion–molecule reactions. Multiple transition states were studied by Chesnavich in the reaction $CH_4^+ \rightarrow CH_3^+ + H$ using a simple model Hamiltonian [37] (see also Ref. [13]). The model system consists of two parts: a rigid, symmetric top representing the CH_3^+ cation, and a mobile H atom. We employ Chesnavich's model restricted to two dimensions (2D) to study roaming.

The Hamiltonian for zero overall angular momentum is:

$$H = \frac{p_r^2}{2\mu} + \frac{p_\theta^2}{2}\left(\frac{1}{I_{CH_3}} + \frac{1}{\mu r^2}\right) + V(r,\theta), \tag{1}$$

where r is the coordinate giving the distance between the centre of mass of the CH_3^+ fragment and the hydrogen atom. The coordinate θ describes the relative orientation of the two fragments, CH_3^+ and H, in a plane. The momenta conjugate to these coordinates are p_r and p_θ, respectively, while μ is the reduced mass of the system and I_{CH_3} is the moment of inertia of the CH_3^+ fragment.

The potential $V(r,\theta)$ describes the so-called transitional mode. It is generally assumed that in ion–molecule reactions the different modes of the system separate into intramolecular (or conserved) and intermolecular (or transitional) modes. The potential $V(r,\theta)$ is made up of two terms:

$$V(r,\theta) = V_{CH}(r) + V_{coup}(r,\theta), \tag{2}$$

with:

$$V_{CH}(r) = \frac{D_e}{c_1 - 6}\{2(3 - c_2)\exp[c_1(1 - x)] \\ -(4c_2 - c_1c_2 + c_1)x^{-6} - (c_1 - 6)c_2x^{-4}\}, \tag{3a}$$

$$V_{coup}(r,\theta) = \frac{V_0(r)}{2}[1 - \cos(2\theta)], \tag{3b}$$

$$V_0(r) = V_e\exp\left[-\alpha(r - r_e)^2\right]. \tag{3c}$$

Here $x = r/r_e$, and the parameters for potential $V(r,\theta)$, Eq. (2), fitted to reproduce data from CH_4^+ species are: dissociation energy $D_e = 47$ kcal/mol; equilibrium distance $r_e = 1.1$ Å. Parameters $c_1 = 7.37$, $c_2 = 1.61$, fit the polarizability of the H atom and yield a stretch harmonic frequency of 3000 cm^{-1}. $V_e = 55$ kcal/mol is the equilibrium barrier height for internal rotation, chosen so that at $r = r_e$ the hindered rotor has, in the low energy harmonic oscillator limit, a bending frequency of 1300 cm^{-1}. The parameter α controls the rate of conversion of the transitional mode from angular to radial mode. By adjusting this parameter one can control whether the conversion occurs 'early' or 'late' along the reaction coordinate r. For our Letter we fix $\alpha = 1$ Å^{-2}, which corresponds to a late conversion. The masses are taken to be $m_H = 1.007825$ u, $m_C = 12.0$ u, and the moment of inertia $I_{CH_3} = 2.373409$ uÅ^2. A contour plot of the PES $V(r,\theta)$ is shown in Figure 1.
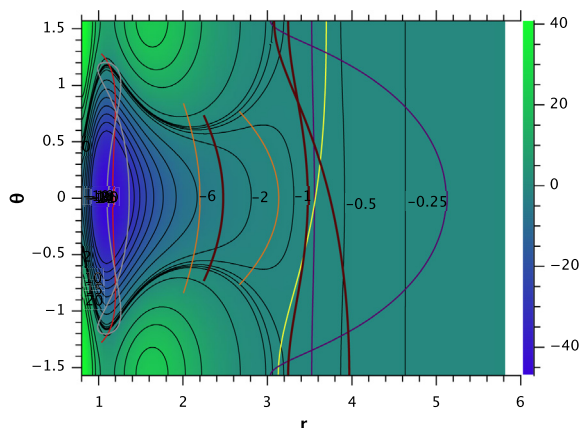
Figure 1. A contour plot of the Chesnavich potential $V(r, \theta)$ (Eq. (2)) and $\alpha = 1$ with projections of representative periodic orbits. Orange lines are POs of the $S2th1$ family (definitions of the symbols are given in Figure 2), at energies -0.252 and 4.993 kcal/mol, purple lines are POs of $S2FR1$ family at energies -0.0602 and 5.005 kcal/mol and yellow line is the period doubling PO ($S2FR12$) at energy 2.035 kcal/mol. The wine color POs, all at energy 1.392 kcal/mol, belong from the left to $S2th1$, $S2FR1$ and $S2FR12$ families, respectively. The red and grey periodic orbits shown in the region of the minimum belong to families of the potential which drive the molecule to isomerization. Distances in Angstroms, angles in radians and energies in kcal/mol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Equilibrium points for potential $V(r, \theta)$ ($\alpha = 1$). (CC) means a center-center equilibrium point (EP), (CS) a center-saddle EP and (SS) a saddle-saddle EP.

Energy (kcal mol^{-1})	r (Å)	θ (radians)	Stability	Label
-47	1.1	0	CC	EP1
8	1.1	$\pi/2$	CS	EP2
-0.63	3.45	$\pi/2$	CS	EP3
22.27	1.62	$\pi/2$	SS	EP4

In Table 1, the stationary points of the potential function are tabulated and are labelled according to their stability. The minimum for CH_4^+ (EP1) is of center-center stability type (CC), which means that it is stable in both coordinates, r and θ. The saddle, which separates two symmetric minima, at $\theta = 0$ and π (EP2), is of center-saddle type (CS), i.e., stable in r coordinate and unstable in θ. The maximum in the PES (EP4) is a saddle-saddle equilibrium point (SS). The outer saddle (EP3) is a CS equilibrium point.

The MEP connecting the minimum EP1 with the saddle EP2 at $r = 1.1$ Å (see Figure 1) describes a reaction involving 'isomerisation' between two symmetric minima. The MEP for dissociation to radical products (CH_3^+ cation and H atom) follows the line $\theta = 0$ with $r \to \infty$ and has no potential barrier. Broad similarities between the features of the Chesnavich model and molecules for which the roaming reaction has been observed can readily be identified. In the Chesnavich model system we recognize two reaction 'channels', one leading to a molecular product, in fact to the same molecule, by passage over an inner TS, and one to radical products via dissociation. Moreover, a saddle (EP3) exists just below the dissociation threshold.

3. Results

Examining the potential in Figure 1 it is not difficult to anticipate the existence of two classes of reactive events, isomerization and direct dissociation to radicals, but the occurence of a 'third way' (roaming [3], see below) is difficult to predict, even for this simple 2D system. Although it is customary to associate aspects of a molecule's dynamics with specific features of the PES

landscape [24], recent progress in non-linear mechanics suggests caution, especially in the interpretation of chemical reactivity. A method to explore the phase space structure of a non-linear dynamical system for extended ranges of energy (or other system parameters) dates back to Poincaré [41], and involves the study of periodic orbits and their continuation as energy or other parameters vary.

Distinct families of POs emanate from equilibrium points, where the number of families is at least as large as the number of DoF [42,43]. POs of the same family can be followed as energy increases. At critical values of energy bifurcations take place and new families are born. Continuation/bifurcation (CB) diagrams are obtained by plotting a property of POs as a function of energy or some other parameter. One important kind of elementary bifurcation is the center-saddle (CS) (saddle-node) [34]. Although periodic orbits, being one dimensional objects, cannot reveal the full structure of phase space, they do provide a 'skeleton' around which more complex structures such as NHIMs develop. Numerous explorations of non-linear dynamical systems by construction of PO CB diagrams have been made (for molecules, see Refs. [44,45]).

In Figure 2 such a CB diagram is shown for the Chesnavich model system with representative POs depicted in Figure 1. Not all families of POs generated from all equilibria are shown, but only those which are relevant to the roaming effect. A detailed description of the various PO families is given in the caption of Figure 2.

The phase space approach to TST requires the identification of NHIMs which serve as 'anchors' for the construction of DSs that locally minimize the flux. For 2 DoF systems, the NHIM is just a periodic orbit, which we call the NHIM-PO. Normal hyperbolicity of the NHIM-PO implies that it possesses one stable and one unstable direction transverse to the PO. The NHIM-PO is a one dimensional object embedded in the four dimensional phase space. A dividing surface at a specific energy is a phase space surface that divides the energy surface into two parts, namely reactants and products. The NHIM-PO being 1 dimensional does not have the right dimensionality to perform as a DS on the three dimensional energy surface embedded in a four dimensional *phase space*. Rather, the NHIM-PO serves as the *boundary* of the relevant DS, which is the NHIM-PODS. The NHIM-PODS at a specific energy is a sphere on which the NHIM-PO is an equator. The NHIM-PO in turn divides
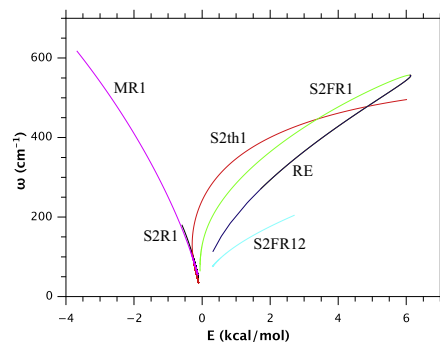

Figure 2. Continuation/Bifurcation diagram of periodic orbits for the Chesnavich potential and $\alpha = 1$. $MR1$ denotes the principal family of POs along r that originates from the minimum of the potential (equilibrium point EP1), whereas $S2R1$ is the corresponding family that emanates from the saddle (EP3). $S2th1$ is the family of POs with hindered rotor behaviour, acting as the TTS (see text) that emanates from a center-saddle bifurcation and appears at about $E = -0.291$ kcal/mol below the dissociation energy. Similarly, $S2FR1$ denotes the family of POs with free rotor behaviour that also originates from a CS bifurcation at energy $E = -0.0602$ kcal/mol, while $S2FR12$ a period doubling bifurcation of $S2FR1$ family, which is generated at energy $E = 2.715$ kcal/mol. At this energy the $S2FR1$ becomes unstable. RE is the family of POs which are near free rotors and act as the OTS. They are relative minima, and have $r \sim const$, $p_r = 0$ and $p_\theta \neq 0$ also approximately constant. This family is the unstable branch of a subcritical CS bifurcation with the $S2FR1$ family the stable branch, and emerges at energy 6.131 kcal/mol.

the NHIM-PODS into two hemispheres, one of which (the forward hemisphere) intersects all the trajectories which evolve from reactants to products, while the other (the backward hemisphere) intersects all the trajectories which travel from products to reactants.

Our first task is then to identify the TTS and the OTS as DSs attached to appropriate NHIM-POs. For a system with a natural Hamiltonian (kinetic plus potential terms), when we plot a suitable PO in the (r, θ) plane we represent simultaneously the NHIM-PO and the DS constructed from it.

The NHIM-PODS associated with the S2th1 family of periodic orbits (see Figure 2) are identified with the TTS. Figure 3 is a color plot of the potential function in the Cartesian (xy) plane and the two blue lines shown are examples of two such NHIM-PODS projected on configuration space at an energy corresponding to a thermal energy of 300 K. There are two symmetry-related NHIM-PODS in Figure 3.
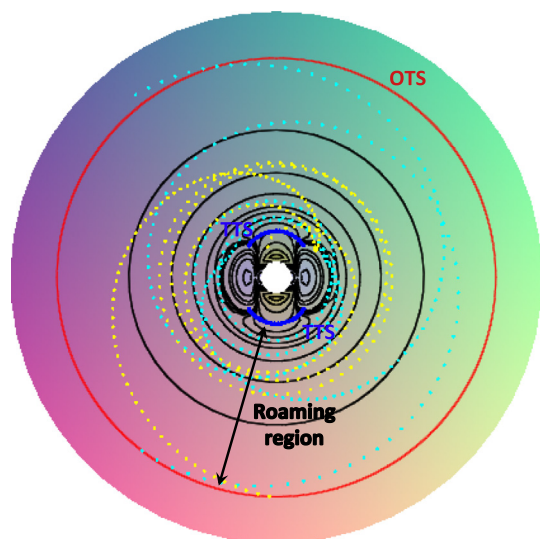
It has been recognised that the OTS is related to the centrifugal barrier arising from the centrifugal term in the kinetic energy, Eq. (1). The PO associated with the centrifugal barrier is a relative equilibrium [40], and this PO belongs to the RE family shown in Figure 2. These RE POs and higher dimensional analogues have been studied by Wiesenfeld et al. [40] in the context of capture theories of reaction rates. An example of such a RE NHIM-PODS is depicted as the red outer circle in Figure 3 at the thermal energy of 300 K. We have therefore associated the TTS and OTS with well defined DSs attached to dynamical objects, i.e., NHIM-PODS.

To investigate the behaviour of the trajectories initiated at the OTS, we sample the DS at the thermal energy 300 K. We sample the backward hemisphere of the DS, which intersects all trajectories passing from large values of r into the interaction region (small values of r). The result of this trajectory simulation is shown in Figure 4. Trajectories are initiated on the black line segment at $r \sim 12$ Å, which is the projection of the OTS on configuration space restricted to the θ range $[-\frac{\pi}{2}; \frac{\pi}{2}]$. The DS is sampled uniformly in θ and the conjugate variable p_θ at effectively fixed r and fixed total energy. For clarity, we do not impose π-periodicity in angle θ on the plotted trajectories, but rather let this coordinate increase or decrease freely as the trajectory evolves in time.

We classify the trajectories into four qualitatively different categories, noting that a reactive trajectory is one which crosses the (inner) TTS passing from large 2r to smaller r. (Integration of reactive trajectories terminates shortly after they cross the TTS.) The four different trajectory categories are:

(a) Direct reactive trajectories: these have no turning points in the r direction, i.e., they react directly without making any oscillations in the r direction.
(b) Roaming reactive trajectories: these react but exhibit *at least* two turning points in the r direction.
(c) Direct non reactive trajectories: these trajectories go to small values of r and are reflected once and recross.
(d) Roaming non reactive trajectories: these trajectories do not react, but are not direct trajectories. They never cross the TTS but eventually recross the OTS to end up at large values of r. However, before recrossing the OTS they exhibit at least three turning points in r.

Figure 3. Contour plot of the PES in a Cartesian coordinate system. The red line is the projection of OTS and the two blue lines are the projections of the TTS. Yellow and cyan dotted lines represent a roaming reactive and non reactive trajectory respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
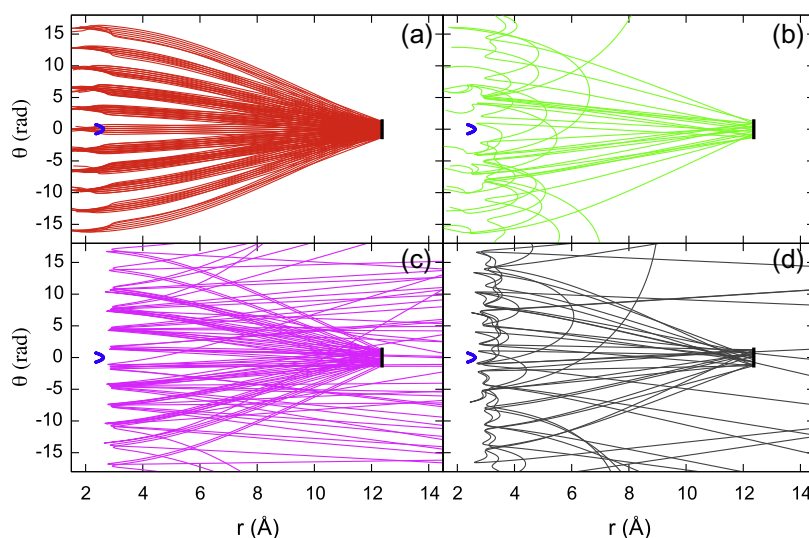

Figure 4. Trajectories initiated on OTS backward hemisphere. The thick black line represents the OTS and the thick blue line the TTS. All trajectories have energy $E = k_B T$, where k_B is Boltzmann's constant and $T = 300$ K. (a) Direct reactive trajectories. (b) Roaming reactive trajectories. (c) Direct non reactive trajectories. (d) Roaming non reactive trajectories. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

These four categories exhaust all possible qualitatively different trajectory behaviors (we ignore measure zero sets of trapped trajectories that approach POs in the roaming region along stable manifolds). In Figure 3 in addition to the TTS and OTS we plot two trajectories, one roaming reactive (yellow dots) and one roaming non reactive (cyan dots).

With this classification of trajectories the existence of the roaming phenomenon is immediately apparent. Panels (b) and (d) of Figure 4 show trajectories which attempt to react but cannot find their way through the TTS, and are reflected back. Close to the TTS exchange of energy between the radial and angular modes takes place and the hydrogen atom starts to orbit the CH_3^+ ion in the *roaming region*, which is the region of *phase space* between the TTS and the OTS, before perhaps returning and crossing the TTS to react (panel (b)) or promptly recrossing the OTS and leaving the interaction region forever (panel (d)).

For the reverse process (photodissociation), we want to know the behaviour of trajectories initiated on the TTS. Thus, the trajectories in panel (b) of Figure 4 can be thought of as those trajectories which start at the TTS, roam and then cross the OTS to give CH_3^+ + H. Again, the roaming mechanism finds a natural explanation once we identify the relevant transition states, i.e., the TTS and the OTS. These two DSs create a trapping region between them, in which some trajectories may be captured circling for arbitrarily long times.

From Figure 4 panels (b) and (d), we can see that trajectories appear to oscillate in the r direction at $r \sim 3.5$ Å. This fact can be explained by the presence of the S2FR1 family of periodic orbits (see Figures 1 and 2), where the H atom makes full rotations in the angle θ and small oscillations in r. In Figure 5 we plot the same trajectories as in panels (b) and (d) of Figure 4 with the projection of this PO (orange line) for the same energy (300 K). We see this PO is actually a 2:1 resonance between the radial and angular modes, since during the time θ covers the range $[0; 2\pi]$ there are two oscillations in the r direction. Trajectories are presumably trapped by the stable and unstable invariant manifold of the S2FR1 PO (and/or POs created by period-doubling bifurcations, such as POs of family S2FR12 in Figure 2), which explains the resemblance of some trajectories to this PO.

We note that the S2FR1 family originates at an energy below the threshold energy for dissociation to radical products, whereas the RE family exists only for positive energies. Hence, we expect that these periodic orbits will explain roaming effects observed for total energies below the threshold to radical products as indeed has been found in formaldehyde [46]. Nevertheless, we emphasize that, despite the existence of the saddle EP3, the transition state that controls the dissociation (association) reaction, and especially
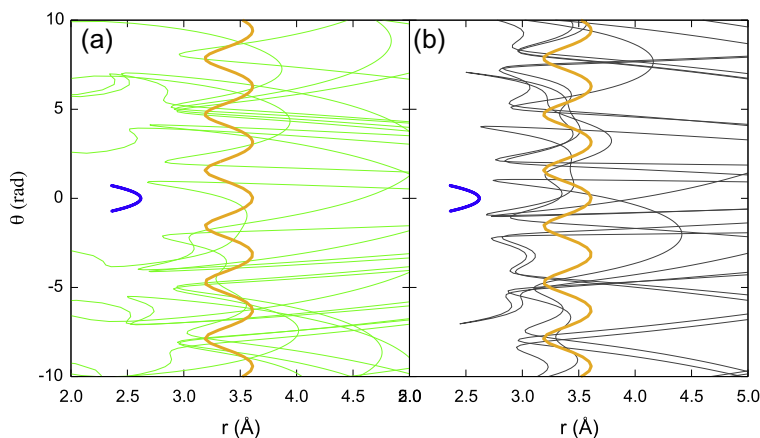

Figure 6. Rotational state distributions for non reactive trajectories initiated on the OTS. Normalized final rotor angular momentum (p_θ) distributions for roaming (blue) and direct (red) non reactive trajectories are shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

roaming, is that related to the RE periodic orbit. Calculation of action integrals for the various periodic orbits shows that for the RE family the action is smaller than S2FR1 POs. The minimum flux criterion required in TST [29] is thus satisfied by the RE POs. Periodic orbits of S2FR1 type and its period doubling bifurcations, which emerge from above the saddle EP3, presumably serve to enhance the roaming effect by increasing the possibilities for trapping of trajectories.

Direct and roaming non reactive trajectories exhibit different final rotational state distributions (see Figure 6), in line with previous findings on the roaming mechanism. Direct non reactive trajectories are more likely to suffer a collision with the inner wall of the potential and to exit the roaming region with large radial kinetic energy, and low final rotor angular momentum. Conversely, trapped (roaming) trajectories are likely to have lower radial kinetic energy and hence larger rotor angular momentum.

4. Discussion

The roaming phenomenon has stimulated much recent research [15] and has led to the identification of the roaming 'mechanism' in the dissociation dynamics of several polyatomic molecules. The roaming effect has brought transition state theory once more to

Figure 5. Trajectories of panels (b) and (d) of Figure 4 with the PO (*S2FR*1) responsible for trapping of these trajectories (orange line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
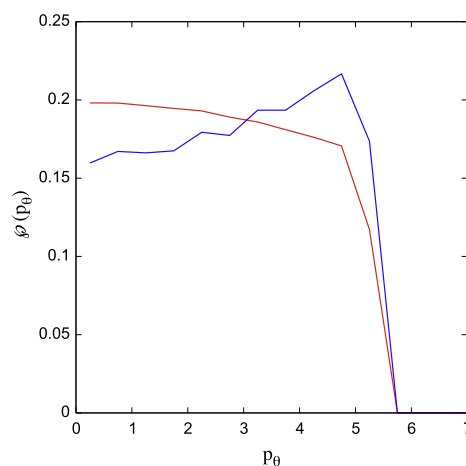
the frontiers of research in chemical dynamics. Despite substantial progress in the development of the phase space approach to fundamental concepts related to TST, such as dividing surface, activated complex and reaction pathways [31], much recent work has shown that adherence to a configuration space viewpoint based on the potential energy surface alone may prohibit the comprehension of the mechanisms of chemical reactions not directly associated with minimum energy paths or saddles on the PES (in the context of organic reaction mechanisms, see, for example, Ref. [47]).

In this article, we have clearly demonstrated that NHIMs and their stable/unstable manifolds exist and define minimal flux/non-recrossing phase space dividing surfaces for ion–molecule association or dissociation reactions. The associated DS rigorously define a roaming region of phase space, in which both reactive and non reactive trajectories can be trapped for arbitrarily long times [36,38,37,27]. Our definition of the roaming region leads naturally to a dynamically based classification of trajectories as either roaming or non-roaming.

Extension of the concepts developed here to higher dimensional ($n \geqslant 3$ degrees of freedom) systems is in principle straightforward, as our framework does not depend essentially on dimensionality. Nevertheless, substantial technical difficulties need to be overcome for accurate computation of NHIM-DS for higher dimensional systems.

Acknowledgments

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