Roming Formaldehyde, a litterature review

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A collection of articles related to roaming, mostly in formaldehyde, H_2CO. *Quoted sections are set in italics.*

There are four prinary groups that have published theories tackling roaming. Harding and Klippenstein take a rather standard transition state theory perspective, but subdivide configuration using "centrifugal" and "entropic" barriers rather than energetic ones alone [23]. Jordan and Kable construct a two-parameter theory based partitioning the results of a variational transition state theory with a phase-space volume summation [29]. Wiggins and Ezra take a dynamical systems perspective and seek phase-space structures giving rise to roaming [34]. Tsai and Lin interpret the output of an impulsive model for photo-fragmentation [38].

[1] Fukui, K. Formulation of the reaction coordinate. *J. Phys. Chem.* **1970**, *74*, 4161–4163.

> Paper in which the "intrinsic reaction coordinate" is defined as the minimum energy (or maximum gradient) path between reactants and products *via* a(ny number of) transition state(s). *"[The Intrinsic Reaction Coordinate is] a curve passing through the initial and the transition points and orthogonal to energy equipotential contour surface."*

[2] Chesnavich, W. J.; Bowers, M. T. Statistical phase space theory of polyatomic systems: Rigorous energy and angular momentum conservation in reactions involving symmetric polyatomic species. *J. Chem. Phys.* **1977**, *66*, 2306–2315.

> Used by [29] in their theory of roaming. Provides a means to measure the phase space volume available to a system composed of symmetric, non-interacting polyatomics while imposing fixed energy and angular momentum.

[3] Carpenter, B. Intramolecular Dynamics for the Organic Chemist. *Accts. Chem. Res.* **1992**, *25*, 520–528.

> A high-level-view article outlining a number of ways the assumptions of transition state theory and the rates predicted from it can break down for moderately size systems (tens of atoms). The author suggests post-transition state bifurcation as well as non-statistical deposition of energy into intermediates as possible culprits. Author then goes on to discuss reduced dimensionality trajectories on free energy surfaces as a way to explore these ideas.

[4] van Zee, R. D.; Foltz, M. F.; Moore, C. B. Evidence for a second molecular channel in the fragmentation of formaldehyde. *J. Chem. Phys.* **1993**, *99*, 1664–1673.

First paper to note appearance of cold shoulder in J_{CO} distribution for H_2CO with increasing dissociation energy. From the abstract:

> *[We report] CO(ν,J) distributions from photolysis on the* $2^1 4^1$, 4^5, $2^1 6^1$, $2^1 4^3$, *and* $2^3 4^1$ *bands of* H_2CO *.... A significant fraction of the CO(*$\nu = 0$*) photofragment is found in low rotational states (*$J_{CO} < 15$*) for excitation above the threshold of the H + HCO dissociation channel. Photolysis on the* $2^1 4^1$ *band, which lies below this radical threshold, shows no measurable population in low-*J_{CO} *states. The fraction of the total population in low-*J_{CO} *states increases with increasing photolysis energy.*

The authors speculated that population of the low-J_{CO} states the signaled the the opening of another reaction pathway; this was later confirmed and dubbed the roaming mechanism by [6].

[5] Peslherbe, G.; Wang, H.; Hase, W. Monte Carlo sampling for classical trajectory simulations. *Adv. in Chem. Phys.* **1999**, *105*, 171–201.

Describes method for microcanonically partitioning energy among the normal modes of a molecule (at some point in configuration space where the gradient vanishes). Includes a correction for the anharmonicity of the surfaces and a means to impose a chosen total angular momentum. We used this method in the preparation of initial conditions for trajectories as did [9].

[6] Townsend, D.; Lahankar, S. A.; Lee, S. K.; Chambreau, S. D.; Suits, A. G.; Zhang, X.; Rheinecker, J.; Harding, L. B.; Bowman, J. M. The Roaming Atom: Straying from the Reaction Path in Formaldehyde Decomposition. *Science* **2004**, *306*, 1158–1161.

Joint experimental/theoretical work which announced the discovery of roaming. Simulation details discussed in [9]. Experimental setup used direct current slice imaging to probe specific ro-vibrational states of CO under dissociation at 329.60 nm. The images give the velocity distribution for the selected CO state and the *"structure of the images reflects the internal energy distribution of the* H_2 *co-product"* by conservation of energy..

- Identified roaming as mechanism leading to cold shoulder in J_{CO} distribution first noticed by [4].
- CO with low J correlated with low rotational and recoil kinetic energy, which implies the associated H_2 product is quite hot.

[7] Zhang, X.; Zou, S.; Harding, L. B.; Bowman, J. M. A Global ab Initio Potential Energy Surface for Formaldehyde. *J. Phys. Chem. A* **2004**, *108*, 8980–8986.

Describes global potential energy surface (PES) used in [6] and in our work. Harmonic estimate of zero-point energy: 5844 cm $^{-1}$

[8] Rheinecker, J.; Zhang, X.; Bowman, J. Quasiclassical trajectory studies of the dynamics of H2CO on a global ab initio-based potential energy surface. *Mol. Phys.* **2005**, *103*, 1067–1074.

> Another companion paper to [6]. Uses the potential described in [7]. From our perspective, the major finding is that initiating trajectories from the saddle point leading to molecular products fails to capture the low end of the J_{CO} distribution. This is presumably because such an ensemble of trajectories does not include roaming events.

[9] Zhang, X.; Rheinecker, J.; Bowman, J. Quasiclassical trajectory study of formaldehyde unimolecular dissociation: $H_2CO \longrightarrow H_2 + CO$, $H + HCO$. *J. Chem. Phys.* **2005**, *122*.

> Description of the trajectories simulated for [6]. This paper deals primarily with the energy-dependence of the competition between the radical and molecular pathways. Roaming is hinted at with mention of a *"second, intramolecular hydrogen abstraction pathway"*. Simulations performed on the energy surface described in [7]. A range of total energies were selected to be commensurate with experiment (34000 cm^{-1} to 38500 cm^{-1} above the potential minimum). Total angular momentum set to 0. Injected energy via the method described in [5]. Used Adams-Moulton predictor-corrector and a time step of 5 $\hbar/E_H$ (0.121 fs). Integrated for 10^5 time steps (12.1 ps) or until the fragments were separated by 14 a_0.

[10] Houston, P. L.; Kable, S. H. Photodissociation of acetaldehyde as a second example of the roaming mechanism. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 16079–16082.

> First authors to postulate roaming in CH_3CHO. Following photo-dissociation at 308 nm, the $P(J_{CO}; \nu = 0)$ distribution was well described by the sum of 2 distinct Gaussians—one at low and the other at (relatively) high J_{CO}. This was the first hint at a plurality of mechanisms. They also noted that the low J_{CO} population was correlated with significantly lower CO recoil velocity; this is in accord with the similar observation for H_2CO. The nail in the coffin was that molecular dynamics studies initiated at the transition state to molecular products did not reproduce the low J_{CO} feature of the distribution. These ideas were confirmed in a followed-up paper [12], which indicated that the majority of molecular products arose via roaming.

[11] Harding, L. B.; Klippenstein, S. J.; Jasper, A. W. Ab initio methods for reactive potential surfaces. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4055–4070.

> Exhaustive review and comparison of sundry *ab initio* methods for electronic structure calculation focusing on their applicability to reacting systems. H_2CO and CH_3CHO were treated and, almost as an aside, saddle points with a H and CH_3 respectively far removed from the formyl were reported (found with CASPT2). These have since been dubbed "roaming saddle points" or "roaming transition states". In each case, the saddle is predicted to lie 0.1-0.2 kcal $\cdot$ mol^{-1} below the radical dissociation threshold. The authors also report the computation of minimum energy paths connecting the reactant and molecular product wells via the roaming saddles.

[12] Heazlewood, B. R.; Jordan, M. J. T.; Kable, S. H.; Selby, T. M.; Osborn, D. L.; Shepler, B. C.; Braams, B. J.; Bowman, J. M. Roaming is the dominant mechanism for molecular products in acetaldehyde photodissociation. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 12719–12724.

> Joint experiment/simulation paper addressing roaming in CH_3CHO as a follow-up to [10]. Authors probed the CH_4 product—which was unseen in the previous paper—and found that it was quite vibrationally hot (as predicted). This is the first paper to verify roaming by moieties larger than hydrogen, namely a whole methyl group. Conclude that roaming accounts for $84 \pm 10\%$ of the flux to molecular products under dissociation at 308 nm. This fraction was estimated by scaling the CH_4 vibrational energy distribution obtained from molecular dynamics initiated at the transition state until the low-energy tail matched with the experimental distribution. Simulations discussed in detail in [16].

[13] Lahankar, S. A.; Goncharov, V.; Suits, F.; Farnum, J. D.; Bowman, J. M.; Suits, A. G. Further aspects of the roaming mechanism in formaldehyde dissociation. *Chem. Phys.* **2008**, *347*, 288–299.

> A follow-up to [6]. Begins with a survey of the energetics of the H_2CO system and reaction pathways available to it. Provides evidence of roaming *below* the radical dissociation threshold and up to 3200 cm^{-1} above it.

[14] Lourderaj, U.; Park, K.; Hase, W. L. Classical trajectory simulations of post-transition state dynamics. *Int. Rev. Phys. Chem.* **2008**, *27*, 361–403.

> A report on using direct dynamics simulations to characterize a number of systems exhibiting "post transition state dynamics". Report gives technical details as well as discussion of the following "science" issues:
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> - **Partitioning of product energies**. Authors initiate trajectories at the transition state saddle[1] and compute product state distributions in reasonable agreement with experiment.
> - **Non-statistical dynamics**. Treating cyclo-propane, which has 3 distinct isomerization pathways, Authors suggest that the dynamics are *"non-statistical"* when the branching fractions of trajectories initiated from the saddles do not agree with that predicted by barrier heights.
> - **Bypassing deep wells by avoiding the intrinsic reaction path**. Discuss a number of systems for which the dynamics are not well described by a minimum-energy reaction path. They mention roaming in H_2CO in passing.
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> This paper essentially says, if you back it up with powerful enough quantum mechanical calculations, direct dynamics initiated from a saddle and with suitably chosen initial momenta, gets the whole story on the dynamics of a reaction, yielding product energies and revealing reaction paths. I think this is just wrong—the situation with H_2CO is a clear counter example.

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[1] Unfortunately, this would be entirely inappropriate for a system exhibiting roaming, however this was not discussed.

[15] Osborn, D. L. Exploring Multiple Reaction Paths to a Single Product Channel. *Adv. Chem. Phys.* **2008**, *138*, 213–265.

A comprehensive review of reactions in which there are multiple distinct paths to chemically identical products. It places roaming within this larger context. About half of the systems discussed involve barrier-branching among traditional, minimum energy paths. Most of the other systems feature "dynamical pathway branching," (of which roaming is a subset) which involves pathways which explicitly avoid transition states or, more generally, minimum energy paths. Systems with this feature are not well explained by most statistical theories, which rely on the notion. Of those presented,

> *The key factor in common is the flatness of the [potential energy surface] in at least one coordinate, which leads to inefficient coupling . . . between this coordinate and the rest of the system and hence the possibility that the non-MEP [minimum energy path] trajectory does not collapse to the MEP.*

Comments on noteworthy systems:

- **H_2CO Photodissociation: Roaming**. The roaming hydrogen wanders about the formyl until approaching a nearly linear CHH configuration.[2] This is near the barrierless transition state for the $H + HCO \longrightarrow H_2 + CO$ abstraction reaction; the low torque exerted by this configuration is the origin of the lower rotational energy in CO generated via this pathway than CO generated via the direct pathway. Roaming occurs instead of radical dissociation when the roaming H finds the other before intramolecular vibrational energy redistribution has time to sufficiently energize the radical dissociation pathway.
- **OH^- + CH_3F: Avoiding the Minimum Energy Path**. After traversing the transition state, almost 90 % of the reactive flux in this system eschews the minimum energy path and bypasses the well representing hydrogen-bonded $CH_3OH{\cdots}F^-$. Instead, unbound $CH_3OH + F^-$ is formed directly. This seems to happen because the energy surface beyond saddle is steep in the C–F coordinate and relatively flat in the FCO bend. The forces along the bend aren't strong enough to pull the system into the well and so the C–F bond lengthens unchecked. (See figure 12 of this article for an evocative representation of the landscape.)
- **CH_3 + O: Two Pathways Around the Transition State**. This system has 2 major product channels and one, resulting in $H_2 + H + CO$, seems not to have a transition state at all, but rather passes over a ridge-line in the energy surface. This channel, which accounts for roughly 20% of the reactive flux, has 2 competing mechanisms: one is the first reported instance of roaming in a bimolecular reaction and the other (the dominant path) approaches no saddle points at all is is entirely distinct from the minimum energy path. Sim-

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[2] This paper is the first mention I've seen of this configuration. It is worth noting that for some notions of "nearly" the saddle to molecular products might be called a nearly linear HHC configuration.

ulations were carried out at $J_{Total} = 50$, which may introduce non-trivial orbital-angular momentum barriers.

- **H_2O Photodissociation: Chemical "Double Slits"**. An interesting quantum effect of multiple competing paths is the appearance of an interference pattern in the distribution of an observable which is a function of some property of the path that differs in each case (here, the path length). This is observed for $H_2O \longrightarrow H + OH$ at 121.6 nm in the OH rotational quantum number distribution. H_2O can decay to its ground electronic state via either of 2 conical intersections and the phase shifts produced as the population moves between them give rise to an even-odd intensity alteration in N.

In all cases of roaming (bi- or uni- molecular), there exists a barrierless radical-radical abstraction pathway leading to excited, closed-shell products. It seems reasonable to infer that all H + C_nH_{2n+1} reactions are candidates for roaming mechanisms. This is later found to be the case by [21]

[16] Shepler, B. C.; Braams, B. J.; Bowman, J. M. Roaming Dynamics in CH3CHO Photodissociation Revealed on a Global Potential Energy Surface. *J. Phys. Chem. A* **2008**, *112*, 9344–9351.

Quasiclassical trajectory study of the photodissociation of CH_3CHO to CH_4 + CO and CH_3 + HCO.

- Energy surface developed from 10^5 single point energy calculations with RCCSD(T) and basis set choice of either cc-pVZT or aug-cc-pVZT (the latter is applied for roughly 1% of points). Harding *et al.* [20] take issue with the lack of multi-reference methods used, though the paper defends its use of energies interpolated from isolated fragments.
- The lower panel of figure 3 shows a J_{CO} distribution for H_2CO decomposed into "Roaming" and "Transition State" curves. Unfortunately the manner of decomposition is not described other than to say:

  > *[The] distribution for H2CO was carefully deconstructed … into TS [Transition State] and non-TS components. The TS component agrees virtually exactly with the results of dynamics initiated at the H2+CO molecular TS of the same PES and also with earlier QCT calculations initiated at the molecular saddle point.*

  The roaming curve shows population for $J_{CO} = 45$ and higher![3] The accompanying text indicates this is data published in [9], but that paper has no such figure.
- Found the branching ratio to molecular products (as opposed to radical) to be of order 0.8 in the experimentally relevant energy range. (On this point did [20] disagree most strongly.) The authors postulate that there are features of the energy landscape, which in directing the system towards non transition state dynamics, "shut-off" the radical channel.

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[3] The curves are in good agreement with our J_{CO} curves, which were partitioned using a configuration space criterion for roaming.

- Conclusion notes that while energetically accessible, the following products are conspicuously absent from the trajectory simulations: $H + CH_2CHO$, $H_2 + CH_2CO$, $H_2O + C_2H_2$, comprising $\ll 1\%$ of products formed.

The introduction also includes a lovely review of non-transition state dynamics. Systems covered include:

- In the system H + ICl $\longrightarrow$ I + HCl, HCl was formed with a bimodal vibrational distribution. This was attributed to two mechanisms, "direct" and "migratory." The non-transition state migratory mechanism was primarily a result of the low barrier to the reaction relative to collision energy. The the deviation shouldn't be too surprising because the energy is well above that of the transition state and therefore the notion of a governing intrinsic reaction coordinate is less appropriate.
- Sometimes an obvious transition state does not tell the whole story. H_2 + CN $\longrightarrow$ HCN + H has a transition state, which dominates the dynamics, but there exists a second pathway over a *ridge* separating $H_2 + CN$ and H_2CN.
- The review concludes by pointing to [15] for more.

[17] Zhang, P.; Maeda, S.; Morokuma, K.; Braams, B. J. Photochemical reactions of the low-lying excited states of formaldehyde: T1/S0 intersystem crossings, characteristics of the S1 and T1 potential energy surfaces, and a global T1 potential energy surface. *J. Chem. Phys.* **2009**, *130*, 114304.

> *Ab initio* investigation of the S_0, S_1, and T_1 electronic surfaces of H_2CO for the purposes of understanding photo-fragmentation. After excitation to the first excited state, H_2CO decomposes into either radical or molecular products. Molecular products are formed in the S_0 state and radical products on the S_0 or T_1 state. It is unclear whether internal conversion, $S_1 \longrightarrow S_0$, or inter-system crossing, $S_1 \longrightarrow T_1 \longrightarrow S_0$, is responsible for the system relaxing back to the ground state. Both mechanisms have issues associated with them: the fist is incapable of explaining a 1 ms lag between the sub microsecond decay of S_1 and the appearance of molecular products; the second is questionable because of the weak coupling between S_1 and T_1.[4]

[18] E, W.; Vanden-Eijnden, E. Transition-Path Theory and Path-Finding Algorithms for the Study of Rare Events. *Annu. Rev. Phys. Chem.* **2010**, *61*, 391–420.

> A review of "Transition Path Theory," a scheme for understanding rare-events in potential systems by studying average flows. The introduction points out that in some systems, entropy effects dominate reaction rate over things like energetic barriers[5].

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[4] In any case, it is well established that dissociation to molecular products occurs on S_0 and therefore investigations of the molecular product channel are well-justified in not considering other electronic states.

[5] This seems to be reasoning similar to that used by our group's in using geodesics to study liquids, however the authors seem entirely ignorant of the group's work—perhaps the ideas should be in conversation.

- techniques provide a prescription for constructing (among other things) the "current" of reactive trajectories between regions of configuration space. The flow lines of which are *"averaged objects in which all unnecessary details have been filtered out."* The authors compute these objects on a ruggedized Muller-Brown potential.
- A generalization to discrete systems can find the shortest path through a two-dimensional maze.
- The authors describe a reaction path which locates the centroid of such flow (the center of a reactive tube) as an alternative to a typical minimum energy path.
- The authors go on to review a number of algorithms for locating minimum energy paths as well as transition tubes.

[19] Grubb, M. P.; Warter, M. L.; Suits, A. G.; North, S. W. Evidence of Roaming Dynamics and Multiple Channels for Molecular Elimination in NO3 Photolysis. *J. Phys. Chem. Lett.* **2010**, *1*, 2455–2458.

Beginning of roaming story in NO_3. Found bimodal O_2 vibrational distribution after photolysis at 588 nm.

[20] Harding, L. B.; Georgievskii, Y.; Klippenstein, S. J. Roaming Radical Kinetics in the Decomposition of Acetaldehyde. *J. Phys. Chem. A* **2010**, *114*, 765–777.

"Reduced Dimensional Trajectory" approach to predict branching between roaming and bond fission channels applied to CH_3CHO. Simulates rigid fragments on 6-dimensional, analytic potential obtained from fits to 10^5 large scale, multi-reference electronic structure calculations (at the (2E,2O)-CASPT2/aug-cc-pvdz level). Provides estimates of *reactive fluxes (reactive numbers of states) between the reactants and different products via the propagation of rigid-body trajectories forward and backward from a dividing surface separating reactants and different products.*

- *"The long-range centrifugal barriers provide an outer transition state that separates the free ion and molecule from the ion-molecule complex."*
- Assumes vibrational modes are decoupled from "transitional" modes in roaming region. "Transitional" modes are all those except for the internal (presumed independent thereof) vibrations of the fragments.
- Transitional modes are typically very low frequency; see [11].
- Assumes that roaming and direct product formation channels are independent.
- Used master equation simulations to transform fixed energy results for comparison with pyrolysis experiments
- Concludes that roaming fraction in acetaldehyde is $18\% \pm 10\%$ of the *total*—this ends up being the great majority of all molecular products. Reports also that the molecular/radical roaming fraction is of order 0.2; these results differed markedly from [16]

[23] notes that this method gave predictions of incorrect order in a joint theory/experiment study of dimethyl ether.

[21] Harding, L. B.; Klippenstein, S. J. Roaming Radical Pathways for the Decomposition of Alkanes. *J. Phys. Chem. Lett.* **2010**, *1*, 3016–3020.

> Computational study (*via* CASPT2) of the pyrolysis of propane, n-butane, isobutane and neopentane suggest that *"for alkanes larger than ethane, roaming radical decomposition paths exist with barriers* ~ 1 *kcal/mol below the lowest bond cleavage paths."* This suggests that thermal decomposition may lead to closed-shell, molecular products rather than the anticipated radical products. This general trend is taken as evidence of the ubiquity of the roaming mechanism (as predicted by [15]).

[22] Bowman, J. M.; Shepler, B. C. Roaming Radicals. *Annu. Rev. Phys. Chem.* **2011**, *62*, 531–553.

> First of Bowman's two major reviews of roaming (the other is [33]). Roaming in H_2CO and other systems is a challenge to conventional transition state theory. This review places roaming in the general context of the theory's limitations. Addresses roaming in the photodissociation of H_2CO and CH_3CHO in great detail and briefly mentions roaming in: photodissociating NO_3 and $(CH_3)_2CO$ and isomerizing HOONO. Notes that all these systems contain a radical-radical abstraction pathway, which suggests that roaming is common. Also discusses some of the practical implications of the competition of a roaming mechanism with a radical pathway.

[23] Klippenstein, S. J.; Georgievskii, Y.; Harding, L. B. Statistical Theory for the Kinetics and Dynamics of Roaming Reactions. *J. Phys. Chem. A* **2011**, *115*, 14370–14381.

> Assuming that the roaming and tight saddles are energetically separated (see [25, 27] for differing opinions on this), describes method for computing branching ratio as a function of energy difference between tight saddle and radical asymptote and the *"dynamics of the roaming process"*. ([29] also uses this energy difference in their theory.) Compares quite favorably to reduced dimension trajectories [20] at energies of less than 1 kcal/mol above the radical asymptote. Suggests that this is unimportant because *"high energy roaming branching is small anyways."*. However, [4] noted that the opposite was the case and [13] found evidence for roaming well out of this range.
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> - In defining roaming, shifts focus from: many paths to the same product, to: any reaction that *"produces an alternate set of products via reorientational motion in the long-range region of the potential."*
> - The above definition and described methods are applicable to roaming radical, roaming ion-molecule, and roaming radical-molecule, for both uni- and bimolecular reactions.
> - Assumes decomposition can be broken into a sequence of steps:

1. *"partial decomposition into two weakly interacting fragments"*
2. *"A statistical competition between dissociation, isomerization, and return to reactants"*. Steady-state kinetics using transition state fluxes for each process then give the relative branching ratios.

- As in [20], this theory requires/assumes relative separation between transitional and internal, non-transitional modes.
- Though there no potential barriers separating H_2CO from HCO···H *"there are entropic barriers that correlate with transition states separating the two."*[6] A similar case is made for centrifugal barriers between HCO···H and HCO + H[6]. Both kinds of barriers are invoked to justify the separation of molecular and radical products from H···HCO (where the two H atoms are close together)[6]. However, there is, in fact, a potential barrier separating HCO···H from H···HCO.
- The analysis does not consider any contribution to molecular products via the tight transition state, which is considered to be independent from roaming. The two contributions can therefore be summed.
- From this, the authors derive an expression for the roaming/radical branching ratio in H_2CO as a function of reactive fluxes between the states enumerated above.

The paper goes on to to generalize the branching ratio for other systems with an arbitrary number of intermediates and for bimolecular reactions. Much care is given to describing how to effect proper state-counting for arbitrary dividing surfaces. These methods are then compared to reduced dimension trajectories[7] for a range of roaming systems and generally agree for energies in the near vicinity of the radical dissociation threshold. Authors conclude that roaming will be particularly important for systems with low-energy roaming saddles, large(r than H) roaming moieties, or cases when bimolecular abstraction is competitive with bimolecular addition for the corresponding radical reactions.

[24] North, S. W. Roaming in the dark. *Nat. Chem.* **2011**, *3*, 504–505.

Brief summary of current understanding of electronic structure of NO_3 and mechanisms for $NO_3 \xrightarrow{h\nu} NO + O_2$ and $NO_3 \xrightarrow{h\nu} NO_2 + O$, both of which involve roaming. Recommended by John Stanton.

[25] Shepler, B. C.; Han, Y.; Bowman, J. M. Are Roaming and Conventional Saddle Points for H2CO and CH3CHO Dissociation to Molecular Products Isolated from Each Other?. *J. Phys. Chem. Lett.* **2011**, *2*, 834–838.

Attempts to determine if there is a barrier separating the conventional transition states and the roaming transition states [11] in H_2CO and CH_3CHO. This is important to statistical theories that assume the two channels are strictly indepen-

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[6] This sounds pretty hand-wavy to me, but the authors state that all is justified in terms of second order saddle points in [27].

[7] Which rely on reciprocally consistent assumptions.

dent (*e.g.* [23, 29]). Gives *upper bounds* for barriers in H_2CO and CH_3CHO as 2 kcal/mol and 6 kcal/mol respectively. On this basis, the authors feel that a single dividing surface containing both transition states is more appropriate than 2 distinct surfaces—that is, the transition states are not separate. See [27] for more on this topic.

[26] Grubb, M. P.; Warter, M. L.; Xiao, H.; Maeda, S.; Morokuma, K.; North, S. W. No Straight Path: Roaming in Both Ground- and Excited-State Photolytic Channels of $NO_3 \longrightarrow NO + O_2$. *Science* **2012**, *335*, 1075–1078.

First conclusive evidence for roaming occurring on multiple electronic surfaces. Authors report that $NO_3 \longrightarrow NO + O_2$ proceeds *exclusively* by roaming.

[27] Harding, L. B.; Klippenstein, S. J.; Jasper, A. W. Separability of Tight and Roaming Pathways to Molecular Decomposition. *J. Phys. Chem. A* **2012**, *116*, 6967–6982.

Provides a good review of transition state theory. Suggests using 2nd order saddle points to determine the separability of 1st order saddle points for transition state theory. There are two issues:

1. While most applications of transition state theory use harmonic approximations to the potential at a single saddle point, in general, the transition state is a global, minimum-flux dividing surface between reactants and products. Surfaces with multiple saddles to the same product may be treated by summing the contributions of each *if* the 1st order saddles are dynamically (if not energetically) separated.
2. The idea is that 2nd order saddles will be flux-minima and therefore should be included in the dividing surface. Therefore, if a 2nd order saddle separates a roaming and a tight saddle point and if it is a sufficiently large barrier, the pathways can be regarded as distinct.

In the case of formaldehyde, instead of a 2nd order saddle point, the authors located a minimum along an S_1/S_0 conical intersection. They suggest that this:

> *"is similar to a second-order saddle point, where, instead of two imaginary frequencies, the conical intersection may be characterized as having two coordinates that break the degeneracy of the intersecting states. The lower-energy state therefore behaves like a second-order saddle point near the conical intersection, except that a two-dimensional cusp (having two "infinite" imaginary frequencies) is formed instead of a second-order saddle point."*

I'm not sure I buy it since this is a *minimum* on the energy surface and we're looking for *classical* flux minima. In any case, the point has an energy 11 kcal/mol ($\sim$ 920 cm^{-1}) above the radical asymptote, which is energetically inaccessible enough to justify separation.

[28] Xiao, H.; Maeda, S.; Morokuma, K. Global ab Initio Potential Energy Surfaces for Low-Lying Doublet States of NO3. *J. Chem. Theory Comput.* **2012**, *8*, 2600–2605.

Created potential energy surfaces for NO_3 in the D_0, D_1, and D_2 states.

- Found intrinsic reaction coordinates for roaming on D_0 and D_1.
- It is quite computationally expensive to find all paths because of how flat the surfaces are in the roaming area.

[29] Andrews, D. U.; Kable, S. H.; Jordan, M. J. T. A Phase Space Theory for Roaming Reactions. *J. Phys. Chem. A* **2013**, *117*, 7631–7642.

This is the best paper I read. The authors present a theory to predict the branching fraction between roaming and barrierless bond fission.

- Requires 2 parameters: *"ΔE_{roam}, the energy difference between bond dissociation threshold and roaming threshold, and P_{roam}, the probability that states that may roam do rather than recombine to form reactants."*
- Theory has 2 premises:
  1. *Roaming is a post-VTST mechanism. This means that the underlying kinetics can be calculated by a VTST calculation of the bond dissociation channel. The total VTST rate is then partitioned into a dissociation fraction and a roaming fraction.*
  2. *The bond dissociation and roaming fractions are determined by the relative phase space theory[2] sum of states for each pathway.* Their phase space theory treats the fragments as non-interacting in the roaming region.
- Unfortunately, there are few experiments available for direct comparison as the theory gives the branching ratio between roaming products (usually molecular) and barrierless bond fission (usually radical). Bowman points out [33] that not providing a framework to consider the products formed via the tight transition state is a shortcoming.
- Tested in 3 systems and found reasonable agreement when taking P_{roam} to be an adjustable parameter: H_2CO, $P_{roam} = 0.99$; NO_3, $P_{roam} = 0.0075$; CH_3CHO, $P_{roam} = 0.21$ (fit to simulated data from [20])

[33] notes that by using a fit to P_{roam}, the model does give roaming fractions in agreement with experiment. However, it provides no way to construct P_{roam} or ΔE_{roam} from the properties of the energy landscape.

[30] Fu, B.; Bowman, J. M.; Xiao, H.; Maeda, S.; Morokuma, K. Quasiclassical Trajectory Studies of the Photodissociation Dynamics of NO3 from the D-0 and D-1 Potential Energy Surfaces. *J. Chem. Theory Comput.* **2013**, *9*, 893–900.

Reports potential fits for the D_0 & D_1 surfaces of NO_3. Ran QCT from the global minimum. 99% of trajectories followed the classically open—though quantum mechanically closed[8]—non-roaming route to NO_2 + O. Roaming trajectories show partially associated O for several picoseconds. This paper reported 2 ps, but Bowman's review [33] has the same figure with a different scale as well as text indicating 30 ps.

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[8] Given endpoints, our method would not be frustrated by such issues.

[31] Homayoon, Z.; Bowman, J. M. Quasiclassical Trajectory Study of CH3NO2 Decomposition via Roaming Mediated isomerization Using a Global Potential Energy Surface. *J. Phys. Chem. A* **2013**, *117*, 11665–11672.

> Describes fit potential energy surface for CH_3NO_2. Quasi-classical trajectories examining the isomerization reaction ($CH_3NO_2 \longrightarrow$ *cis*$-CH_3ONO$) found the system straying far from the identified transition state (TS1)

[32] Li, A.; Li, J.; Guo, H. Quantum Manifestation of Roaming in H + MgH $\longrightarrow$ Mg + H_2: The Birth of Roaming Resonances. *J. Phys. Chem. A* **2013**, *117*, 5052–5060.

> Analyzes H + MgH $\longrightarrow$ Mg + H_2 via quasi-classical trajectories and quantum wave packet methods.
>
> - There is good agreement between the product state distributions generated via trajectory-based and wavepacket-based methods. The authors then conclude that analyzing the dynamics from the classical perspective is therefore reasonable.[9]
> - Roaming channel accounts for %20 of products in this system at lost collision energies.
> - *"...roaming is manifested quantum-mechanically by a large-amplitude vibration that emerges just below the reaction threshold and is guided by the roaming transition state."*

[33] Bowman, J. M. Roaming. *Mol. Phys.* **2014**, *112*, 2516–2528.

> Major review article; updated earlier article [22], though covers new material. Describes roaming mechanism, relevant systems, and several attempts at statistical theories.
>
> - *A key characteristic of the roaming pathway is that it passes through a high-energy, flat region of the potential energy surface (PES). In this region the forces are relatively weak and so the dynamics exhibits large amplitude motion.*
> - The roaming pathway 'entangles' routes to molecular and radical products and that it is a failing of *the most widely used statistical and even dynamical approaches to describe the rates ... [to] treat them as separate and thus non-interacting pathways.*
> - In H_2CO roaming trajectories visit high energy region of HCOH isomers prior to roaming. Suggests the *possible role of isomers in the roaming region as being an aspect of potentials that keeps the incipient radicals from dissociating and also 'steers' them from recombining in the region of the global minimum and instead of the self-abstraction configurations.*[10].

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[9] This is great for us because of all systems where one might worry about quantum effects, H + MgH ought be near the top of the list.

[10] This also occurs in the CH_3NO_2 system and sounds like a good candidate for "large" barriers in the bird's nest

- Cites [19] to introduce roaming in NO_3. [26] gave “conclusive” evidence for roaming on two electronic surfaces (D_0 & D_1). Bowman’s own group simulated dissociating NO_3 in [30].
- Intrinsic reaction coordinates [1] including roaming saddles have been computed for NO_3 [28] and CH_3NO_2 [31]. In all roaming systems, the dynamics show large deviations from these paths and *“large amplitude motion”* in the vicinity of the saddles[11]. This has terminally frustrated attempts at a statistical theory for the prediction of branching ratios.
- Quantum roaming in Mg + H_2 [32]: vibrational wave functions for bound states just below break-up energy showed much amplitude in region of neither the tight nor the “roaming” saddle point. Conclude: the wave functions are highly delocalized.
- Speculates that “post-transition state branching” [14, 3] is the norm for large systems with a roaming saddle point.
- Cites [29, 23, 34] as theories proposed to treat roaming.
- Counts “roughly 20” systems which are reported to roam.
- Suspects that transition state theory may yet have something to say about roaming, but not via any “constructive”, canned theory—likens the situation to that of the n-body problem, which only yields to numerical analysis.

[34] Mauguiere, F. A. L.; Collins, P.; Ezra, G. S.; Farantos, S. C.; Wiggins, S. Multiple transition states and roaming in ion-molecule reactions: A phase space perspective. *Chem. Phys. Lett.* **2014**, *592*, 282–287.

This paper was a bit of a let-down. I wanted their phase-space/orbit-bifurcation analysis to yield more than it did. It’s worth mentioning because Wiggins and Ezra are one of only 4 teams trying to provide theoretical insight into roaming.

- Uses a 2-dimensional model (due to Chesnavich) of $CH_3^+ + H \longrightarrow CH_4^+$ to apply a phase space analysis to ion-molecule reactions. The model is envisions a symmetric top (CH_3^+) interacting with a point mass (H) in the plane. The authors are particularly interested in roaming and suggest that Orbiting Transition States identified in ion-molecule reactions are an instance of this.
- Roaming is not easy to predict from the energy landscape alone, even in a simple, two-degree-of-freedom system.
- The orbiting transition state is related to a centrifugal barrier arising in the kinetic energy. In particular, for the Chesnavich model, the orbiting transition state is not associated with any potential feature.
- In their notion of roaming, the authors include “reactive” and “non-reactive” roaming paths. Roaming just means having some finite number of turning points. Reactive trajectories have an even number and non-reactive an odd number.

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[11] I don’t think this should be a surprise given the “flat” landscape in the vicinity of the saddles and the high energies involved.

- Authors identified a periodic orbit and phase space dividing surface (based on a *normally hyperbolic invariant manifold*) associated with the orbiting transition state in the model system. Then initiated trajectories from this surface and classified them based on their reactivity and number of turning points in a special coordinate[12]. This dividing surface and another, from the tight transition state, define a “roaming region”, between then within which trajectories may oscillate for some time.
- The paper goes on to suggest that the origins of the roaming behavior is in a particular family of periodic orbits within the identified roaming region.
- In the conclusion, the authors suggest that their method, involving normally hyperbolic invariant manifolds, can be used to define minimal flux phase space dividing surfaces for other reactions, but concede that *“substantial technical difficulties need to be overcome”* for the method to be practical.
- Points out that the statistical theory elaborated in [23] relies on approximate dividing surfaces in configuration space, which do not satisfy a no-recrossing criterion. Discrepancies between [23]’s predictions and trajectory simulations can be attributed to this or simply non-statistical dynamics.

[35] Mauguiere, F. A. L.; Collins, P.; Ezra, G. S.; Farantos, S. C.; Wiggins, S. Roaming dynamics in ion-molecule reactions: Phase space reaction pathways and geometrical interpretation. *J. Chem. Phys.* **2014**, *140*.

A report expanding on [34]. They studied the CH_3^+ + H system. Observations of note:

- There exists a 1st order saddle on the Chesnavich model potential (see [34]), which could be called a roaming saddle. However the orbiting transition state dividing surface is rather far from this saddle.
- Notion of roaming was refined from the previous definition (involving only turning points) to require recrossings of another dividing surface connected to an intermediate (between the tight and orbiting transition state in r) periodic orbit dubbed the “free rotor” periodic orbit.
- **Their first major finding was around the distribution of *gap times*** for trajectories initiated on the orbiting transition state dividing surface. The gap time is the time required for such a trajectory to traverse the region between the orbiting and tight transition state (including exiting by not reacting). *“The statistical assumption of TST [transition state theory] is equivalent to the requirement that the gap time [s] distribution is the random, exponential distribution $P(s) = k\exp(-ks)$.”* Their results show gap time distributions for a range of energies that decidedly do not have this form.
- **Fractal nature of phase-space bands of initial conditions** leading to different products was also intriguing. A figure constructed by plotting the fate $((roaming|direct) \otimes (reactive|non-reactive))$ of trajectories initiated on

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[12] In this case, the easily identifiable CH_3^+ – H separation distance. I think this classification isn’t particularly useful without a prescription for identifying the key coordinate.

the dividing surface in one degree of freedom and its conjugate momentum showed that the interfaces between regions are quite complex.[13] Additionally, along the boundaries of these regions, the gap times diverged.

[36] Coutinho, N. D.; Silva, V. H. C.; de Oliveira, H. C. B.; Camargo, A. J.; Mundim, K. C.; Aquilanti, V. Stereodynamical Origin of Anti-Arrhenius Kinetics: Negative Activation Energy and Roaming for a Four-Atom Reaction. *J. Phys. Chem. Lett.* **2015**, *6*, 1553–1558.

Attempts to recover dynamical information from constant *temperature* simulations. That doesn't make any sense. All the same, they present evidence for roaming in the $OH + HBr \longrightarrow H_2O + Br$ system. At higher temperatures, the H was in a "roaming" state longer and the authors suggest this is tied to the negative dependence on temperature of the reaction rate.

[37] Mereshchenko, A. S.; Butaeva, E. V.; Borin, V. A.; Eyzips, A.; Tarnovsky, A. N. Roaming-mediated ultrafast isomerization of geminal tri-bromides in the gas and liquid phases. *Nat. Chem.* **2015**, *7*, 562–568.

Reports first instance of roaming in the liquid phase. $CHBr_3$ is shown to exhibit a roaming-mediated isomerization to $BrHCBr-Br$ in both the gas and liquid phase. In this system, "roaming" occurs on a 100 fs time-scale, but with large amplitude motion and on a flat region of the potential energy surface. Further experiments and quantum simulations of XBr_3 (X=CH, B, or P) suggest the phenomena is general for polybromides. The isomer is also accessible via a solvent-mediated mechanism which takes several picoseconds. The isomer is stable for several hundred picoseconds by which point the system will have undergone radical dissociation or re-isomerization back to XBr_3. Roaming in the tribromides is rather directional because the flat region of the energy surface is accessed after relaxation from the *"Franck-Condon region, where the energy gradient comprises a significant driving force."*. Consequently the system has accrued nontrivial nuclear velocity by the time it arrives in the flat area.

[38] Tsai, P.-Y.; Lin, K.-C. Insight into photofragment vector correlation by a multi-center impulsive model. *Phys. Chem. Chem. Phys.* **2015**, *17*, 19592–19601.

This work was published 6 months after and is an extension to [39], which I found to have some problems. However, some of the vector-correlation results presented here were found to be consistent with quasi-classical trajectory simulations of H_2CO. For the roaming pathway, Authors used progress along the reaction coordinate as fitting-parameter to select the "key configuration" that gave results most consistent with [6]. Noteworthy observations/findings follow:

- Dissociation via the tight saddle point yields fragment angular momentum vectors perpendicular to the velocity vectors, $v \perp j$. Dissociation via the roaming pathway leads to no such vector correlation–*"implying the photofragments are produced* via *a floppy, unconstrained reaction pathway."*

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[13] This is interesting to us, because it suggests that the subspace leading to roaming is highly variegated. In H_2CO, the question is still open as to whether the space is even compact.

- The impulsive model is frustrated by a curved intrinsic reaction coordinate; the authors posit that a curved minimum energy path (via the tight saddle point) is responsible for discrepancies (between their theory and experiment) in the polar angle distribution of $\mu - j$ correlation for the CO fragment. (μ is the transition dipole moment.)
- For the following measures, **distributions were substantially *broader* in the roaming case** than in the direct dissociation case: $v_{H_2} - j_{H_2}$, $v_{CO} - j_{CO}$, and transition dipole moment & CO-H_2 relative velocity[14].
- Authors go on to say that the floppy nature of the roaming path is *not* responsible for the loose correlations, but rather the relative norms of the impulse and transverse vibrations at the "key configuration." If the transverse norm is much larger than the impulse norm, then the distribution will be broad because of the necessarily wider space into which the zero-point vibrations may send the system.
- Authors concede that it is unknown if it is valid to separate statistical and impulsive reservoirs when treating vector quantities.

[39] Tsai, P.-Y.; Lin, K.-C. Insight into the Photodissociation Dynamical Feature of Conventional Transition State and Roaming Pathways by an Impulsive Model. *J. Phys. Chem. A* **2015**, *119*, 29–38.

> Impulsive models posit that the product energy distribution can be determined by a single instantaneous impulse applied to a "key configuration". This paper develops a multi-center impulsive model in an attempt to construct product energy distributions consistent with the photo-dissociation of H_2CO via the tight saddle point as well as the roaming mechanism. The authors succeed in constructing product state distributions for dissociation via the tight saddle point that align well with experiment without the need for adjustable parameters. However, for the roaming case, identifying the "key configuration" was not straightforward and the authors offer no prescription for doing so. They were also, therefore, unsuccessful in predicting branching ratios or much of anything else about the roaming pathway. The majority of the paper is, unfortunately, incoherent.

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[14] Looks an awful lot like the randomization we're seeing. However, this is being detected using a single configuration beyond the roaming saddle point along the minimum energy path.