Phase Space Structures Explain Hydrogen Atom Roaming in Formaldehyde Decomposition

Frédéric A. L. Mauguieière,*† Peter Collins,‡ Zeb C. Kramer,§ Barry K. Carpenter,* Gregory S. Ezra,* Stavros C. Farantos, ¶ and Stephen Wiggins†

†School of Mathematics, University of Bristol, Bristol BS8 1TW, United Kingdom
‡Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853, United States
§School of Chemistry, Cardiff University, Cardiff CF10 3AT, United Kingdom
¶Department of Chemistry, University of Crete and Institute of Electronic Structure and Laser, Foundation for Research and Technology - Hellas, Iraklion 711 10, Crete, Greece

Supporting Information

ABSTRACT: We re-examine the prototypical roaming reaction—hydrogen atom roaming in formaldehyde decomposition—from a phase space perspective. Specifically, we address the question "why do trajectories roam, rather than dissociate through the radical channel?" We describe and compute the phase space structures that define and control all possible reactive events for this reaction, as well as provide a dynamically exact description of the roaming region in phase space. Using these phase space constructs, we show that in the roaming region, there is an unstable periodic orbit whose stable and unstable manifolds define a conduit that both encompasses all roaming trajectories exiting the formaldehyde well and shepherds them toward the \( \text{H}_2 \rightarrow \text{CO} \) well.

A significant challenge to conventional understanding of reaction mechanisms is provided by the recently discovered class of roaming reactions. The roaming mechanism was identified in 2004 in a study of the photodissociation of formaldehyde.1 When excited by photons of energy greater than 30300 cm\(^{-1}\), the formaldehyde molecule can dissociate via two channels: \( \text{H}_2\text{CO} \rightarrow \text{H} + \text{HCO} \) (radical channel) or \( \text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO} \) (molecular channel). Above the threshold for the \( \text{H} + \text{HCO} \) dissociation channel, the CO rotational state distribution exhibits an intriguing "shoulder" at lower rotational levels correlated with a hot vibrational distribution of \( \text{H}_2 \) coproduct.2 The observed product state distribution is not in accord with the traditional picture of the dissociation of formaldehyde via the well-characterized saddle point transition state for the molecular channel. Instead, a new pathway is followed that is dynamical in nature, and such dynamical reaction paths or roaming mechanisms are the central topic of this Letter.

For the case of formaldehyde photodissociation, classical trajectory simulations establish that the roaming manifests itself by a hydrogen atom nearly dissociating and orbiting the HCO fragment at long distances before returning to abstract the other hydrogen and form the molecular products \( \text{H}_2 \) and \( \text{CO} \).1 Long-range interactions between dissociating fragments allow for reorientational dynamics that can result in a different set of products and/or energy distributions than the one expected from a reaction following the minimum energy path (MEP), while a dynamical bottleneck prevents facile escape of the orbiting H atom.

Following this work on formaldehyde, roaming has been recognized as a ubiquitous phenomenon in unimolecular decomposition3–6 and has been identified in a variety of different types of reactions. Examples of known roaming reactions now include those involving excited electronic states7 while a dynamical bottleneck prevents facile escape of the orbiting H atom.

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The standard picture in reaction dynamics is firmly 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, is the path that a system follows (with small fluctuations) as reaction occurs. Broadly speaking, reactions occurring via the roaming mechanism avoid the IRC and follow alternative reaction pathways. Reactions involving dynamics that avoid the IRC, so-called non-MEP reactions, were extensively studied before the term "roaming" was coined.11–16

A central ingredient of standard reaction rate theories such as transition state theory (TST) is the concept of a dividing

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surface (DS), which is a surface that the system must cross in order to pass from reactants to products (or the reverse).17–19
Association of transition states with saddle points on the potential energy surface (PES) has a long history of successful applications in chemistry and has provided great insight into reaction dynamics.20–22 Accordingly, much effort has been devoted to connecting roaming reaction pathways with the existence or nonexistence of putative “roaming” saddle points on the PES.23

However, in cases where reactions proceed without a clear correlation to PES features such as IRCs or saddles, as appears to be the case for several roaming examples, they are mediated by transition states that are dynamical in nature, that is, phase space structures. The phase space formulation of TST has been known since the beginning of the theory17 but has only recently reached conceptual and computational maturity for systems with more than two degrees of freedom.25 Fundamental to this development is the recognition of the role of phase space objects, namely, normally hyperbolic invariant manifolds (NHIMs),26 in the construction of relevant DSs for chemical reactions. The NHIM approach to TST has enabled a deeper understanding of reaction dynamics for systems with many (≥3) degrees of freedom (DoF).25,27,28 For dynamical systems with two DoF, the NHIMs are just unstable periodic orbits (POs), which have long been known in this context as periodic orbit dividing surfaces (PODS).19

A characteristic of many systems exhibiting roaming reactions studied so far is the presence of long-range interactions between the fragments of the dissociating molecule. This characteristic is typical of ion–molecule reactions, and roaming is clearly expected to be at play in these reactions. The simple model introduced by Chesnavich29 has all of the ingredients required to manifest the roaming effect. In recent studies,30–32 we have revisited the Chesnavich model for ion–molecule reactions39 in light of recent developments in TST. We have shown that, for barrierless systems such as ion–molecule reactions, the concepts of orbiting transition state (OTS) and tight transition state (TTS) (see ref 33 and also the unified statistical theory of Miller34) can be clearly formulated in terms of well-defined phase space geometrical objects. (For recent work on the phase space description of OTS, see ref 35.) We demonstrated how OTS and TTS can be identified with well-defined phase space dividing surfaces attached to NHIMs.

In the present Letter, we re-examine the prototypical roaming reaction—hydrogen atom roaming in formaldehyde decomposition—from a phase space perspective. Specifically, we address the question “why do trajectories roam rather than dissociate through the radical channel?” Roaming has been found in formaldehyde for total energies from below to above the threshold to radical products,30 so that a fundamental understanding of the roaming mechanism requires elucidating why some trajectories do not follow a path leading directly to the radical products, even when they have enough energy to do so. In this work, we describe and compute the phase space structures that define and control all possible “reactive events” for this reaction, as well as provide a dynamically exact description of the “roaming region”.

To investigate roaming dynamics in formaldehyde decomposition, we use a reduced 2 DoF model. The model assumes that the HCO fragment is a rigid body and describes the dynamics of the other hydrogen atom moving with respect to the HCO fragment restricted to a plane. The angle θ describes the orientation of the hydrogen atom with respect to the HCO fragment, and the radial coordinate R describes the distance from the center of mass of the HCO fragment to the hydrogen atom. The Hamiltonian for this model is obtained by deriving an expression for the kinetic energy for motion in the plane in terms of the conjugate momenta pR and pθ (and the total angular momentum J, set equal to zero, J = 0) and by constructing a potential energy function V(R, θ) from the full six-dimensional PES produced by Bowman.37 The Hamiltonian as well as the way that the PES was obtained are described in the Supporting Information (SI) accompanying this Letter. The PES and the coordinate system used are shown in Figure 1.

Figure 1. Two DoF potential energy surface and coordinates employed in the reduced dimensional model.

This model describes the long-range part of the potential, and it 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 H2 + CO.

The roaming phenomenon is manifested as follows. Trajectories initiated in the formaldehyde well leave the well and follow a path to dissociation to the radical products H + HCO. However, in the course of their evolution, 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 H2 + CO.

In order to analyze the questions raised above, we first identify the relevant “reactive events” and then determine the unstable POs (NHIMs for 2 DoF systems) from which we construct DSs, the crossing of which determines these reactive events. In one relevant reactive event, the formaldehyde molecule breaks into the radical products H + HCO. The PO identified with this event is associated with the centrifugal barrier (and is referred to as a “relaxed equilibrium” or “relaxed periodic orbit” in the mathematics literature) and has been labeled POOTS in Figure 2. This PO 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. A second reactive event occurs when the system escapes from the formaldehyde well and reaches the flat region of the PES. In our model, this occurs for R at around 6–8 au and θ in the region of 0–2 rad.
We have located an unstable PO that defines the DS for passage from formaldehyde to the complex HCO···H. This PO has been labeled POTTS1 in Figure 2. The final reactive event that we consider consists of the binding of the two hydrogen atoms just before the molecule breaks into the molecular products, H₂ + CO. The PO defining the DS for this event is similar to the one just described and is located in approximately the same range of the R coordinate with θ varying from 4.5 to 6 rad and has been labeled PO_TTS2 in Figure 2. Figure 2 shows the projections of these 3 POs into configuration space along with the contours of the PES and a PO labeled PO_ROT (magenta curve) that will be discussed below.

Each of the POs is 1D and defines a 2D DS. Ignoring overall rotation in the plane, the molecular phase space is four-dimensional, so that the DS serves to partition the 3D constant energy surface. Each of the three POs that 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 radical products H + HCO. For our model, this threshold is at 33558 cm⁻¹, and the energies of the POs have been taken to be 200 cm⁻¹ above this threshold. The DSs constructed from the POs are surfaces in phase space at the same total energy of the POs. The DSs consist of two parts, one which intersects trajectories that evolve from reactants to products (forward) and the other which intersects trajectories that evolve from products to reactants (backward).

We have constructed the DS attached to POTTS1 associated with the reactive event H₂CO → HCO···H. Our algorithm to sample points of the DS is explained in the SI. Figure 3a shows the projection of the reactant-to-product half (i.e., hemisphere) of this DS on the space (θ, p_θ, p_R) with POTTS1 depicted as a magenta line. This DS hemisphere intersects all trajectories.

Figure 2. POs from which DSs that describe different reactive events in formaldehyde decomposition are constructed as well as resonant (also orbiting) PO in the roaming region. The energy units are cm⁻¹.

Figure 3. Trajectory propagation from the DS. (a) We show 9846 initial conditions on the DS. Initial conditions corresponding to the three types of trajectories (see text) have been assigned different colors. Red denotes initial conditions for roaming trajectories (669 initial conditions), black denotes initial conditions corresponding to trajectories that return to the formaldehyde well (22 initial conditions), and cyan denotes initial conditions corresponding to H + HCO trajectories, that is, dissociating trajectories (9155 initial conditions). The next three panels illustrate some trajectories of each type. (b) Roaming trajectories. (c) Trajectories returning to the formaldehyde well. (d) H + HCO trajectories.
undergoing the reaction $\text{H}_2\text{CO} \rightarrow \text{HCO} \cdots \text{H}$. To investigate the
dynamics of formaldehyde dissociation, we sampled this DS
hemisphere (see the SI) and initiated trajectories at the
sampled points. We then propagated the trajectories until they
crossed the DSs associated with the other POs (or the same
PO). We focus on roaming trajectories initiated on the DS
controlling the escape from the formaldehyde well and ending
up in the $\text{H}_2 \cdots \text{CO}$ well by crossing the DS associated with $\text{POTTS}_1$ (Figure 3b). Finally,
the reaction $\text{HCO} \cdots \text{H} \rightarrow \text{H}_2\text{CO}$, when the trajectories cross the
backward DS associated with $\text{POTTS}_1$ (Figure 3c). Finally, the
reaction $\text{HCO} \cdots \text{H} \rightarrow \text{H} + \text{HCO}$ occurs when the system
crosses the DS associated with $\text{POOTS}$ at a large value of $R$
(Figure 3d).

Therefore, for trajectories initiated on the DS controlling the
escape from the formaldehyde well, there are three possible
outcomes: the roaming behavior just described, a return to the
formaldehyde well by recrossing the other hemisphere of the
DS from which they were initiated, and dissociation to the
radical product by crossing the DS at a large value of $R$
(Figure 3d).

We now consider the dynamical “mechanism” that causes
roaming trajectories to turn in the $\theta$ direction instead of
evolving directly to the radical products. To identify the
mechanism, we must consider the dynamics in the region
where a trajectory has the three possible fates. This is the region
bounded by the three DSs associated with the three POs
$\text{PO}_{\text{TTS1}}, \text{PO}_{\text{TTS2}},$ and $\text{PO}_{\text{OTS}}$ discussed above. These DSs bound
a region in phase space that is the roaming region, associated
with the flat region of the PES, and this is the location where
the dynamical complex $\text{HCO} \cdots \text{H}$ is defined. In this region,
the molecule is not yet dissociated, and couplings between the
two degrees of freedom are still present, which enable the
system to transfer energy between these DoF. Note that there
is no arbitrariness in our definition of the roaming region once
we have identified the relevant DSs.

Figure 3b shows a relatively small spread of roaming
trajectories in configuration space, in the $R$ range of $[6.5,$
$9.5]$ au. The roaming trajectories appear to approximately
follow the nearby orbiting periodic orbit $\text{POROT}$, also shown as
a magenta curve (as in Figure 2). We show, in Figure 1 of the
SI, a few trajectories from the ensemble of trajectories in Figure
3b. From $\text{POROT}$, which passes directly through the roaming
region, emerge the phase space structures that cause the $\text{H}$
atom to roam.

We analyze the behavior of trajectories in the vicinity of
$\text{POROT}$ by computing 2D surfaces in phase space (the stable
and unstable invariant manifolds) associated with $\text{POROT}$.
These surfaces can intersect to form a phase space conduit that
envelopes the roaming trajectories and leads them to particular
regions of phase space. In the case of formaldehyde, we will
see that this phase space shepherd is the mechanism for
transferring energy from the radial to the angular mode.

To visualize the shape of the phase space conduit composed
of segments of the stable and unstable manifolds of $\text{POROT}$, we
construct Poincaré surfaces of section (PSS) by fixing one of
the two coordinates and recording every time a trajectory crosses the plane. These plots provide a well-known method to explore the phase space structures in 2 DoF dynamical systems.

To show the role of the invariant stable and unstable manifolds of PO\textsubscript{ROT} we plot in Figure 4 pieces of these manifolds (green for the stable and red for the unstable) on several PSS constructed by fixing \( \theta \) at different values and taking \( p_\theta > 0 \). Along with these manifolds on the different PSS, we also plot the traces that the roaming trajectories leave on the plane (black dots). The blue bullet marks the intersection of PO\textsubscript{ROT} with the PSS. This figure strikingly reveals 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\textsubscript{ROT} (depicted by the cyan bullet), which is referred to as a homoclinic point. The area confined by the stable and unstable manifolds of PO\textsubscript{ROT} is conserved, but it does change shape as \( \theta \) varies. In fact, Figure 4 shows that as \( \theta \) increases, this region deforms and moves toward the DS controlling the access to the H\textsubscript{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\textsubscript{2}−CO well.

We have considered the prototypical roaming reaction—hydrogen atom roaming in formaldehyde decomposition—from a phase space perspective. We have constructed DSs in phase space that are bottlenecks associated with the relevant reactive events and that enable us to define the roaming region dynamically. These DSs have the “no-recrossing” and minimal flux properties. We are thereby able to sample the DS associated with escape from the formaldehyde well and determine how these particular trajectories evolve throughout the roaming region and undergo the different reactive events. The phase space perspective allows us to determine why trajectories roam rather than dissociate through the radical channel. It turns out that in the roaming region, there is an unstable PO, PO\textsubscript{ROT} whose stable and unstable manifolds trap all roaming trajectories that exit the formaldehyde well and shepherd them toward the H\textsubscript{2}−CO well. This finding provides a very compelling dynamical explanation for roaming in formaldehyde.

Roaming in formaldehyde has been treated by statistical theories.\(^{39,40}\) Our analysis indicates that the dynamics in the roaming region is nonstatistical, as is evidenced by the distributions of the different types of trajectories in Figure 3a. 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. Nonstatisticality in roaming dynamics in formaldehyde will be explored further in a future paper.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01930.

Hamiltonian and PES for the model and DS associated with a PO (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: frederic.mauguiere@bristol.ac.uk.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


