

Introduction

Following recent developments in the understanding of the roaming mechanism in molecular dynamics (Townsend et al. 2004; Bowman and Shepler 2011; Bowman 2014; Mauguère et al. 2014a, 2014b, 2015, 2016; Bowman and Houston 2017; Krajčák and Waalkens 2018), the results of Heazlewood et al. (Heazlewood et al. 2008) on roaming being the dominant mechanism for acetaldehyde photodissociation triggered the following question: Can some of the standard parameter values in Chesnavich’s CH_4^+ model (Chesnavich 1986) be altered so that it admits roaming as the dominant form of dissociation? It is well known that roaming plays a minor role in the dissociation of Formaldehyde (Townsend et al. 2004). Since acetaldehyde dissociates into $\text{CH}_4 + \text{CO}$, one of the obvious differences in the dissociation of Formaldehyde into $\text{H}_2 + \text{CO}$ is the mass ratio of the products. Therefore we investigate the influence of various masses of the free atom on roaming in Chesnavich’s CH_4^+ model. Furthermore we consider different values of parameter a , the coupling parameter of the angular and radial degrees of freedom in Chesnavich’s potential, and deduce its impact on roaming. Physically speaking, a controls the strength of the short range anisotropy of the CH_3^+ molecule and its precise role in the potential is discussed in Section 2.

Chesnavich’s CH_4^+ model (Chesnavich 1986) is a phenomenological 2 degree of freedom model introduced that was introduced to study the transition from vibrational reactants to rotational products in the presence of multiple transition states. We use it to study the first stage of roaming, where a hydrogen atom separates from the rigid CH_3^+ molecule and instead of dissociating, it roams in a region of nearly constant potential only to return to the molecule without forming a bond. The process of intramolecular abstraction and subsequent dissociation requires both H atoms to be mobile and thus requires at least 4 degrees of freedom. At the moment no tools for a qualitative dynamical study that would explain roaming in its entirety in 4 degrees of freedom have been developed.

We study the system in a polar centre of mass frame, where r is the distance of the mobile H atom from the centre of mass of the system in Å and θ is the angle describing the relative orientation of H and CH_3^+ in radians. The momenta p_r and p_θ are canonically conjugate to r and θ respectively.

The model we study is defined by the Hamiltonian

$$H(r, \theta, p_r, p_\theta) = \frac{1}{2\mu} p_r^2 + \frac{1}{2} p_\theta^2 \left(\frac{1}{I} + \frac{1}{\mu r^2} \right) + U(r, \theta),$$

where $\mu = \frac{m_{\text{CH}_3} m_H}{m_{\text{CH}_3} + m_H}$, with $m_H = 1.007825$ u and $m_{\text{CH}_3} = 12.0$ u, is the reduced mass of the system, and $I = 2.373409$ uÅ² is the moment of inertia of the rigid body CH_3^+ . Chesnavich’s potential $U(r, \theta)$ has the form

$$U(r, \theta) = U_{\text{CH}}(r) + U_{\text{coup}}(r, \theta), \quad (1)$$

and it is the sum of radial long range potential U_{CH} and short range “hindered rotor” potential U_{coup} , that represents the anisotropy (Chesnavich 1986; Jordan, Smith, and Gilbert 1991) of the rigid molecule CH_3^+ . We use the standard definition of U_{CH} and U_{coup} and standard parameter values as suggested by Chesnavich (Chesnavich 1986) and used in recent publications (Mauguière et al. 2014a, 2014b; Krajňák and Waalkens 2018), namely

$$U_{CH}(r) = \frac{D_e}{c_1 - 6} \left(2(3 - c_2)e^{c_1(1-x)} - (4c_2 - c_1c_2 + c_1)x^{-6} - (c_1 - 6)c_2x^{-4} \right), \quad (2)$$

where $x = \frac{r}{r_e}$, $D_e = 47$ kcal/mol, $r_e = 1.1$ Å, $c_1 = 7.37$ and $c_2 = 1.61$, and

$$U_{coup}(r, \theta) = \frac{U_e e^{-a(r-r_e)^2}}{2} (1 - \cos 2\theta), \quad (3)$$

where $U_e = 55$ kcal/mol. The parameter a (in Å⁻²) influences the value of r at which the transition from vibration to rotation occurs, for example $a = 1$ represents a late transition (Mauguière et al. 2014b, 2014a; Krajňák and Waalkens 2018) and $a = 4$ an early transition (Mauguière et al. 2014b). In this paper we shall explore all values of a that may be relevant to roaming.

The total energy $H(r, \theta, p_r, p_\theta) = E$ is given in kcal/mol with respect to the dissociation energy 0.

We introduce the potential in more detail and explain the role of the parameter a in Section 2. Subsequently we give an overview of roaming up to date in Section 3, we explain how phase space structures influence the dynamics in Section 4 and focus on how these structures cause roaming in 5.

To study the dependence of roaming on the mass of the free atom, we replace the free H atom by a atom of mass m , so that the reduced mass of the system is $\mu_m = \frac{m_{CH_3}m}{m_{CH_3}+m}$ and the Hamiltonian then is

$$H_m(r, \theta, p_r, p_\theta) = \frac{1}{2\mu_m} p_r^2 + \frac{1}{2} p_\theta^2 \left(\frac{1}{I} + \frac{1}{\mu_m r^2} \right) + U(r, \theta). \quad (4)$$

In this work we consider $m < m_{CH_3}$, since the free atom is usually the lighter of the two dissociated products. For comparison, the free atom would have to weight $m = 8.57$ to be in the same proportion as in acetaldehyde.

Since m is only present in the kinetic part of the Hamiltonian ([eq:Hamm]), its influence cannot be seen in configuration space. We explain how variations in mass of the free atom influence the system, phase space structures and roaming in different parts of phase space in Sections 6, 7 and 8.

The phase space structures that enable us to study dynamics in phase space are normally hyperbolic invariant manifolds (NHIMs) and the corresponding stable and unstable invariant manifolds. We build upon the understanding of the role

of NHIMs and invariant manifolds in governing dynamics as described in Refs. in great detail.

Role of a in Chesnavich's CH_4^+ potential

The potential $U(r, \theta)$ as defined by ([eq:U]), ([eq:UCH]) and ([eq:Ucoup]), has the following characteristics:

- potential wells near $\theta = 0$ and $\theta = \pi$ representing the two isomers of CH_4^+ ,
- areas of high potential near $\theta = \frac{\pi}{2}$ and $\theta = \frac{3\pi}{2}$ creating a potential barrier between the two wells,
- an area where the potential is monotonic and nearly constant due to $U(r, \theta) \in o(r^{-4})$ as $r \rightarrow \infty$, representing the dissociated state.

Note that due to the rotational symmetry $U(r, \theta) = U(r, \theta + \pi)$ and reflectional symmetry $U(r, \theta) = U(r, -\theta)$ of U that follows from the anisotropic term U_{coup} in ([eq:Ucoup]), the wells and areas of high potential are symmetric.

All of the characteristics listed above can be derived from the critical points of $U(r, \theta)$. Table [table:equil] shows critical points of U for $0 \leq \theta < \pi$, while symmetric counterparts exist in $-\pi \leq \theta < 0$. We denote critical points by q , the subscript indicates the index of the saddle and the superscript indicates the half plane in which the critical point lies: $+$ for $0 \leq \theta < \pi$, $-$ for $-\pi \leq \theta < 0$.

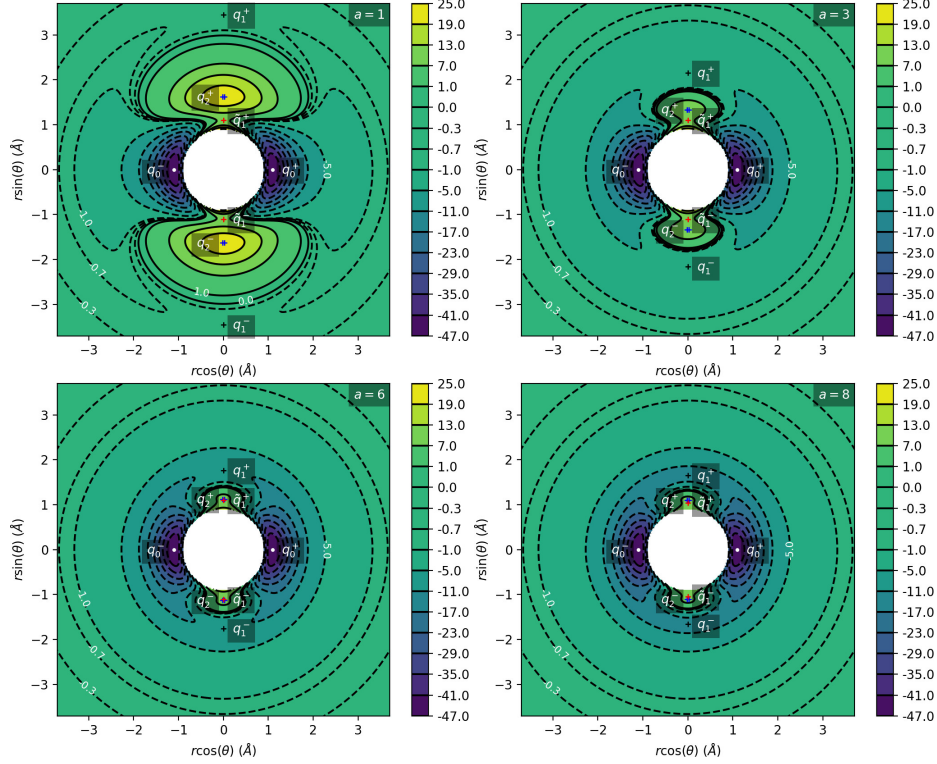
Table 1: Equilibrium points for potential $U(r, \theta)$. Energy and radial coordinate of q_1^+ , q_2^+ and \tilde{q}_1^+ varies with a and is shown graphically in Figure [fig:thpi2].

Energy (kcal mol ⁻¹)	r (Å)	θ (radians)	Significance	Label
-47	1.1	0	potential well	q_0^+
> 0	< 1.1	$\pi/2$	isomerisation saddle	q_1^+
> 0	> 1.1	$\pi/2$	local maximum	q_2^+
< 0	> 1.1	$\pi/2$	isomerisation saddle	\tilde{q}_1^+

We remark that q_1^+ and q_2^+ are energetically inaccessible at energies considered in this work. Four more critical points q_0^- , q_1^- , q_2^- and \tilde{q}_1^- are related to the ones above by symmetry. The location of the critical points in configuration space can be seen in Figure [fig:pot] for $a = 1, 3, 6, 8$.

The coupling term U_{coup} through which a influences the potential, vanishes around $\theta = 0$ and $\theta = \pi$ and is maximal around $\theta = \pm \frac{\pi}{2}$. Therefore variations of a leave most of the well unaffected, while the potential maxima and associated critical points vary significantly. Figure [fig:thpi2] illustrates how the potential barrier between the wells recedes with increasing a . The figure also shows how

q_1^+ , q_2^+ and \tilde{q}_1^+ are affected by a , note the decrease of energy of q_1^+ . When considered in context of the contour plots in Figure [fig:pot], for $a = 6$ and larger the wells merge into one from an energetic perspective, but dynamically remain distinct.



: Contour plots of the potential energy surface U for $a = 1, 3, 6, 8$. Dashed lines correspond to $U < 0$, solid lines correspond to $U \geq 0$. Contours correspond to values of potential shown on the colorbar right, with some values indicated in the plot. Critical points of the potential q_0^- , q_1^- , q_2^- and \tilde{q}_1^- , as introduced in Table [tab:equil] are indicated.

Due to the exponential decay of the anisotropic term U_{coup} and the $o(r^{-4})$ decay of U as a whole, the area of flat potential that can be seen in Figures [fig:pot] and [fig:thpi2] remains unchanged. In this area U is negative, monotonic in r , very close to zero and certainly has no saddles.

Apart from different values of the potential, the wells also differ from the area of flat potential dynamically. In the potential well trajectories vibrate, i.e. oscillate in the angular direction, as they are bounded by the two areas of high potential. Outside of the wells, especially in the flat area, the absence of potential barriers enables unlimited movement in the angular direction that is manifested in trajectories completing full rotations around the centre of mass. The transition from one type of dynamics to the other depends heavily on the size and height

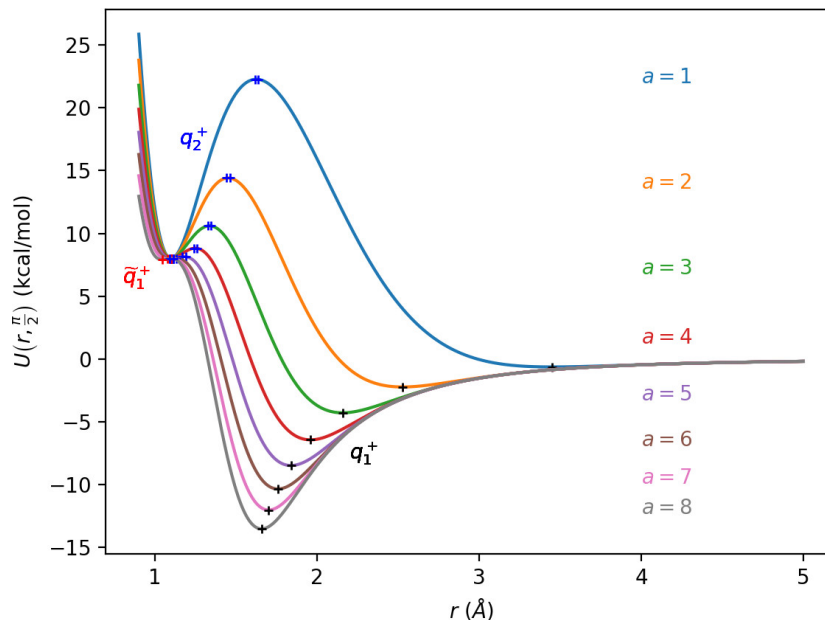


Figure 1: Radial sections of the potential U along $\theta = \frac{\pi}{2}$ for $a = 1, 2, 3, 4, 5, 6, 7, 8$.

of the areas of high potential that is influenced by a as described above.

Roaming

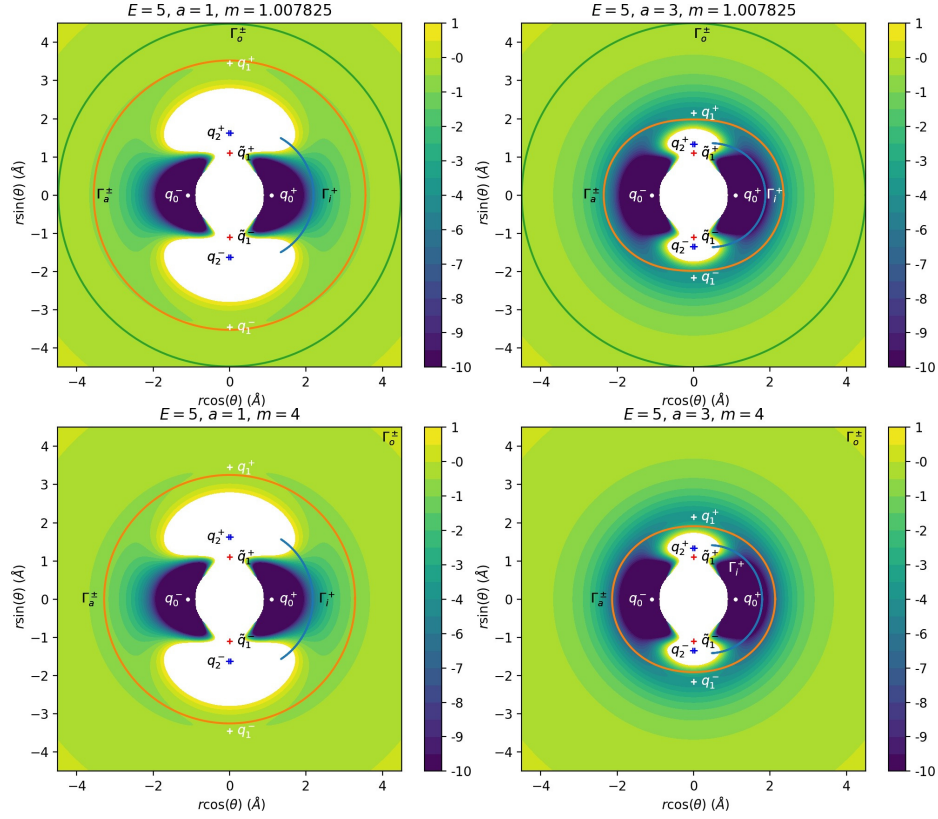
Roaming was discovered in the study of photodissociation of formaldehyde (Townsend et al. 2004) (H_2CO) and explained the unusual energy distribution between H_2 and CO experimentally observed previously (Zee, Foltz, and Moore 1993). Since then roaming was reported in a number of other molecules (Bowman and Houston 2017). Initial states of roaming resemble radical dissociation, when a single H atom escapes from HCO by breaking a single covalent bond and immediately dissociates. Instead of dissociating, the free hydrogen ‘roams’ around a flat monotonic region of the potential near HCO and returns to the molecule to abstract the remaining hydrogen. Ultimately, the products of this dissociation are identical to the products of molecular dissociation. While molecular dissociation requires the system to pass over a potential saddle, no saddle is involved in roaming. Consequently the distribution of energy between the products can differ significantly. Following a study (Bowman and Shepler 2011) of H_2CO and CH_3CHO it was established that regardless of similarity of products, roaming is actually closer to radical dissociation than to molecular dissociation and further evidence was published subsequently (Huston, Conte, and Bowman 2016).

In light of developments following a phase space approach to chemical reaction dynamics (Wiggins et al. 2001; Uzer et al. 2002; Waalkens and Wiggins 2004), we employ the definition of roaming introduced in Ref. . This definition considers the number of intersections of a trajectory with a dynamically justified dividing surface and thereby accounts for the influence of various phase space structures. The dividing surface is constructed using an unstable periodic orbit that is not associated with any potential saddle. It was shown (Mauguière et al. 2015) how invariant manifolds of unstable periodic orbits convey trajectories between two potential wells in what is called a ‘shepherding mechanism’. The exact phase space structure, an intersection of invariant manifolds of unstable periodic orbits, responsible for roaming was since identified (Krajňák and Waalkens 2018). The key to understanding roaming follows from the use of toric surfaces of section (MacKay and Strub 2014, 2015; Mauguière et al. 2016) to study invariant manifolds.

Phase space structures governing transport {#sec:phase transport}

There are three important families of periodic orbits (Mauguière et al. 2014a, 2014b; Krajňák and Waalkens 2018) in Chesnavich’s CH_4^+ model. By family of periodic orbits we mean a continuum of periodic orbits parametrised by energy, so that each family contains two orbits related by (reflectional) symmetry for a given E . We will refer to these orbits as the inner (Γ^i), middle (Γ^a) and outer (Γ^o) periodic orbit based on the radii of the orbits and their significance in dissociation. For a given E , the middle and outer families consist of two orbits with the same configuration space projections but opposite orientation, one with $p_\theta > 0$ and one with $p_\theta < 0$, hence clearly distinct in phase space. In a configuration space projection these orbits rotate counterclockwise and clockwise respectively. The inner family consists of two orbits, one on the edge of each potential well. In the following, statements regarding one of the orbits of a family automatically hold for the other one due to symmetry. If we only refer to one orbit, we refer to Γ^a and Γ^o with $p_\theta > 0$ and Γ^i oscillating around $\theta = 0$.

Configuration space projections are shown in Figure [fig:poconfig]. Note that none of these families is associated with a saddle point on the potential energy surface.



The family of outer periodic orbits Γ^o is proven (Krajňák and Waalkens 2018) to exist due to a centrifugal barrier for a class of systems including the one considered here. It was also shown that the orbits in this family are unstable. States of the system beyond the outer orbits correspond to dissociated states $\text{CH}_3^+ + \text{H}$. Orbits of this family are therefore the outer boundary of the roaming region (Mauguière et al. 2014a). We prefer to use the more general term interaction region as the phase space structures responsible for roaming and isomerisation among trajectories that leave the well, also arbitrate whether incoming trajectories originating at $r = \infty$ react (reach the well) or not. In the context of transition state theory, this region is sometimes also called the collision complex.

The potential wells represent the region where the CH_4^+ molecule is in a stable configuration and orbits of the inner family Γ^i naturally delimit this region. All inner periodic orbits are unstable and form the inner boundary of the interaction region.

Inside the interaction region lies the family of middle orbits, which are crucial in the definition of roaming. These orbits are unstable for small positive energies ($E < 2.72$ for $a = 1$ and $m = m_H$) and stable after a period doubling bifurcation involving a family denoted sometimes by FR12 (Mauguière et al. 2014a, 2014b)

or Γ^b (Krajňák and Waalkens 2018) that is of no further importance. The exact energy of the period doubling bifurcation varies with m and a , but for $m = m_H$ and $a = 1$ is at approximately $E = 2.72$. The family is also subject to bifurcations at negative energies, but these are not relevant for roaming.

The definition of roaming as introduced in Ref. requires us to construct a dividing surface in phase space based on the configuration space projection of Γ^a . We shall denote the dividing surface associated with Γ^a as DS^a . For a given energy E , DS^a consists of all points $(r, \theta, p_r, p_\theta)$ on the energy surface $H_m(r, \theta, p_r, p_\theta) = E$, such that (r, θ) is a point on the configuration space projection of Γ^a .

It is known that a spherical dividing surface may in the neighbourhood of an index-1 saddle bifurcate into a torus (MacKay and Strub 2014, 2015) and it was recognised (Mauguière et al. 2016) that dividing surfaces constructed using periodic orbits that rotate such as DS^a , as opposed to vibrate, are tori. In addition, if Γ^a is unstable, then DS^a does not admit local recrossings.

Indeed one can see that for every point $(r_{\Gamma^a}, \theta_{\Gamma^a})$ on the configuration space projection of Γ^a , the corresponding phase space structure is a circle implicitly defined by ([eq:Hamm]) as

$$E - U(r_{\Gamma^a}, \theta_{\Gamma^a}) = \frac{1}{2\mu_m} p_r^2 + \frac{1}{2} p_\theta^2 \left(\frac{1}{I} + \frac{1}{\mu_m r^2} \right).$$

Note that the radius of the circle never vanishes along Γ^a as the kinetic energy never vanishes along Γ^a .

A trajectory is considered a roaming trajectory if it originates in the potential well and crosses DS^a at least three times before dissociating. If a trajectory crosses DS^a an even number of times and enters either one of the potential wells, it is an isomerisation trajectory.

Roaming can be reformulated as a transport problem (Krajňák and Waalkens 2018) in the following manner. Let DS^i and DS^o be defined using Γ^i and Γ^o analogously to DS^a . It is well known that a dividing surface associated with a periodic orbit that reaches two equipotentials, such as Γ^i , is a sphere. Using reasoning similar to the above one can see, that because the kinetic energy along Γ^i vanishes when it reaches the equipotentials, DS^i consists of circles except for the poles which are points, thus a sphere. Γ^i , being the equator of this sphere, divides it into two hemispheres with unidirectional flux - trajectories leaving the well cross the outward hemisphere while trajectories entering the well cross the inward hemisphere.

DS^a and DS^o are tori, but they too can be divided into two parts of unidirectional flux. This can be easily seen on DS^o , but a similar argument applies to DS^a . Since Γ^o has a constant radius and $p_r = 0$, the two orbits are characterised by p_θ^2 being maximal for the given energy along the orbit. Any trajectory crossing DS^o must therefore have $p_r \neq 0$. All trajectories with $p_r > 0$ cross the outward

annulus of DS^o bounded by the two orbits Γ^o , while all with $p_r < 0$ cross the inward annulus and enter the interaction region.

Note that because dividing surfaces divide the energy surface into two separate partitions, the dividing surfaces defined above have the following roles. Since Γ^i lies on the edge of the potential well, the role of DS^i is to divide the the energy surface region associated with the potential well from the rest of the energy surface. Every trajectory that enters or exists the well must cross DS^i . Similarly, DS^o is used to divide the dissociated states from the rest of the energy surface and every trajectory going from one part of the energy surface into the other must cross DS^o . DS^a divides the the energy surface interaction region between DS^i and DS^o into two, but neither of the two partitions bears a relevant meaning. The definition of roaming is the sole purpose of this surface in this investigation.

We can formulate dissociation as a problem of transport of trajectories between dividing surfaces in the following manner. By definition, trajectories that leave the well must cross the outward hemisphere of DS^i . Trajectories that leave the interaction region (dissociate), cross the outward annulus of DS^o . Dissociation is therefore a question of how trajectories from the outward hemisphere of DS^i reach the outward annulus of DS^o .

In the process of being transported from DS^i to DS^o , dissociating trajectories originating must cross the outward annulus of DS^a . Roaming trajectories cross the torus DS^a at least three times, first the outward annulus and then alternately the inward and the outward annulus. It should be noted that trajectories originating in either of the wells have to cross the outward annulus of DS^a before they can reach its inward annulus. Similarly trajectories going from the inward annulus of DS^a to the outward annulus of DS^o must cross the outward annulus of DS^a . Therefore trajectories that originate in the well and cross the inward annulus of DS^a before dissociating are roaming trajectories.

The role of phase space structures in reaction dynamics has been explained on many occasions (Wiggins et al. 2001; Uzer et al. 2002; Waalkens and Wiggins 2004). Dividing surfaces as defined above can be shown to be the surfaces of minimal flux (Waalkens and Wiggins 2004) and therefore sit in the narrowest part of the bottleneck, be it a sphere such as DS^i or a torus such as DS^a and DS^o . Structures that convey trajectories across such a bottleneck were identified to be stable and unstable invariant manifolds of the unstable periodic orbit. These invariant manifolds have a cylindrical structure and form a barrier between trajectories that are lead through the bottleneck (inside) and those are not (outside).

For each unstable orbit Γ , there are two branches of stable invariant manifold, i.e. manifolds consisting of a continuum of trajectories that are asymptotic to the orbit in forward time, and two branches of unstable invariant manifold, asymptotic in backward time. We shall denote the invariant manifolds of Γ by W_Γ , we distinguish stable and unstable by a superscript, W_Γ^s and W_Γ^u , and if we refer to an individual branch, we add a $+$ or $-$ to the superscript to indicate,

whether the branch leaves the neighbourhood of Γ to the $r > r_\Gamma$ side (+) or to the $r < r_\Gamma$ side (-).

The precise cylindrical structure of the manifold reflects the geometry of the corresponding periodic orbit in a similar way as it is reflected by the corresponding dividing surface. Manifolds W_{Γ^i} are spherical cylinders, whereas W_{Γ^a} and W_{Γ^o} are toric cylinders. The different geometries can be understood from a phase space perspective.

For any fixed energy, Γ^i is a (topological) circle with its center, due to symmetry of the system, on the ray $\theta = 0$, $p_r = p_\theta = 0$. This property is passed on to all four branches of W_{Γ^i} , these too are always centered at/symmetric with respect to $\theta = 0$, $p_r = p_\theta = 0$, no matter how heavily they are deformed by the flow which is smooth.

In contrast, W_{Γ^a} and W_{Γ^o} are centered at $r = 0$, just like the corresponding orbits Γ^a and Γ^o . This property is independent of energy.

All of this is a consequence of the local energy surface geometry that is not uniform throughout the energy surface and can be observed as qualitatively different forms of dynamics - vibration and rotation.

Phase space structures responsible for roaming {#sec:phase roaming}

We study invariant manifolds and their intersections on a surface of section, namely on an accurate approximation of the outward annulus of DS^a . Both annuli of DS^a are transversal to the flow and are bounded by Γ^a . Suppose the configuration space projection of Γ^a can be parametrised using the function $\bar{r}(\theta)$ as $(\bar{r}(\theta), \theta)$ and define

$$\rho(r, \theta) = r - \bar{r}(\theta).$$

Clearly Γ^a is then given by

$$\rho(r, \theta) = 0,$$

and the outward annulus of DS^a is defined by all points $(r, \theta, p_r, p_\theta)$ on the energy surface, such that

$$\rho(r, \theta) = 0, \quad \dot{\rho}(r, \theta) > 0.$$

Note that $\dot{\rho}(r, \theta) > 0$ is not equivalent to $\dot{r} > 0$.

Most notably, we are interested in the interaction between $W_{\Gamma^i}^{u+}$, the manifold guiding trajectories that leave the potential well into the interaction region, and $W_{\Gamma^o}^{s-}$, the manifold guiding trajectories out of the interaction region into dissociated states. Figure [fig:middlesec] illustrates intersections of these manifolds with the outward annulus of DS^a .

Note that the section of $W_{\Gamma^i}^{u+}$ with the outward annulus of DS^a produces a topological circle (further denoted γ_i^{u+}) centered at $\theta = 0, p_\theta = 0$. Recall from Section 4 that all branches of W_{Γ^i} are centered at/symmetric with respect to $\theta = 0, p_r = p_\theta = 0$. The shape of γ_i^{u+} is just a consequence of this fact.

Similarly the section of $W_{\Gamma^o}^{s-}$ with the outward annulus of DS^a (further denoted γ_o^{s-}) reflects the fact that Γ^o and all branches of W_{Γ^o} are centered at $r = 0$. Although γ_o^{s-} seem like lines, these are two circles concentric with DS^a . For simplicity, we omit one of the γ_o^{s-} circles in all following figure and concentrate on the upper half plane $p_\theta > 0$.

All of the figures displaying intersections of invariant manifolds with the outward annulus of DS^a should be understood as follows. Note that for the sake of simplicity we take advantage of symmetry of the system and usually restrict ourselves to $\theta \in [-\pi/2, \pi/2], p_\theta \geq 0$ when considering the outward annulus of DS^a . Consequently, with the exception of Figure [fig:middlesec], we only show manifolds corresponding to one of the orbits of Γ^i and one of Γ^o .

Recall that the interior of γ_i^{u+} contains trajectories that leave the well, while γ_o^{s-} contains dissociating trajectories which do not return to the surface of section as indicated in Figure [fig:middlesec]. The intersection must therefore contain trajectories that lead to immediate dissociation, such as the radial trajectory $\theta = 0, p_\theta = 0$.

Roaming trajectories do not dissociate immediately, therefore they are contained γ_i^{u+} , but not in γ_o^{s-} . These trajectories have too much energy in the angular degree of freedom, i.e. $|p_\theta|$ is large. The other kind of trajectories contained in $\gamma_i^{u+} \setminus \gamma_o^{s-}$ are those that re-enter either of the wells, these correspond to isomerisation.

If γ_i^{u+} and γ_o^{s-} do not intersect, that is, all of $W_{\Gamma^i}^{u+}$ is contained in $W_{\Gamma^o}^{s-}$, roaming is not present in the system for the given parameter values. For this reason the system does not admit (Krajňák and Waalkens 2018) roaming for $E \geq 2.5$, $m = m_H$ and $a = 1$.

While it is true that $\gamma_i^{u+} \setminus \gamma_o^{s-}$ contains roaming trajectories, it is not true that the area of the intersection is proportional to the amount of roaming trajectories. Since $\gamma_i^{u+} \setminus \gamma_o^{s-}$ tends to grow together with γ_i^{u+} and γ_i^{u+} can only grow at the cost of $\gamma_o^{s-} \setminus \gamma_i^{u+}$, the areas $\gamma_i^{u+} \setminus \gamma_o^{s-}$ and $\gamma_o^{s-} \setminus \gamma_i^{u+}$ behave like complements. Therefore the amount of roaming is limited by $\gamma_o^{s-} \setminus \gamma_i^{u+}$, the area where roaming and nonreactive trajectories (see Figure [fig:middlesec]) cross the outer annulus of DS^a for the last time before dissociating.

To see how m and a influence roaming, we will study how γ_i^{u+} and γ_o^{s-} change by calculating the areas $\gamma_i^{u+} \setminus \gamma_o^{s-}$ and $\gamma_o^{s-} \setminus \gamma_i^{u+}$. The size of $\gamma_i^{u+} \setminus \gamma_o^{s-}$ is correlated with the maximal value of p_θ along γ_i^{u+} and the minimal p_θ along γ_o^{s-} . Once we know this area, it is easy to determine $\gamma_o^{s-} \setminus \gamma_i^{u+}$ using the actions of the orbits Γ^i and Γ^o .

The area $\gamma_i^{u+} \setminus \gamma_o^{s-}$ grows with increasing m . Consequently we arrive at one of the main conclusions of this work, namely that roaming diminishes for large and small values of m (Figure [fig:Wiincr]) with an optimum inbetween. This can be seen for $a \leq 2$, but for larger values of a , the optimum may move towards masses unreasonable for roaming. Disappearance of roaming for large masses is due to a slowdown in the radial degree of freedom and the significant variation of position of Γ^o with mass. We explain these two effect separately in Sections 6 and 7. The reason for the disappearance of roaming for low masses is due to a stronger coupling of the degrees of freedom in the kinetic part of the Hamiltonian ([eq:Hamm]) that we deal with in Section 8.

The parameter a influences the transition between vibration and rotation by controlling the amplitude of the anisotropy in the potential. As noted in Section 2, the larger a is, the more the potential wells open up in the angular direction allowing easier access of the wells by trajectories from the interaction region. Instead of promoting roaming, this favours isomerisation, because at the same time the height of the potential barrier between the wells decreases as shown in Figure [fig:thpi2]. We explain the process in Section 9.

Simplification of the system and inner orbits

The mass of the free atom m is only present in terms of the kinetic part of the Hamiltonian ([eq:Hamm]) and therefore cannot be studied from a configuration space perspective. From the Hamiltonian equations of motion

$$\begin{aligned}\dot{r} &= \frac{1}{\mu_m} p_r, \\ \dot{p}_r &= \frac{p_\theta^2}{\mu_m r^3} - \frac{\partial U}{\partial r}, \\ \dot{\theta} &= \left(\frac{1}{\mu_m r^2} + \frac{1}{I} \right) p_\theta, \\ \dot{p}_\theta &= -\frac{\partial U}{\partial \theta},\end{aligned}$$

one can see, that m influences the relation between momenta p_r , p_θ and velocities \dot{r} , $\dot{\theta}$ as well as the centrifugal contribution in \dot{p}_r . All of these are weakened with increasing m .

Provided m is sufficiently large (in practice $m > 4$), $\frac{1}{\mu r^2}$ is small compared to $\frac{1}{I}$ in the interaction region. For the purposes of the following argument we can neglect the term $\frac{1}{\mu r^2}$ and consider the Hamiltonian

$$\tilde{H}_m(r, \theta, p_r, p_\theta) = \frac{1}{2\mu_m} p_r^2 + \frac{1}{2I} p_\theta^2 + U(r, \theta).$$

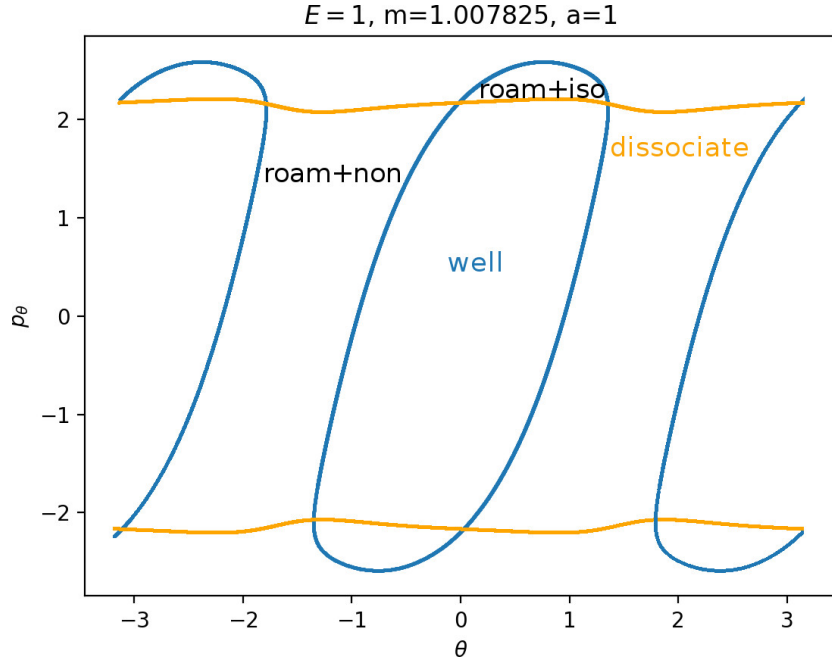


Figure 2: Intersection of $W_{\Gamma_o}^{s-}$ (orange) and $W_{\Gamma_i}^{u+}$ (blue) with the outward annulus of the DS^a for $E = 1$, $m = 1.007825$ and $a = 1$, indicating where trajectories corresponding to different types of dynamics intersect the surface. Area enclosed by γ_i^{u+} is crossed by trajectories that are leaving the well, while γ_o^{s-} leads dissociating trajectories out of the interaction region, $\gamma_i^{u+} \setminus \gamma_o^{s-}$ contains roaming and isomerisation trajectories, and $\gamma_o^{s-} \setminus \gamma_i^{u+}$ is crossed by roaming and non-reactive trajectories.

The associated equations are

$$\begin{aligned}\dot{r} &= \frac{1}{\mu_m} p_r, \\ \dot{p}_r &= -\frac{\partial U}{\partial r}, \\ \dot{\theta} &= \frac{1}{I} p_\theta, \\ \dot{p}_\theta &= -\frac{\partial U}{\partial \theta}.\end{aligned}$$

The degrees of freedom in the resulting system are only coupled via $U(r, \theta)$ and the mass parameter m only influences \dot{r} .

Let $m_0 < m_1$, $H_{m_0} = H_{m_1} = E$ and p_θ be such that it satisfies the fixed energy constraint. Denote by $p_{r_{m_0}}, p_{r_{m_1}}$ the momenta given by the Hamiltonians defined as follows:

$$\begin{aligned}p_{r_{m_0}} &= \sqrt{2\mu_{m_0} \left(E - U(r, \theta) - \frac{p_\theta^2}{2I} \right)}, \\ p_{r_{m_1}} &= \sqrt{2\mu_{m_1} \left(E - U(r, \theta) - \frac{p_\theta^2}{2I} \right)}.\end{aligned}$$

Then provided p_θ is not maximal, by

$$\frac{\mu_{m_0}}{\mu_{m_1}} = \frac{\frac{m_{CH_3} m_0}{m_{CH_3} + m_0}}{\frac{m_{CH_3} m_1}{m_{CH_3} + m_1}} = \frac{m_0 m_{CH_3} + m_0 m_1}{m_1 m_{CH_3} + m_0 m_1} < 1,$$

we have that

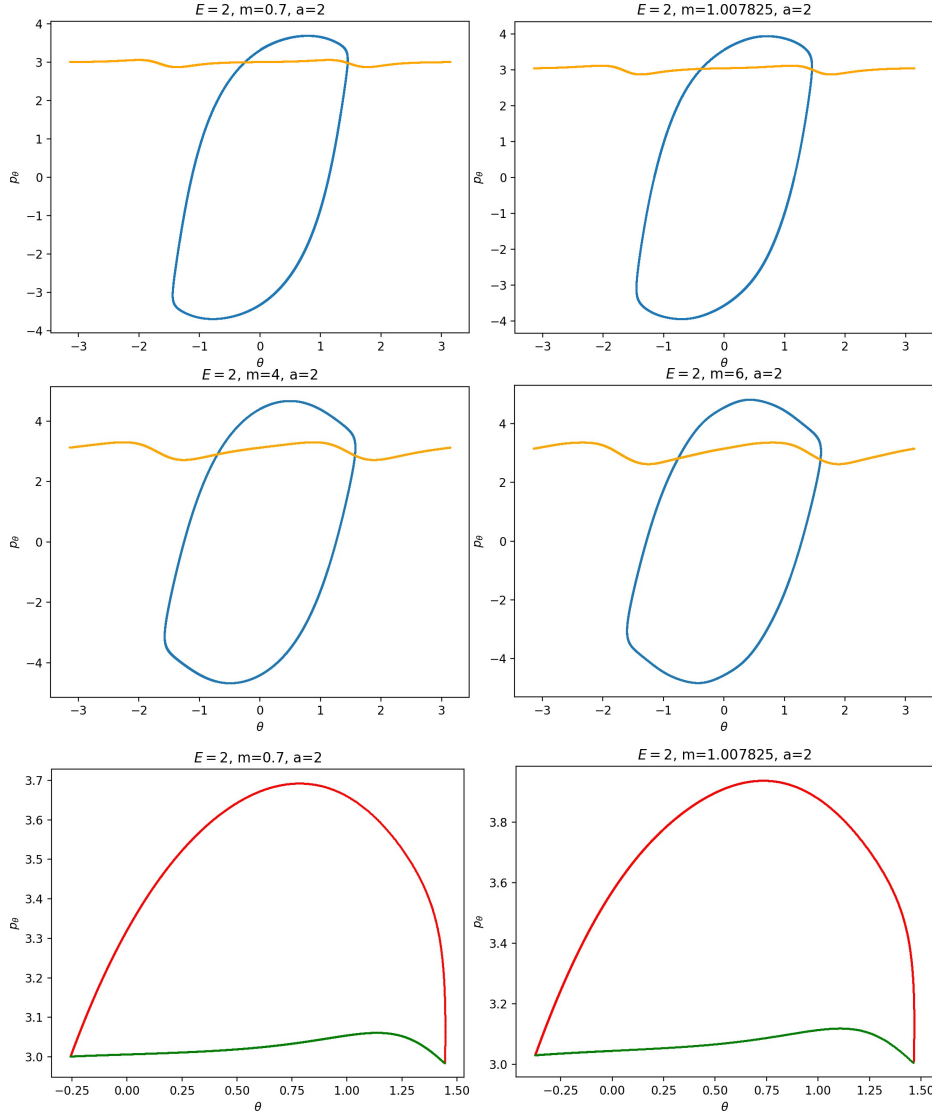
$$\frac{p_{r_{m_1}}}{\mu_{m_1}} = \frac{1}{\mu_{m_1}} \sqrt{2\mu_{m_1} \left(E - U - \frac{p_\theta^2}{2I} \right)} = \sqrt{\frac{\mu_{m_0}}{\mu_{m_1}}} \frac{1}{\mu_{m_0}} \sqrt{2\mu_{m_0} \left(E - U - \frac{p_\theta^2}{2I} \right)} = \sqrt{\frac{\mu_{m_0}}{\mu_{m_1}}} \frac{p_{r_{m_0}}}{\mu_{m_0}} < \frac{p_{r_{m_0}}}{\mu_{m_0}}.$$

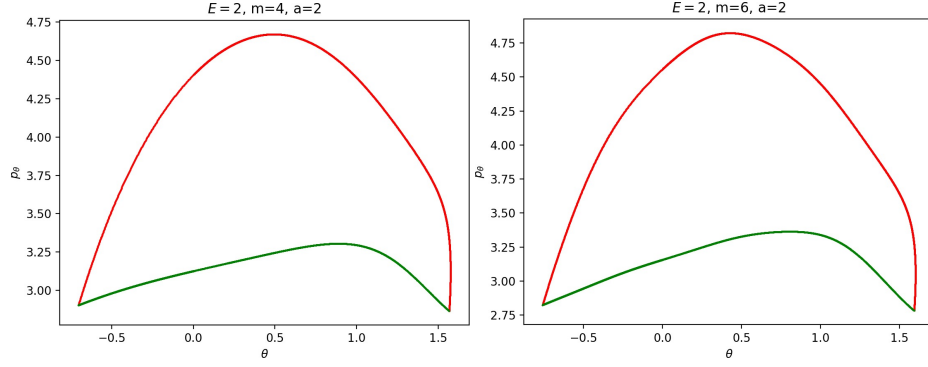
For p_θ maximal we trivially have $p_{r_{m_1}} = p_{r_{m_0}} = 0$. Trajectories therefore slow down in the radial direction with increasing m for each r, θ, p_θ on the energy surface.

Implications for the section of $W_{\Gamma_i}^{u+}$ with the DS^a:

- Slowdown in radial direction, whereby $W_{\Gamma_i}^{u+}$ is more likely to hit the potential island.
- The interaction of $W_{\Gamma_i}^{u+}$ with the potential island is the only mechanism to transfer energy between the degrees of freedom.
- A push from the potential island in the radial direction means decrease in p_θ along $W_{\Gamma_i}^{u+}$.

Note that Figures [fig:Wiincr] and [fig:Wiincrdetail] seem to contradict the last point. This is due to the varying radial position of DS^a , when Γ^a comes closer to Γ^i as m increases (see Figure [fig:poconfig]). The decrease can be observed on surfaces with constant radius, however $W_{\Gamma^i}^{u+}$ can become tangent to such surfaces when m is varied.





Reduction of the system and outer orbits

If r is sufficiently large, U is rotationally symmetric and

$$V_{red}(r) = \frac{p_\theta^2}{2mr^2} + U(r),$$

where p_θ becomes a constant of motion. $U(r)$ is monotonic, $U(r) < 0$ and $U \in o(r^{-2})$ as $r \rightarrow \infty$, therefore the reduced system admits an equilibrium given by $r = r_{po}$, $p_r = 0$, where r_{po} is the solution of

$$\dot{p}_r = -\frac{\partial H}{\partial r} = \frac{1}{\mu r_{po}^3} p_\theta^2 - U'(r_{po}) = 0,$$

or equivalently

$$\frac{p_\theta^2}{\mu r_{po}^2} = r_{po} U'(r_{po}). \quad (5)$$

In the full system this relative equilibrium is manifested as a periodic orbit with initial conditions $r = r_{po}$, $\theta = \text{const}$, $p_r = 0$ and p_θ^\pm such that $H(r_{po}, 0, \theta, p_\theta^\pm) = E$.

To understand the influence of m on the periodic orbit, let us first establish the relationship between r_{po} and p_θ^\pm and incorporate the dependence on μ_m subsequently. Combining $H(r_{po}, 0, \theta, p_\theta^\pm) = E$, i.e.

$$E = \frac{p_\theta^{\pm 2}}{2I} + \frac{p_\theta^{\pm 2}}{2\mu_m r_{po}^2} + U(r_{po}), \quad (6)$$

with ([eq:pr]) yields

$$E = \frac{p_\theta^{\pm 2}}{2I} + \frac{1}{2} r_{po} U'(r_{po}) + U(r_{po}).$$

If $\frac{1}{2}rU'(r) + U(r)$ is monotonic in r (for r sufficiently large), then we find that r_{po} increases or decreases with $p_\theta^{\pm 2}$. In case of Chesnavich's CH_4^+ model, $\frac{1}{2}rU'(r) + U(r)$ is positive and monotonically decreasing. This is due to the leading term of U for large r being $-cr^{-4}$, where $c > 0$, while that of $\frac{1}{2}rU'(r)$ must be $2cr^{-4}$. It is sufficient that $U(r) < 0$ and $U \in o(r^{-2})$ as $r \rightarrow \infty$. Consequently we see that an increase in $p_\theta^{\pm 2}$ must lead to an increase in r_{po} and vice versa for every fixed energy E .

To gain insight on the influence of m , we rewrite ([eq:pr]) as

$$p_\theta^{\pm 2} = \mu_m r_{po}^3 U'(r_{po}),$$

and plug it into ([eq:Epr0]) to obtain

$$E = \frac{\mu_m r_{po}^3 U'(r_{po})}{2I} + \frac{\mu_m r_{po}^3 U'(r_{po})}{2\mu_m r_{po}^2} + U(r_{po}) = \frac{\mu_m r_{po}^3 U'(r_{po})}{2I} + \frac{1}{2} r_{po} U'(r_{po}) + U(r_{po}).$$

We have already noted that (for r sufficiently large) $\frac{1}{2}rU'(r) + U(r)$ is positive and monotonically decreasing. As a function of r (where r is sufficiently large), $\frac{\mu_m r^3 U'(r)}{2I}$ is also positive and monotonically decreasing, provided $U \in o(r^{-3})$ which is the case for Chesnavich's potential. Therefore to maintain a fixed energy E and increase in μ_m must be compensated by an increase in r_{po} .

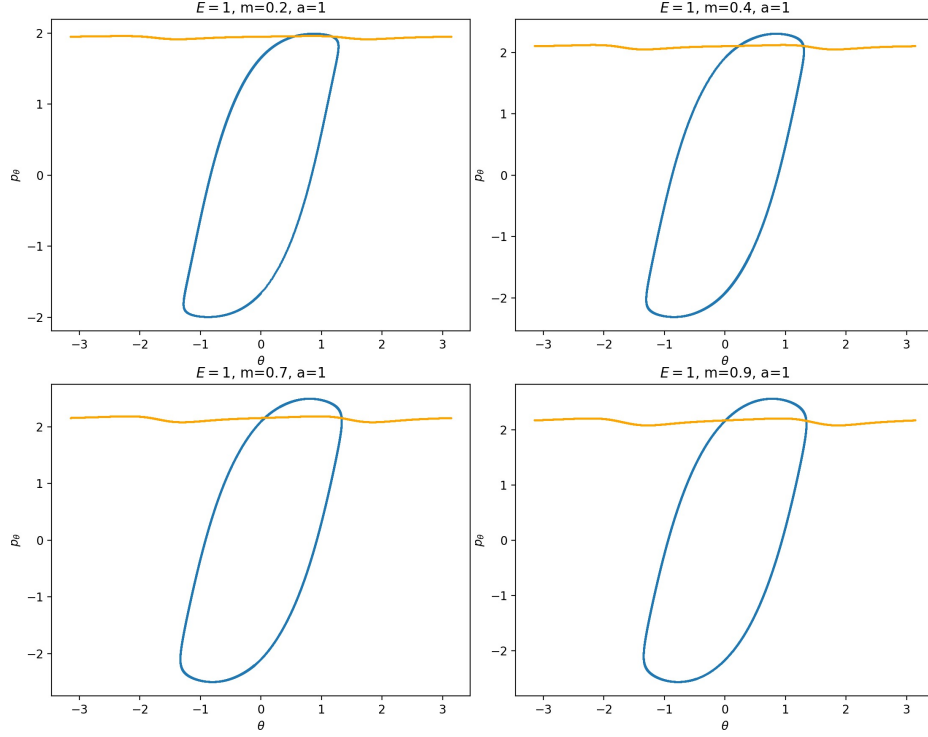
We see that r_{po} and $p_\theta^{\pm 2}$ increase with m . Note that the reasoning remains true any potential that is rotationally symmetric, monotonic and in the class $o(r^{-3})$ for r sufficiently large and can be extended to systems with non-zero total angular momentum.

Implications for γ_o^{s-} :

- Γ_\pm^o moves away with increasing m .
- p_θ increases along γ_o^{s-} with m and it is less influenced by the radial degree of freedom.

Small masses

As justified in Section 7, r_{po} and $p_\theta^{\pm 2}$ increase with m . Therefore for $m < m_H$ we see that Γ_\pm^o moves inward and p_θ along γ_o^{s-} decreases. This alone does not suffice to make conclusions regarding roaming, because we know that roaming does not exist for atoms with very small masses as suggested by Figure [fig:middlesmallm].



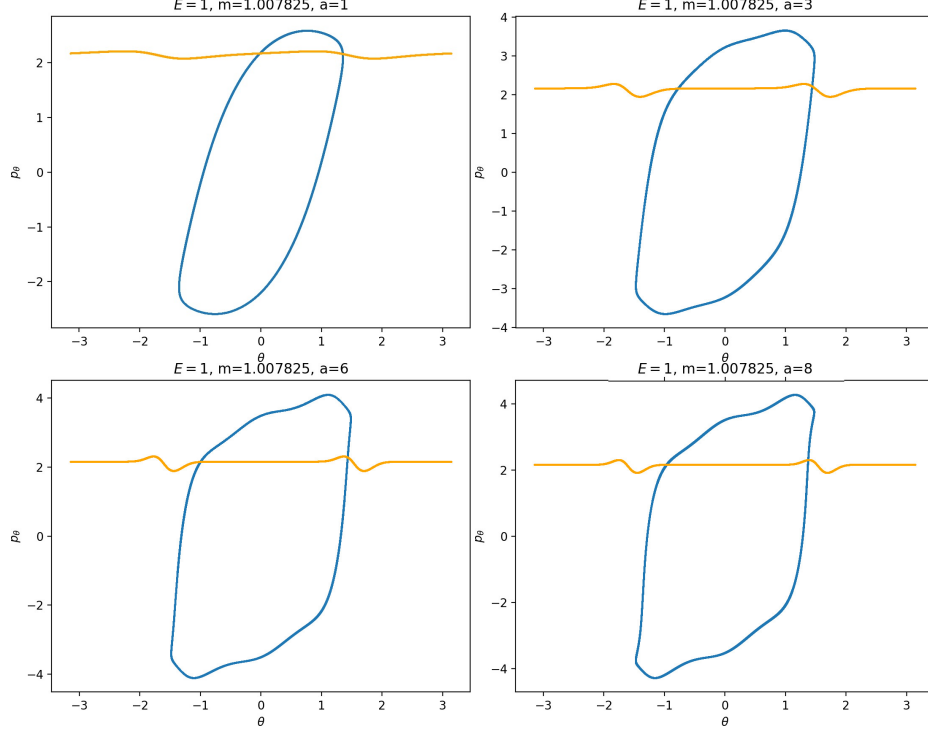
For $m < m_H$, p_θ^2 has a significant influence on \dot{p}_r , especially in the wells where r is small, and also $\dot{r} = \frac{1}{m}p_r$ grows faster. This prevents $W_{\Gamma_i}^{u+}$ from entering areas of high potential near the potential islands and limits the transfer of energy into the angular degree of freedom, since the contribution of the potential in the interaction region is minimal. Although p_θ along Γ^o decreases, fewer and shorter segments of $W_{\Gamma_i}^{u+}$ can gain sufficient angular momentum to be repelled by the centrifugal barrier back into the interaction region.

Influence of a on roaming

The parameter a influences the strength of coupling of the degrees of freedom via the potential and thereby it influences (Chesnavich 1986) how early (e.g. $a = 4$) or late (e.g. $a = 1$) the transition from vibration to rotation occurs. An investigation of the differences in dynamics for $a = 1$ and $a = 4$ can be found in Ref. . In physical terms, a controls the anisotropy of the rigid molecule CH_3^+ .

It turns out that the expansion of the potential wells and the reduction of potential islands around the index-2 saddles with increasing a does have a significant impact on roaming. As can be seen from Figure [fig:middleE1aa], the area $\gamma_i^{u+} \setminus \gamma_o^{s-}$ increases with a . However, as pointed out in Section 5 if $\gamma_i^{u+} \setminus \gamma_o^{s-}$ grows, $\gamma_o^{s-} \setminus \gamma_i^{u+}$ must shrink and therefore larger values of a result

all other classes of dynamics diminishing in favour of isomerisation.



Resulting upper bound on roaming

Below we give the upper bound on roaming, which is the ratio of the minimum of the areas $\gamma_i^{u+} \setminus \gamma_o^{s-}$ and $\gamma_o^{s-} \setminus \gamma_i^{u+}$ to the energy surface volume for $r = \infty$. As explained above, the area $\gamma_i^{u+} \setminus \gamma_o^{s-}$ contains all isomerisation and roaming trajectories, while $\gamma_o^{s-} \setminus \gamma_i^{u+}$ contains all roaming and nonreactive trajectories. The energy surface volume at $r = \infty$ corresponds to all trajectories in the system with the exception of stable islands, which are not relevant in the context of roaming. This measure does not account for isomerisation trajectories, because these are cut off when they re-enter one of the wells. Since all trajectories with the exception of stable islands must eventually leave the wells and the interaction region, we effectively avoid double-counting. Values of the upper bound can be found in Table [tab:1] as well as in Figure [fig:corrroam].

We do not provide values for $E = 0.5$ and $m > 4$ due to the large radius of Γ^o ; for $E = 1$, $a = 8$ and $m < 0.9$ due to a bifurcation of Γ^i around $m = 0.856$ after which DS^i no longer delimits the corresponding potential well in a reasonable manner and similarly for $E = 2$ and $a = 8$.

As the values in Table [tab:1] show, the prominence of roaming does not evolve in a simple manner. In agreement with conclusions in Sections 6, 7, 8, the proportion of roaming decreases or even disappears for very large and very small masses of the free atom and we know it also recedes in favour of isomerisation with increasing a . Unlike the area of $\gamma_i^{u+} \setminus \gamma_o^{s-}$, which grows monotonically both in m and a , our upper bound on roaming being the smaller of $\gamma_i^{u+} \setminus \gamma_o^{s-}$ and $\gamma_o^{s-} \setminus \gamma_i^{u+}$ does not. Figure [fig:corrroam] suggest that while there is an optimum at a reasonable mass for $a = 1$ and occasionally $a = 2$, the bound otherwise decreases with m with an optimum at a value of m smaller than considered in this work.

The strange evolution of the bound with respect to a , which is shown in Figure [fig:corrroam], is probably due to the inaccuracy of the bound. Overall it seems that the proportion of roaming mostly decreases, which is due to prevalence of isomerisation as a increases.

An estimate of the amount of roaming in the system can be obtained via an approximation of the proportion of nonreactive trajectories in $\gamma_o^{s-} \setminus \gamma_i^{u+}$ either via a computationally expensive brute force method or from the intersection of invariant manifolds with a surface $\theta = \text{const}$ that does not suffer from transition between spherical and toric local geometries. Such an estimate is outside of the scope of this work.

$E = 0.5$

Table 2: Ratio of the minimum of the areas $\gamma_i^{u+} \setminus \gamma_o^{s-}$ and $\gamma_o^{s-} \setminus \gamma_i^{u+}$ to the measure of all trajectories in the system (for details see text) for $E = 0.5, 1, 2$ and various values of m and a .

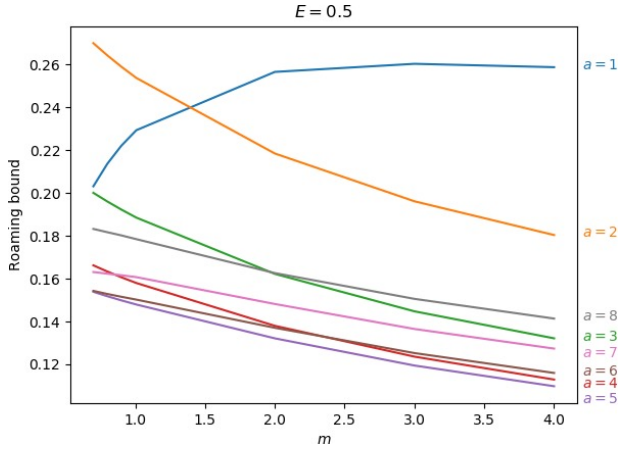
	0.7	0.8	0.9	m_H	2	3	4	5	6	7	8	m
1	0.203	0.214	0.222	0.229	0.257	0.260	0.259					
2	0.270	0.264	0.259	0.254	0.218	0.196	0.180					
3	0.200	0.196	0.192	0.189	0.162	0.145	0.132					
4	0.166	0.163	0.161	0.158	0.138	0.124	0.113					
5	0.154	0.152	0.150	0.148	0.132	0.119	0.110					
6	0.154	0.153	0.152	0.150	0.137	0.125	0.116					
7	0.163	0.162	0.162	0.161	0.148	0.137	0.127					
8	0.183	0.182	0.180	0.178	0.163	0.151	0.141					
a												

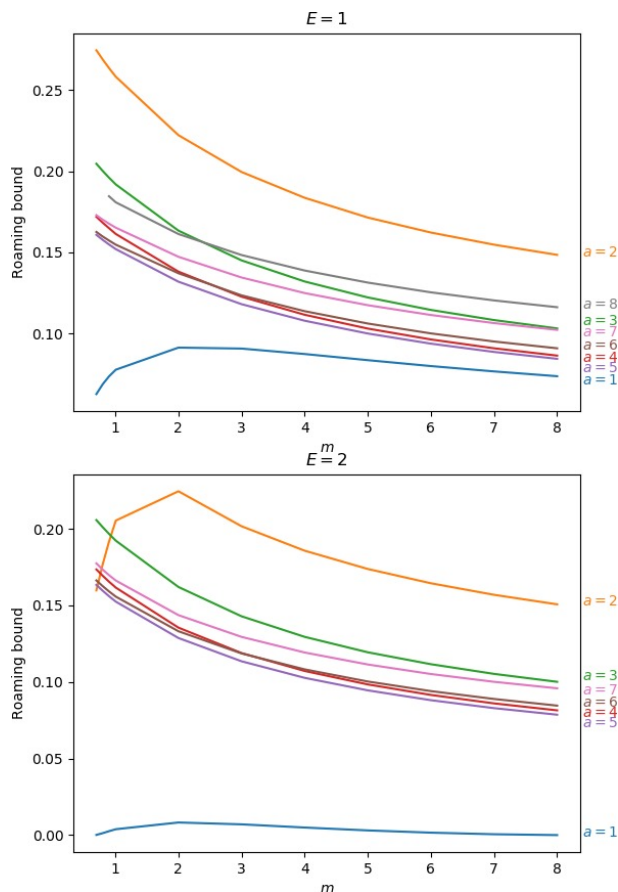
$E = 1$

	0.7	0.8	0.9	m_H	2	3	4	5	6	7	8	m
1	0.063	0.069	0.074	0.078	0.091	0.091	0.087	0.084	0.080	0.077	0.074	
2	0.274	0.269	0.264	0.258	0.222	0.200	0.184	0.171	0.162	0.155	0.148	
3	0.205	0.200	0.196	0.192	0.163	0.145	0.132	0.122	0.115	0.108	0.103	
4	0.172	0.168	0.165	0.161	0.138	0.123	0.112	0.103	0.096	0.091	0.086	
5	0.161	0.158	0.155	0.152	0.132	0.118	0.108	0.100	0.094	0.089	0.084	
6	0.163	0.160	0.157	0.155	0.137	0.124	0.114	0.106	0.100	0.095	0.091	
7	0.173	0.170	0.168	0.165	0.147	0.135	0.125	0.117	0.111	0.106	0.102	
8			0.185	0.181	0.161	0.148	0.139	0.131	0.125	0.120	0.116	
a												

$E = 2$

	0.7	0.8	0.9	m_H	2	3	4	5	6	7	8	m
1	0.000	0.001	0.003	0.004	0.008	0.007	0.005	0.003	0.002	0.001	0.000	
2	0.160	0.177	0.192	0.205	0.224	0.202	0.186	0.174	0.164	0.157	0.151	
3	0.206	0.201	0.197	0.192	0.162	0.143	0.129	0.119	0.112	0.105	0.100	
4	0.173	0.169	0.165	0.162	0.135	0.119	0.107	0.098	0.092	0.086	0.081	
5	0.163	0.160	0.156	0.152	0.129	0.113	0.103	0.095	0.088	0.083	0.079	
6	0.166	0.163	0.159	0.156	0.133	0.119	0.108	0.100	0.094	0.089	0.085	
7	0.177	0.173	0.170	0.166	0.144	0.129	0.119	0.111	0.105	0.100	0.096	
a												





Summary and conclusion

We have shown how invariant manifolds that are responsible for roaming evolve with respect to the mass of the free atom m and coupling parameter a that controls the geometry of the potential energy surface. Moreover we provided arguments that follow from the role of parameters in the equations of motion to justify the evolution. These arguments make it also possible to predict behaviour outside of the studied parameter intervals relevant for roaming.

From a quantitative perspective we established an upper bound on the prominence of roaming in Chesnavich's CH_4^+ model. The bound only highlights the intricacy of roaming as a type of dynamics on the verge between isomerisation and nonreactivity. It relies on a generous access to the potential wells to allow reactions as well as a prominent area of high potential that aids sufficient transfer of energy from angular motion to radial motion to prevent isomerisation.

We conclude that it is not possible to choose realistic values of m and a , such that roaming becomes the dominant form of dissociation such as found in acetaldehyde (Heazlewood et al. 2008). Therefore the dominance of roaming must be due to other properties of the system than only mass of the free atom and strength of potential coupling of the degrees of freedom. Our investigation shows that roaming is prone to being dominated by other types of dynamics. Therefore the path to dominance of roaming lies in, as our investigation shows, potential wells that are easily accessible by being ‘open’ in the angular direction to discourage nonreactivity, yet are separated by a sufficiently high isomerisation barrier.

It is interesting to speculate about the relationship between the roaming mechanism and reactions of floppy molecules, such as HCN and KCN. Both types of reaction are focussed on large-amplitude motions. As we have described, in Chesnavich’s model it is the relatively long-range part of the potential that is of interest; that is where dissociation, roaming, and the passage from one inner DS to the other occurs.

With HCN, for example, the focus is on isomerisation dynamics. In the setting of Chesnavich’s model, this means the concern is about the properties of the ‘inner’ region of the potential energy surface. In the study of roaming in Chesnavich’s model the inner region of the potential energy surface (interior to the inner DS) is basically left unspecified.

Nevertheless, as noted in discussions of Ezra and Houston, it is probably true that roaming is just a special case of large-amplitude motions. Consequently, it may well be possible to identify large amplitude eigenstates of floppy molecules, such as HCN or KCN, that correspond to roaming motion, and these may be associated with periodic orbits in the interaction region. This is an interesting topic for further investigation.

Bowman, J. M. 2014. “Roaming Radicals.” *Mol. Phys.* 112 (19): 2516–28. <https://doi.org/10.1080/00268976.2014.897395>.

Bowman, J. M., and P. Houston. 2017. “Theories and Simulations of Roaming.” *Chem. Soc. Rev.* 46: 7615–24. <https://doi.org/10.1039/C7CS00578D>.

Bowman, J. M., and B. C. Shepler. 2011. “Roaming Radicals.” *Annu. Rev. Phys. Chem.* 62: 531–53. <https://doi.org/10.1146/annurev-physchem-032210-103518>.

Chesnavich, W. J. 1986. “Multiple Transition States in Unimolecular Reactions.” *J. Chem. Phys.* 84 (5): 2615–9. <https://doi.org/10.1063/1.450331>.

Heazlewood, B. R., M. J. T. Jordan, S. H. Kable, T. M. Selby, D. L. Osborn, B. C. Shepler, B. J. Braams, and J. M. Bowman. 2008. “Roaming Is the Dominant Mechanism for Molecular Products in Acetaldehyde Photodissociation.” *Proc. Nat. Acad. Sci.* 105: 12719–24. <https://doi.org/10.1073/pnas.0802769105>.

Huston, P. L., R. Conte, and J. M. Bowman. 2016. “Roaming Under the Microscope: Trajectory Study of Formaldehyde Dissociation.” *J. Phys. Chem. A* 120: 5103–14. <https://doi.org/10.1021/acs.jpca.6b00488>.

- Jordan, M. J. T., S. C. Smith, and R. G. Gilbert. 1991. "Variational Transition State Theory: A Simple Model for Dissociation and Recombination Reactions of Small Species." *J. Phys. Chem.* 95 (22): 8685–94. <https://doi.org/10.1021/j100175a050>.
- Krajňák, V., and H. Waalkens. 2018. "The Phase Space Geometry Underlying Roaming Reaction Dynamics." *J. Math. Chem.* 56 (8): 2341–78. <https://doi.org/10.1007/s10910-018-0895-4>.
- MacKay, R. S., and D. C. Strub. 2014. "Bifurcations of transition states: Morse bifurcations." *Nonlinearity* 27 (5): 859–95. <https://doi.org/10.1088/0951-7715/27/5/859>.
- . 2015. "Morse Bifurcations of Transition States in Bimolecular Reactions." *Nonlinearity* 28 (12): 4303. <https://doi.org/10.1088/0951-7715/28/12/4303>.
- Mauguière, F. A. L., P. Collins, G. S. Ezra, S. C. Farantos, and S. Wiggins. 2014a. "Multiple Transition States and Roaming in Ion–Molecule Reactions: A Phase Space Perspective." *Chem. Phys. Lett.* 592: 282–87. <https://doi.org/10.1016/j.cplett.2013.12.051>.
- . 2014b. "Roaming Dynamics in Ion-Molecule Reactions: Phase Space Reaction Pathways and Geometrical Interpretation." *J. Chem. Phys.* 140 (13). AIP Publishing: 134112. <https://doi.org/10.1063/1.4870060>.
- Mauguière, F. A. L., P. Collins, Z. C. Kramer, B. K. Carpenter, G. S. Ezra, S. C. Farantos, and S. Wiggins. 2015. "Phase Space Structures Explain Hydrogen Atom Roaming in Formaldehyde Decomposition." *J. Phys. Chem. Lett.* 6 (20): 4123–8. <https://doi.org/10.1021/acs.jpcclett.5b01930>.
- . 2016. "Phase Space Barriers and Dividing Surfaces in the Absence of Critical Points of the Potential Energy: Application to Roaming in Ozone." *J. Chem. Phys.* 144 (5): 54107. <https://doi.org/10.1063/1.4940798>.
- Townsend, D., A. Lahankar, S. K. Lee, S. D. Chambreau, A. G. Suits, X. Zhang, J. Rheinecker, L. B. Harding, and J. M. Bowman. 2004. "The Roaming Atom: Straying from the Reaction Path in Formaldehyde Decomposition." *Science* 306 (5699): 1158–61. <https://doi.org/10.1126/science.1104386>.
- Uzer, T., C. Jaffé, J. Palacián, P. Yanguas, and S. Wiggins. 2002. "The Geometry of Reaction Dynamics." *Nonlinearity* 15: 957–92. <https://doi.org/10.1088/0951-7715/15/4/301>.
- Waalkens, H., and S. Wiggins. 2004. "Direct Construction of a Dividing Surface of Minimal Flux for Multi-Degree-of-Freedom Systems That Cannot Be Recrossed." *J. Phys. A* 37: L435. <https://doi.org/10.1088/0305-4470/37/35/L02>.
- Wiggins, S., L. Wiesenfeld, C. Jaffé, and T. Uzer. 2001. "Impenetrable Barriers in Phase-Space." *Phys. Rev. Lett.* 86 (24): 5478–81. <https://doi.org/10.1103/PhysRevLett.86.5478>.

Zee, R. D. van, M. F. Foltz, and C. B. Moore. 1993. "Evidence for a Second Molecular Channel in the Fragmentation of Formaldehyde." *J. Chem. Phys.* 99 (3): 1664–73. <https://doi.org/10.1063/1.465335>.