

Roaming Radical Reactions

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ABSTRACT: An unusual decomposition mechanism of highly vibrationally excited molecules, dubbed the “roaming mechanism”, has recently been discovered and is now an active area of investigation. In these reactions, a molecule undergoes partial dissociation to radical fragments by simple bond fission. When the fragments separate to 3–4 Å, roaming reorientation becomes feasible as the kinetic energy is low and the angular forces may be comparable to the radial forces. If this leads the system to access a distinct reactive domain, intramolecular abstraction may take place, giving molecular products with large vibrational excitation. This pathway may deviate substantially from the nominal minimum-energy path and in some cases appears to avoid the normal transition-state geometry entirely. Many of the details have come to light through high-resolution ion imaging studies of formaldehyde, in concert with quasi-classical trajectory calculations from Bowman and co-workers. Many other examples of roaming dynamics have recently been reported, both in experiment and theory. In this Perspective, we highlight key aspects of roaming reactions and point to some interesting future directions for study.



The dissociation of a highly vibrationally excited molecule is a violent event; atoms thrash about, energy flows here and there, and in some sense, it is over very quickly, perhaps nanoseconds for a medium sized molecule in a combustion environment. However, in another sense, when measured by the number of vibrational periods of the bond that finally breaks, it is a remarkably slow process. For a vibrational period of tens of femtoseconds, for example, this nanosecond lifetime represents on the order of a million oscillations. From this point of view, we might well ask why it should it take so long. The simple answer is that enough energy must accumulate in one bond to break it. To determine the dissociation rate, statistical theories in effect simply count the number of ways that the energy may be partitioned in a bond in excess of the energy needed to break it and divide this by the total number of ways the energy may be distributed in the molecule. For a polyatomic molecule with its $3N - 6$ vibrational degrees of freedom, there is an enormous density of states at these energies; therefore, is unlikely for all of the energy to happen to appear in a single bond at one time. It is far more likely that only a few vibrational quanta will be found in any one mode at any one time, and such conditions thus arise much more often. Similarly, one can readily imagine it more likely that a given vibrational mode will possess almost enough energy to dissociate rather than more than enough energy to dissociate. What happens in this case? If the energy is very close to the dissociation limit (we will see that it must be within a few hundred cm^{-1}), the bond can very nearly break, and the fragments separate to very long range. Of course, they may promptly fall back together, and the energy that had accumulated in the “reaction coordinate” may again be shared with the other modes for more thrashing about. However, there is another possibility. As the incipient fragments move out to long range, they will find themselves in a very flat region of the intermolecular potential and with vanishing kinetic energy. There, these

radical fragments may be subject to subtle influences of the potential and begin to wander around. They may escape the forces drawing them back into the well, instead exploring remote regions of the potential surface, perhaps eventually finding a second attractive and highly reactive domain. Reaction may then occur leading to unanticipated chemical products and surprising internal energy distributions. We refer to this phenomenon as “roaming,” and it is the subject of this Perspective. Although the evidence that we will present in what follows has emerged clearly only after much experimental and theoretical effort, simple reflection on the points presented above are enough to suggest that this phenomenon could make a significant contribution to product branching in unimolecular dissociation, and it might well be nearly universal. This subject has been reviewed in some detail recently;^{1–3} therefore, our goal here will be to sketch a picture of roaming on this intuitive foundation, emphasizing the experimental results and pointing to some future directions for investigation.

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Although there had been some suggestion of such behavior in a variety of systems over the years,^{4,5} the first clear demonstration of roaming and identification of the underlying dynamics were reported in a series of combined theoretical and experimental studies^{6–10} of formaldehyde dissociation. Because this system so clearly illustrates the phenomenon, we will devote some attention to the formaldehyde results before turning to the broader evidence and implications of roaming.

A schematic view of the relevant part of the formaldehyde potential energy surface¹¹ is shown in Figure 1. In the photodissociation experiments, electronic excitation takes place to metastable levels of the S_1 state, after which there is internal conversion to the ground state prior to dissociation. The details of this internal conversion remain an area of interest but are beyond the scope of what is considered here. On the ground state, there are two primary decomposition pathways; one leads over a high barrier to closed-shell products H_2 and CO with subsequent release of all of the barrier energy. At slightly higher energy, there is a second, barrierless dissociation path to radical products HCO and H. A 1993 study from the Moore group¹² at Berkeley showed evidence for a “second molecular channel” in the dissociation of formaldehyde. Their CO rotational distributions showed large excitation as the repulsive potential energy from the barrier shown in Figure 1 was efficiently converted to

translational and rotational energy. However, CO rotational distributions obtained for dissociation above the energy of the radical channel showed, in addition, a pathway producing CO with very little rotational excitation. This was rather surprising; one set of products, $CO + H_2$, seemed to be influenced by the opening of another channel leading to radical products. Moore and co-workers believed that this bimodal rotational distribution was most likely related to interaction between the radical and molecular dissociation pathways, but they also considered an alternative explanation involving extreme anharmonicity of the transition state (TS) leading to dissociation from distinct geometries. We will return to these two alternative views below.

Ion imaging results^{6,8} obtained a decade later in our group, reproduced in Figure 2, provided something not available to Moore and co-workers, state-correlated product distributions. High-resolution velocity map images for specific CO quantum states give the corresponding internal state distribution for the H_2 partner by virtue of energy and momentum conservation. It

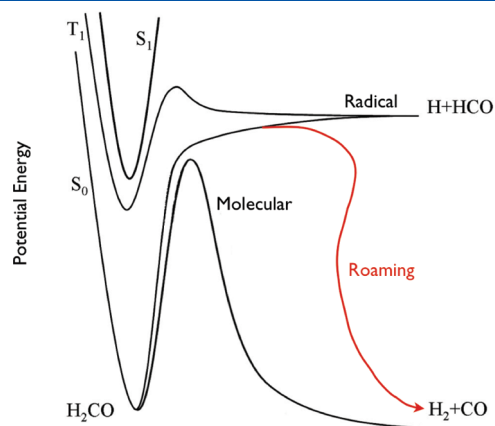


Figure 1. Schematic potential energy curves for formaldehyde dissociation.

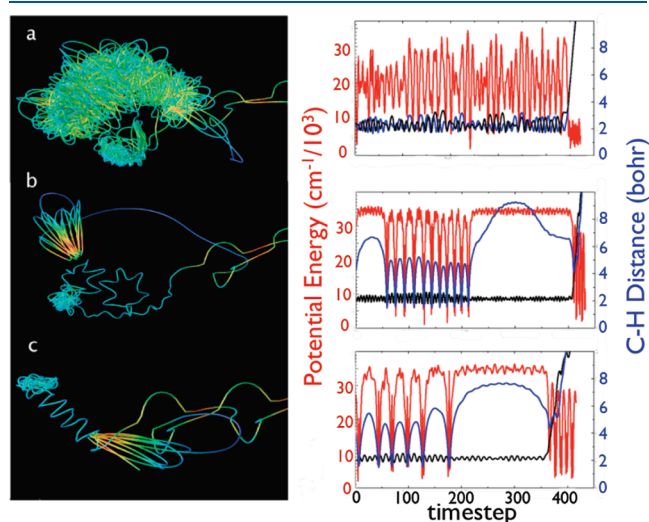


Figure 3. (Left) Visualizations of selected trajectories. Only H atom motions are shown, with the CO moiety omitted for clarity. The instantaneous speed is encoded in color. (A) Nonroaming event; (B, C) roaming events. (Right) Plots of C—H distances (black, blue) and the total potential energy (red) for each trajectory on the left.

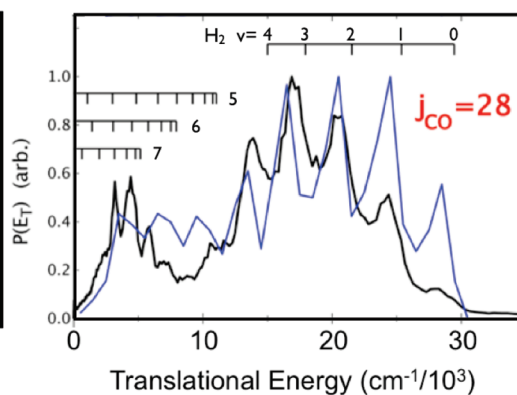
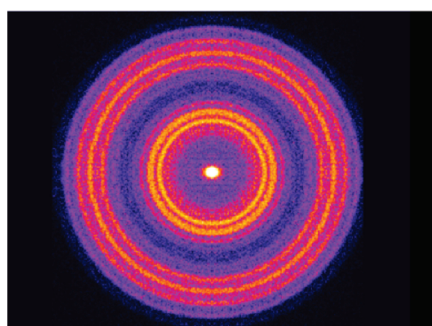


Figure 2. DC slice image CO ($\nu = 0, j = 28$) for dissociation of H_2CO at 30340 cm^{-1} (left) and translational energy distributions (right) obtained from the image. Markers indicate correlated H_2 vibrational levels for $j_{H_2} = 5$ (for $\nu = 0-4$) or full rovibrational levels (for $\nu = 5-7$). The blue line is the result of QCT calculations.

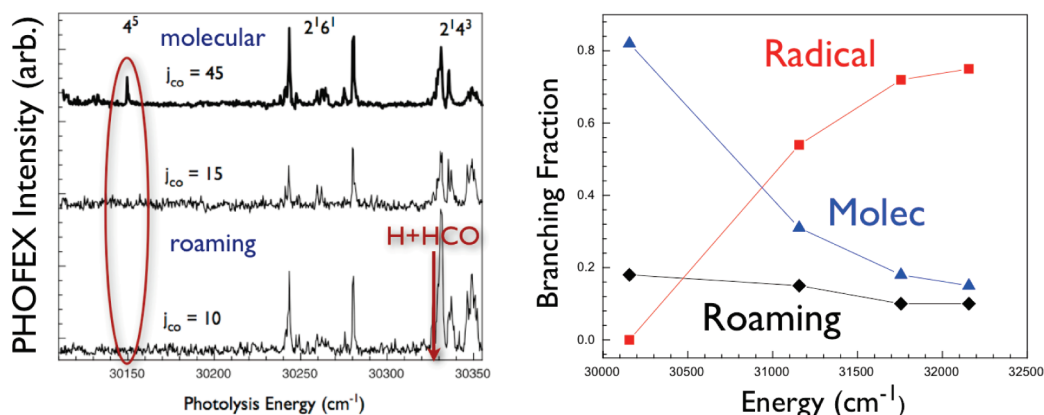


Figure 4. (Left) PHOFEX scan across the radical dissociation threshold (30329 cm^{-1}) for indicated CO rotational levels. The red oval shows the absence of roaming at energies 180 cm^{-1} below the radical threshold. (Right) Energy-dependent multichannel branching for formaldehyde.

became clear from the imaging results shown in Figure 2 that the anomalous low rotational levels highlighted in Moore's paper are associated with the production of very high vibrational levels of H_2 . This surprising combination could not plausibly arise from dissociation via the normal TS geometry; therefore, an alternative pathway was clearly needed.

The definitive answer came from quasi-classical trajectory (QCT) calculations from the Bowman group^{6,13} at Emory that were obtained on a newly developed, high-quality ab initio potential energy surface¹¹ for H_2CO . Their calculations, performed under conditions chosen to mimic the experiment, gave bimodal distributions in good agreement with the imaging results. Furthermore, the trajectory calculations provided the ability to make movies of the reaction, slowed down by a factor of 10^{10} or so. These trajectory animations clearly revealed the nature of the dynamics underlying the distinct sets of products; reactions that produced rotationally excited CO and vibrationally cold H_2 all followed the "normal" dissociation path and at some point passed through a geometry closely resembling that of the TS structure shown in Figure 1. In contrast, trajectories giving highly vibrationally excited H_2 followed a very different path, never visiting that geometry. Instead, one of the hydrogen atoms always ventured out 3.5 or 4 \AA from the HCO fragment and then slowly roamed over the plane of the HCO, eventually finding the other H atom for reaction. Figure 3 shows such a roaming trajectory contrasted with a normal over-the-barrier trajectory in remarkable visualizations by F. Suits at IBM, based on the Bowman group QCT calculations.¹⁰

This roaming may be viewed as a frustrated radical dissociation that leads, instead, to an intramolecular abstraction, just as we had envisioned in the introductory paragraphs above. Production of highly vibrationally excited H_2 and rotationally cold CO can be seen as a natural consequence of the extremely exoergic $\text{H} + \text{HCO}$ reaction; therefore, the distinct product state distributions for the formaldehyde roaming events are easy to understand in this light. For such an "early barrier" reaction, we expect the new bond to be highly excited and the old bond to behave as a spectator. Indeed, Bowman and co-workers have shown in trajectory calculations on the reaction of H with HCO that one component of the product distribution gives H_2 in vibrational levels of $6-7$ along with CO in low rotational levels, exactly analogous to the roaming products of H_2CO dissociation.¹⁴

These initial formaldehyde results provided insight into the dynamics underlying the distinct product distributions but raised

many questions as well. Is roaming simply a threshold phenomenon, and if not, what is its energy dependence? Is this behavior restricted to formaldehyde, or is it more general? Is it exclusively a H atom phenomenon, or may other species be involved in roaming? What are the implications of this for transition-state theory (TST), on which we base much of our theoretical understanding of chemical reactions? And what might be the practical implications of roaming if indeed this is a general but overlooked molecular decomposition mechanism?

The initial results were obtained at energies just $30-40 \text{ cm}^{-1}$ above the radical threshold. Can roaming occur below the radical threshold? One way of examining this question is to scan the excitation laser around the radical threshold while monitoring CO products in low rotational levels (associated with roaming) or high rotational levels (representing dissociation over the barrier), an example of photofragment excitation (PHOFEX) spectroscopy. The results obtained in the vicinity of the radical threshold and below are shown¹⁰ in Figure 4. Each peak represents a transition from the ground state to the first excited state that ultimately leads to the indicated CO quantum state that is being detected after dissociation. No mode specificity has been observed; therefore, the nature of the excited-state preparation is not significant. This is because decomposition takes place on the ground state long after the initial excitation. The threshold for the radical dissociation is marked on the plot. The top panel shows CO in $j = 45$, representing the normal molecular product. Peaks are seen corresponding to well-known metastable levels in the excited state. In the lower two panels, we see the same region of the spectrum probed on low CO rotational levels that come from roaming. As shown in the lower two spectra, roaming products are clearly seen as low as 90 cm^{-1} below the radical threshold, but by 180 cm^{-1} below, they are gone. The conventional molecular channel, on the other hand, persists down to the level of the barrier, well below the radical threshold.

Harding and co-workers¹⁵ reported a distinct roaming transition-state region for formaldehyde. They refer to this as a "region" because it is so flat, and several of the frequencies are so low that it is unrealistic to consider it a normal TS for the purpose of calculating rates. Nevertheless, there are several noteworthy features of the saddle point that they have identified. One is that it features the roaming H atom out of the plane of HCO, about $3.5-4 \text{ \AA}$ away. This is quite consistent with the trajectory calculations, which also seem to pass through this part of the potential surface before leading to the roaming abstraction.

The second key aspect of this is that the location of this saddle point is about 40 cm^{-1} below the radical asymptote. This is consistent, within plausible uncertainty in the calculation, with the PHOFEX data in Figure 4.

One interesting question is whether there is any connection between this saddle point and the tight TS that leads to the normal molecular channel. Although the products seem to follow one pathway or the other, are these two saddle points related? Bowman and co-workers have recently reported³ that one may trace a path from the roaming saddle point directly to the molecular saddle point, and this path rises only 2.5 kcal/mol above the roaming saddle point. This suggests that these two saddle points may indeed be connected, and both of the explanations given in the paper by van Zee et al. are correct; that is, the second molecular channel represents extreme anharmonicity of the TS, and at the same time, this is a consequence of the opening of the radical channel. Indeed it is the anharmonicity associated with the opening of the radical channel that is responsible for roaming.

The second molecular channel represents extreme anharmonicity of the transition state, and at the same time, this is a consequence of the opening of the radical channel. Indeed, it is the anharmonicity associated with the opening of the radical channel that is responsible for roaming.

Roaming in formaldehyde is seen to occur at energies in the immediate vicinity of the radical threshold, but does this mean that it is strictly a threshold phenomenon? Again, PHOFEX spectra can shed light on this point. Such spectra, obtained up to 3000 cm^{-1} above the radical asymptote,⁹ when analyzed and scaled using imaging data, yield the multichannel branching also shown in Figure 4. As expected, the loose TS leading to radical products means that this channel rapidly dominates once it is open, at the expense of the normal molecular channel. However, as the roaming channel is derived from the radical channel, it shows only a weak energy dependence, decreasing gradually with increasing energy.

The next question to address is that of generality. Are there other systems that demonstrate roaming behavior? The answer is a resounding yes. Acetaldehyde has been studied quite extensively in this regard, first with a report of CO Doppler profiles and vector correlations from Kable and Houston.¹⁶ This was followed by extensive theoretical and experimental measurements that have consistently confirmed roaming behavior in acetaldehyde, only disagreeing over its extent.^{17–21} FTIR measurements showed very hot methane, with up to 4 eV of internal energy, from acetaldehyde photodissociation at 308 nm. This internal state distribution was consistent with trajectory calculations on a full dimensional potential surface starting from the equilibrium geometry, which

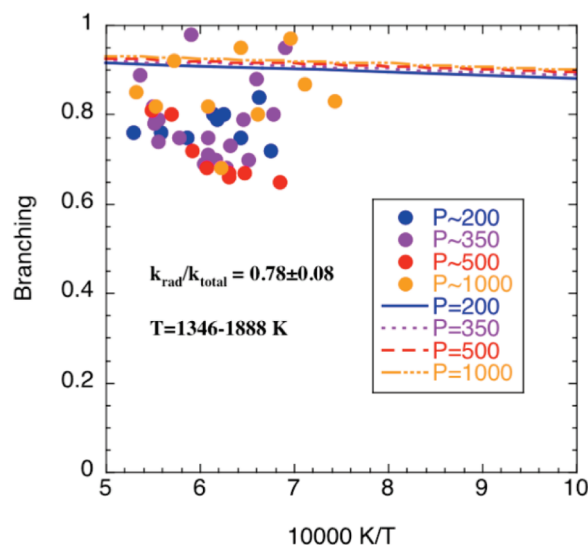


Figure 5. Points show results of shock tube measurements of H atom yield (corresponding to the radical channel) in acetaldehyde pyrolysis by Michael and co-workers from ref 19. Lines are the result of RDT modeling (see ref 21). *P*: pressure in Torr.

suggested that roaming was the dominant decay mechanism at these energies. Shock tube measurements¹⁹ of the H atom yields (taken as a marker for the HCO product of the radical channel) indicated a 23% branching to the roaming radical pathway in thermal pyrolysis of acetaldehyde at temperatures of 1346–1888 K and pressures of several hundred Torr. These experimental points are shown in Figure 5, paired with reduced dimensional trajectory (RDT) calculations²¹ employing a six-dimensional surface (with the radicals frozen in their equilibrium geometries). The theoretical results underestimate the roaming yield slightly compared to the shock tube experiment, but all studies to date confirm roaming dynamics in this system, even under atmospheric pressure, high temperature, thermal conditions.

Many additional examples of roaming dynamics have been reported. Acetone dissociation at 230 nm was recently found to give a significant yield of very slow CO products in low rotational levels, ascribed to intramolecular abstraction by a roaming methyl group.²² Recent theoretical results²³ have found a new pathway to the ground state in acetone from the initially prepared electronically excited state that may be involved; some pathway to the ground state is necessary to support roaming dynamics as the barrier on T_1 would preclude roaming.²² A fascinating recent development is reported in a theoretical study of the ground-state decomposition of a series of alkanes, propane to neopentane, by Harding and Klippenstein.²⁴ Two key findings result from this investigation, (1) roaming radical pathways exist with barriers roughly 1 kcal/mol below the lowest bond fission asymptote in all cases, and these lead to exoergic abstraction pathways, giving closed-shell products, and (2) the roaming minimum energy paths may be divided into two classes; one, Woodward–Hoffmann-allowed, involves an inversion of one of the radicals along the intrinsic reaction coordinate, while the other, Woodward–Hoffmann-forbidden, does not. The calculations suggest that for smaller radicals, the former case applies, while for larger systems, the greater dispersion interaction relative to orbital phase contribution in the saddle point region relaxes this constraint. It will be very interesting to see experimental verification of these observations.

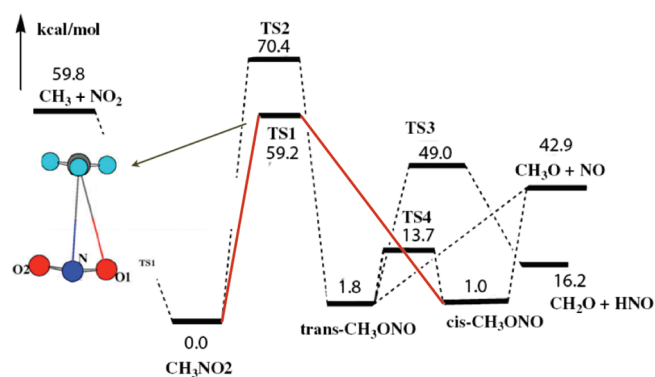


Figure 6. Potential energy diagram for nitromethane showing roaming-like isomerization TS. The roaming-mediated isomerization pathway is indicated by red lines. Adapted from ref 30.

We have so far discussed roaming dynamics in closed-shell systems. Can radicals exhibit roaming dissociation dynamics? There are several recent examples worthy of note. A joint theoretical and experimental study of allyl radicals by Chen et al.²⁵ reported that the H migration channel shows a pathway dynamically similar to the roaming mechanism. Photodissociation of the allyl radical was shown to have three H migration channels producing C_2H_2 . Two of them were classified as conventional channels, taking place at lower energies via tight TSs. The third channel clearly involved formation of $H_2CC\cdot + CH_3$ at much higher energy. Although this did not take place via an intramolecular abstraction, it resembles roaming in that it involves a distinct pathway to the same products that becomes important at higher energy owing to a loose TS.

Another radical that shows strong evidence of a roaming decomposition pathway is nitrate, NO_3 , which is an important atmospheric intermediate.²⁶ This system can dissociate to $O_2 + NO$ and $O + NO_2$ in the visible region. However, the molecular products are only seen at energies below, but within 250 cm^{-1} , of the simple bond fission threshold.²⁷ Above that threshold, only $O + NO_2$ is seen. Simply on the basis of the discussion above, this alone strongly suggests a roaming mechanism involving near-dissociation to $O + NO_2$, followed by intramolecular abstraction leading to O_2 formation. Recent imaging results from North and co-workers²⁶ show that the O_2 product is formed in vibrational levels up to $v = 9$, entirely consistent with intramolecular abstraction at long range as in formaldehyde and acetaldehyde.

In a sense, the nitrate radical case may be seen as representative of another class of roaming events, what we will term “roaming-mediated isomerization”, exemplified by nitromethane dissociation. Nitromethane was found to give both $CH_3 + NO_2$ and $CH_3O + NO$ in infrared multiphoton dissociation experiments.²⁸ The latter products were ascribed to the isomerization $CH_3NO_2 \rightarrow CH_3ONO$ followed by decomposition of the nitrite, and the energy of the isomerization barrier was estimated to be 55.5 kcal/mol ($\sim 5\text{ kcal/mol}$ below the simple bond fission asymptote) based on the observed branching. However, numerous theoretical and experimental investigations over the years failed to identify a suitable isomerization pathway, so that by 2003, M. C. Lin and co-workers entitled their investigation of the situation²⁹ “Nitromethane–Methyl Nitrite Rearrangement: A Persistent Discrepancy Between Theory and Experiment”. Theoretical methods consistently found TSs that were both above the bond fission threshold and too tight to

account for the substantial branching that was seen experimentally. By 2009, in light of the roaming reports on other systems, Zhu and Lin had found a new roaming-like TS (see Figure 6) within 1 kcal/mol of the bond fission energy.³⁰ This TS contrasts with the tight isomerization barrier about 10 kcal/mol higher in energy. The key characteristic of the surface shown in Figure 6 is that there are similar energies for the $R-NO_2$ and $R-ONO$ bonds; this will be the case quite generally for many nitro compounds, suggesting that this roaming-mediated isomerization may be an important aspect of the decomposition of energetic materials. Other systems that possess energetically similar isomers with low dissociation thresholds may well show similar roaming-mediated isomerization.

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We have seen that roaming radicals result when a molecule undergoes a barrierless near-dissociation to produce two fragments with very low relative energy. This makes them susceptible to the weak anisotropy of the potential at long range, and they may reorient themselves to access a distinct, highly reactive region if one is available. We believe this is likely a near-universal phenomenon because the large A factors associated with the barrierless decomposition means that the simple bond fission is always a dominant pathway, and, in general, it is more likely for such a system to have almost enough energy to dissociate than more than enough energy. Many systems have been shown to exhibit this behavior. For the future, there are a number of important avenues to follow in these investigations; from theoretical studies, roaming in alkane dissociation is expected to be quite general, but it will be important to document this experimentally and to explore the orbital phase questions mentioned above. Roaming requires a barrierless bond fission pathway; therefore, in general, it will be more important on the ground electronic state. Infrared multiphoton dissociation, pyrolysis, and

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chemical activation will thus be promising excitation mechanisms to probe roaming that can avoid the problem of interference from excited-state dissociation pathways following electronic excitation. Further examples of roaming-mediated isomerization and demonstration of this phenomenon in trajectory calculations will be interesting to pursue. Perhaps most important will be studies to gauge the practical importance of roaming dynamics in combustion, in the decomposition of energetic materials, and in atmospheric and interstellar chemistry. These studies are currently underway.

BIOGRAPHIES

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