Roaming: Dynamical Reaction Pathways in Phase Space

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Plan for the talk

• Explanation, and brief background, of “roaming”, with a focus on formaldehyde
• The potential for formaldehyde (thanks to Joel Bowman).
• Set-up for the Analysis—Define reactive events and construct phase space dividing surfaces
• Trajectory behaviour.
• The main result—The answer to the question “Why do trajectories “roam” and not dissociate through the radical channel? The phase space mechanism.” (And the implications of the answer to this question.)
• Final remarks—generality of our approach

But this is a mathematics talk. Some general, underlying themes of the talk.

- Where is the mathematics?
- Can mathematicians make a contribution to chemistry?
- What “skills and knowledge” are required?
- A change in our understanding of “the form” of ODEs (the “rise of data”—very similar to the program on “Dynamical Systems Analysis of Lagrangian Transport in Oceanic Flows”.)
What is “Roaming”?


Roaming reactions: The third way

Joel M. Bowman and Arthur G. Suits

Chemists have long held that there are two ways in which a molecule can break apart. But recent results show a third possibility, and its discovery may have far-reaching implications.
Roaming reactions

Figure 1. Two reaction pathways and hints of a third. (a) In conventional dissociation to molecular products, the system must surmount a potential-energy barrier as old bonds are broken and new ones are formed. (b) In dissociation to radical products, one bond stretches until it breaks, and no new bonds are formed. The energy required for the reaction is the energy needed to break the bond, with no additional barrier. (c) A roaming reaction begins like a dissociation to radical products, with the stretching of one bond. But then the trajectory veers away to explore new regions of the potential energy surface. The PES for formaldehyde (H₂CO), or any other nonlinear four-atom system, is a six-dimensional hypersurface. A 3D perspective plot is shown here.
“Roaming—sketch”

Formaldehyde  \( \text{H}_2\text{CO} \)  dissociation

roaming
“Roaming”

Figure 4. A roaming trajectory in the dissociation of formaldehyde. One carbon–hydrogen bond stretches and nearly breaks, but then the H atom roams around to the other side of the molecule to interact with the other H atom. (Animations of this trajectory and of other, nonroaming dissociation trajectories are included in the online version of this article.)
Roaming—a little background

Formaldehyde—the prototypical “roaming reaction”


Following this work, “roaming” has been found in many reactions

For example...


Ketene Isomerization


Also


Review papers


Roaming—Precursor Work

Large body of work on reactions that avoid the MEP, e.g.,

F\(^-\) + CH\(_3\)I → FCH\(_3\) + I\(^-\) Reaction Dynamics. Nontraditional Atomistic Mechanisms 
and Formation of a Hydrogen-Bonded Complex. 

Ion-molecule reactions


Two interesting, and relevant, papers


The Model: 2 DoF Model
(thanks to Joel Bowman for providing the potential)

H₂CO well → H₂ + CO

OC⁻⁻H₂ well → H₂ + CO

V (x10⁴ cm⁻¹)

R (au)

θ (rad)

Radical channel

roaming

H + HCO
Identify the “Reactive Events” of Interest, and Construct Dividing Surfaces the Crossing of which Defines these Reactive Events

We consider dynamics on a fixed energy surface—200 cm\(^{-1}\) above dissociation (33558 cm\(^{-1}\))
But what are these blue curves? The Nature and Structure of the DSs

Analysis and computation in phase space—“the setting for dynamics”

DS is a 2-sphere in the 3D energy surface

It is divided into two hemispheres by an unstable periodic orbit (PO)

These hemispheres control entrance and exit to the well
They have the “no-recrossing” property and “minimal flux”

Periodic orbit dividing surface (“PODS”)—Work of Pollak, Pechukas, and Child from the late 70s. early 80’s (e.g. E. Pollak and M. S. Child [1980] Classical mechanics of a collinear exchange reaction: A direct evaluation of the reaction probability and product distribution. J. Chem. Phys. 73, 4373).

Generalized to more than 2 DoF in recent years using the idea of a normally hyperbolic invariant manifold (NHIM).
Panel (a)—initial conditions

669 red—H’...HCO well (roaming—panel (b))

9155 blue—H + HCO (dissociating—panel (d))

22 green—return to H_2CO well (panel (c))
Why do trajectories “roam”, rather than dissociate?

There is an unstable PO in the “roaming region”.
Projection of the unstable PO in the roaming region into configuration space

Its effect on the dynamics is understood in phase space
A “short” digression into some phase space notions—Poincare maps, and stable and unstable manifolds of unstable POs

1 DoF saddle \((H=p^2-q^2)\)
2 DoF—Unstable POs, their stable and unstable manifolds, and Poincare maps
Poincare maps associated with the unstable PO in the roaming region
The roaming trajectories in relation to this structure: Shepherding Mechanism
Summary—For the 2 degree-of-freedom model we have...

- Identified the “reactive events of interest”
- Constructed the phase space dividing surfaces (with “nice properties”) whose crossing defines these reactive events
- This allowed a sampling of the dividing surfaces in order to determine the nature of trajectories “encountering” the different reactive events
- Determined the phase space mechanism that “decides” whether trajectories roam or dissociate

But what about more than 2 degrees-of-freedom?
“The key idea”—Find a “saddle-like structure” on which to construct a dividing surface (with “properties”), and that has stable and unstable manifolds with one less dimension than the energy surface

For a $n$ degree-of freedom Hamiltonian system..

- 2$n$ dimensional phase space
- 2$n$-1 dimensional energy surface

The key “building block” (a phase space generalisation of a “saddle point” with the “right dimensions”

Normally hyperbolic invariant spheres of dimension 2$n$-3, $S^{2n-3}$

These are examples of normally hyperbolic invariant manifolds (NHIMs)
NHIMs generalize unstable periodic orbits to more the 2 DoF

Recall from previous slide

Normally hyperbolic invariant spheres of dimension 2n-3, \( S^{2n-3} \)

For 2 DoF, \( n=2 \), \( 2n-3=1 \), \( S^1 \) —a periodic orbit

If you look at things “in the right way” similar ideas have been “almost there” in the chemistry literature (just lacking the necessary mathematics in order to elucidate their properties and develop related computational methods).

e.g.


Cornell University Press, Ithaca.
Reacting By Roaming
Studies strengthen role for alternative to transition-state pathways

“We are indeed coming to the conclusion that these roaming mechanisms are quite common,” says Lawrence B. Harding, a research fellow at Argonne National Laboratory who has done several computational studies on roaming and is now investigating alkyl halides. He and others emphasize that the reason roaming mechanisms hadn’t been identified earlier is simply because people hadn’t looked in the parts of potential energy surfaces where the roaming pathways lie.

Adds Suits, “If we had just looked at and thought about this 50 years ago with an open mind, we could have anticipated roaming easily.”
Some references


Extra slides
Critical points on the PES

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Dissociation Energy

\[ V \ (\text{cm}^{-1}) \]

\[ \theta \ (\text{rad}) \]
Procedure for Computing the 2 DoF Model from Bowman’s Potential

1) Bowman’s code works with cartesian coordinates for the 4 atoms. Cartesian coordinates are in 3-space \((x,y,z)\). To obtain a planar model we just set \(z=0\) for all atoms.

2) We fixed the origin to the center of mass of the HCO fragment. Bowman gave us the inter-particle distances for the minimum of the formaldehyde well. So we can fix the origin of the coordinate frame and calculate the \((x,y,z)\) coordinates of each atom. Since the formaldehyde minimum is planar, \(z\) can be taken equal to 0.

3) We oriented the \(x\) axis parallel to the CO axis.

4) We then calculated the \((x,y,z=0)\) coordinates of the 3 atoms of the HCO fragment taken at the formaldehyde minimum. These coordinates don’t change from now on.

5) The position of the remaining hydrogen is obtained from the polar coordinates \((R,\theta)\) and then converted to \((x,y,z=0)\) coordinates.

6) Then Bowman’s code has a subroutine where you provide the \((x,y,z)\) coordinates of the 4 atoms and it converts them to inter-particle distances and from these distances returns the value of the potential.

7) We recorded for a grid in \((R,\theta)\) the values of the potential and then did a spline interpolation.