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## Report Title

Final Report: Roaming Reactions and Roaming-Mediated Isomerization in the Decomposition of Energetic Materials

### ABSTRACT

In the course of this project, roaming reactions and roaming-mediated isomerization were studied in a range of nitro compounds. To this end, infrared multi photon dissociation was coupled to state-resolved velocity map imaging for the first time. Systems studied in detail included nitromethane, nitroethane, 1-nitropropane and nitrobutane, as well as the corresponding nitrites. In addition, these same techniques were applied to vinyl chloride dissociation, where state-resolved imaging clearly showed the ground state dissociation at threshold proceeds by 3-center elimination to give the elusive vinylidene reaction intermediate as a product.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
08/27/2012	1.00 Michael L. Hause, Nuradhika Herath, Rongshun Zhu, M. C. Lin, Arthur G. Suits. Roaming-mediated isomerization in the photodissociation of nitrobenzene, <i>Nature Chemistry</i> , (11 2011): 932. doi: 10.1038/nchem.1194
10/01/2014	5.00 Kirill Prozument, G. Barratt Park, Rachel G. Shaver, AnGayle K. Vasiliou, James M. Oldham, Donald E. David, John S. Muentner, John F. Stanton, Arthur G. Suits, G. Barney Ellison, Robert W. Field. Chirped-pulse millimeter-wave spectroscopy for dynamics and kinetics studies of pyrolysis reactions, <i>Physical Chemistry Chemical Physics</i> , (07 2014): 0. doi: 10.1039/C3CP55352C
10/01/2014	3.00 Zahra Homayoon, Joel M. Bowman, Arghya Dey, Charmara Abeysekera, Ravin Fernando, Arthur G. Suits. Experimental and Theoretical Studies of Roaming Dynamics in the Unimolecular Dissociation of CH, <i>Zeitschrift für Physikalische Chemie</i> , (07 2013): 0. doi: 10.1524/zpch.2013.0409
10/01/2014	4.00 Ravin Fernando, Chamara Abeysekera, Zahra Homayoon, Joel M. Bowman, Arthur G. Suits, Arghya Dey. Photodissociation dynamics of nitromethane and methyl nitrite by infrared multiphoton dissociation imaging with quasiclassical trajectory calculations: Signatures of the roaming pathway, <i>The Journal of Chemical Physics</i> , (02 2014): 0. doi: 10.1063/1.4862691
12/02/2015	9.00 Ravin Fernando, Chen Qu, Joel M. Bowman, Robert W. Field, Arthur G. Suits. Does Infrared Multiphoton Dissociation of Vinyl Chloride Yield Cold Vinylidene?, <i>The Journal of Physical Chemistry Letters</i> , (07 2015): 0. doi: 10.1021/acs.jpcllett.5b01031
12/02/2015	11.00 Ravin Fernando, Arghya Dey, Bernadette M. Broderick, Bina Fu, Zahra Homayoon, Joel M. Bowman, Arthur G. Suits. Visible/Infrared Dissociation of NO, <i>The Journal of Physical Chemistry A</i> , (07 2015): 0. doi: 10.1021/jp509902d
12/02/2015	12.00 Kirill Prozument, Yury V. Suleimanov, Beat Buesser, James M. Oldham, William H. Green, Arthur G. Suits, Robert W. Field. A Signature of Roaming Dynamics in the Thermal Decomposition of Ethyl Nitrite: Chirped-Pulse Rotational Spectroscopy and Kinetic Modeling, <i>The Journal of Physical Chemistry Letters</i> , (11 2014): 0. doi: 10.1021/jz501758p

**TOTAL: 7**

Number of Papers published in peer-reviewed journals:

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

Received

Paper

10/01/2014 6.00 Arthur G. Suits, David H. Parker. Hot Molecules: Off the Beaten Path, Science, (10 2014): 30. doi:

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**(c) Presentations**

Number of Presentations: 0.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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Paper

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**(d) Manuscripts**

<u>Received</u>	<u>Paper</u>
10/01/2014	7.00 Bernadette M. Broderick, Bina Fu, Zahra Homayoon, Joel M. Bowman, Arthur G. Suits, Ravin Fernando, Arghya Dey. Visible/Infrared Dissociation of NO <sub>3</sub> : Roaming in the Dark or Roaming on the Ground?, Journal of Physical Chemistry A (Submitted) (09 2014)
10/01/2014	8.00 James M. Oldham , Kirill Prozument, Yury V. Suleimanov, Beat Buesser, William H. Green, Arthur G. Suits, Robert W. Field. A Signature of Roaming Dynamics in the Thermal Decomposition of Ethyl Nitrite: Chirped-Pulse Rotational Spectroscopy and Kinetic Modeling, ( )
12/02/2015	10.00 Ravin Fernando, Nuwandi Ariyasinghe, Arthur G. Suits. Imaging NO elimination in the infrared multiphoton dissociation of nitroalkanes and alkyl nitrites, Chem. Phys. Lett (09 2015)
<b>TOTAL:</b>	<b>3</b>

**Number of Manuscripts:**

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**Books**

Received      Book

**TOTAL:**

Received      Book Chapter

**TOTAL:**

## Patents Submitted

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## Patents Awarded

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## Awards

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## Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Ravin Fernando	0.50	
Steven Lingenfelter	0.50	
Chamara Abeysekera	0.50	
<b>FTE Equivalent:</b>	<b>1.50</b>	
<b>Total Number:</b>	<b>3</b>	

## Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Arghya Dey	0.20
<b>FTE Equivalent:</b>	<b>0.20</b>
<b>Total Number:</b>	<b>1</b>

## Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Arthur Suits	0.08	
<b>FTE Equivalent:</b>	<b>0.08</b>	
<b>Total Number:</b>	<b>1</b>	

## Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Michael Doyle	0.08	mathematics
Nicholas Rombes	0.08	
<b>FTE Equivalent:</b>	<b>0.16</b>	
<b>Total Number:</b>	<b>2</b>	

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This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 1.00

**Names of Personnel receiving masters degrees**

NAME

**Total Number:**

**Names of personnel receiving PHDs**

NAME

Lu Yan  
Chamara Abeysekera

**Total Number:** 2

**Names of other research staff**

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

**Technology Transfer**

# Roaming Reactions and Roaming-Mediated Isomerization in the Decomposition of Energetic Materials

Arthur G. Suits  
Wayne State University

## Scientific Progress and Accomplishments Final Report, November 2015

### 1. Statement of the Problem Studied

An understanding of the elementary steps in the decomposition of energetic materials is essential to prediction of their performance, long-term stability, and sensitivity to heat and shock. A variety of sophisticated experimental approaches have thus been employed over the years for these purposes. However, even for the best available experimental and theoretical methods, gaining this fundamental understanding is quite challenging owing to the size and complexity of the molecules and the extreme conditions under which these reactions take place. Given this complexity, at every step we must be guided by our chemical intuition in choosing the experiments we will pursue and in interpreting the results we obtain. Recent work has revealed an important new mechanism in molecular decomposition, termed “roaming,” that has prompted a significant shift in our views of the dynamics of unimolecular dissociation.<sup>1-9</sup> This development shows that we have overlooked a significant pathway in chemical reactivity, and it compels us to reframe how we see the decomposition of energized molecules in general, and of high-energy-density materials in particular. Our goal in this program is thus *to explore in detail the potentially profound impact of hitherto overlooked roaming dynamics in decomposition of energetic materials*. This is achieved using a suite of powerful, complementary experimental techniques.

### 2. Summary of the Most Important Results

#### 2.1 Roaming-dynamics and electronic relaxation pathways in the nitrate radical

The nitrate radical,  $\text{NO}_3$ , is an extraordinary molecule that has fascinated and challenged chemists for many years.<sup>10,11</sup> It possesses several low-lying electronically excited states showing complex vibronic interactions accessible via visible excitation.<sup>12-15</sup> Its photochemistry is also quite unusual, with two dissociation channels:  $\text{NO} + \text{O}_2$  and  $\text{NO}_2 + \text{O}$ , showing nearly the same energy threshold and accessible in the visible<sup>16,17,18</sup>, giving it an important role in the atmosphere.<sup>19</sup> In hindsight, the close connection between these two reaction channels may be seen as a portent of the recent recognition of the key role of roaming dynamics in this system.<sup>20,21</sup> Roaming in the case of  $\text{NO}_3$  is quite unusual, however. In some ways it is analogous to nitromethane, in that it involves a roaming isomerization process. However,  $\text{NO}_3$  clearly has been shown to involve excited electronic states as illustrated in Fig. 1. In recent imaging studies, Grubb et al.<sup>20</sup> found that rotationally-selected NO translational energy distributions fell into two distinct groups associated with distinct  $\text{O}_2$  vibrational distributions. The low rotational levels



were formed with vibrationally excited  $O_2$ , while higher rotational levels were associated with vibrationally colder  $O_2$ . Based on a careful search of the stationary points and the intersections among the relevant potential energy surfaces, Morokuma and coworkers<sup>22</sup> suggested the following picture of its dissociation dynamics: After optical excitation to the  $D_3$  state (the lower member of the Jahn-Teller distorted  $E'$  pair), the system relaxes via the  $D_3/D_2$  and  $D_2/D_1$  conical intersections (CIs) to arrive on the dark  $D_1$  state. They argued that the vibrationally colder  $O_2$  product arises from roaming dynamics on  $D_1$  (via the  $D_1$  roaming saddle point (RSP) given in Fig 1), while the vibrationally excited  $O_2$  arises via dissociation from the ground electronic state via the  $D_0$  RSP. Strong support for this assignment was seen in the lambda doublet propensities, which were found to be opposite and perhaps near-limiting for the two distributions,<sup>21,23</sup> as well as in subsequent quasiclassical trajectory (QCT) calculations on separate, uncoupled  $D_0$  and  $D_1$  potential surfaces.<sup>24</sup> These remarkable results prompt several questions: What is the branching for dissociation on these two surfaces? What determines this branching? Does roaming take place exclusively on the dark state, or on the ground state, with branching upon exit, or on both? Is the branching determined at the intersection between the  $D_1$  and  $D_0$  surfaces in the course of electronic relaxation, or possibly from  $D_0$  up to  $D_1$  after an initial relaxation directly from the bright  $D_3$  state to  $D_0$ ? To begin addressing these questions, we combined state-selected DC slice imaging of the NO product following visible or a combination of visible and infrared excitation from a  $CO_2$  laser, along with additional QCT calculations.

Ideally, to probe the question whether roaming takes place exclusively on the excited state or the ground state, one might contrast dissociation following electronic excitation with that arising from infrared multiphoton excitation. Unfortunately,  $NO_3$  has no infrared active bands that overlap the  $CO_2$  laser lines, so direct  $CO_2$  laser excitation is not readily achieved. However, several of the unusual properties of  $NO_3$  allow us to begin an investigation along these lines using state-selected DC slice imaging as in the earlier experiments, but contrasting pure electronic excitation with a *combination* of electronic and infrared excitation. We obtained the total translational energy distributions (P(E)'s) from the images and although we see distinct differences for each probed rotational level and detection pathway, the results for prompt dissociation with purely electronic excitation show little difference when compared to dissociation with a combination of visible and infrared after a 0.7  $\mu s$  delay. We first obtain an estimate of the branching between the two dissociation paths based on the measured distributions. Our strategy here is first to create composite translational energy distributions by weighting the distributions using the appropriate linestrength factors<sup>25</sup>, then fitting the composite distribution with separate  $D_0$  and  $D_1$  components obtained from the QCT calculations from Bowman and coworkers. The agreement is generally satisfactory. The relative yields for  $D_0:D_1$  from the fits were found to be 0.92, 0.49, 0.31 and 0.44 for rotational levels 21.5, 30.5, 33.5 and 36.5, respectively. Lower rotational levels are associated exclusively with  $D_0$ . This state-dependent branching was then used, with linear interpolation over the rotational distributions given by Wittig and coworkers<sup>17</sup>, to obtain a final branching for dissociation of 6.1:1  $D_0:D_1$ .

We now turn to a consideration of the electronic relaxation and dissociation dynamics. The main possibilities, highlighted in Fig. 1, include: initial excitation to the  $D_3$  bright state, followed by internal conversion (IC1) through  $D_2$  and  $D_1$  to  $D_0$  via the

conical intersections that were found by Morokuma and coworkers.<sup>24</sup> This pathway is shown as “IC1” in Fig. 1. The branching for dissociation along  $D_1$  or  $D_0$  that we measure may then reflect the branching at the  $D_1/D_0$  CI as it is encountered during the relaxation. This is the pathway implicit in the treatment of Grubb et al.<sup>21</sup> Alternatively, excitation to the bright state maybe followed by IC to the ground state directly from  $D_3$ , shown as “IC0” on Fig. 1. The distinction here is that we recognize that  $D_3$  and  $D_0$  are directly

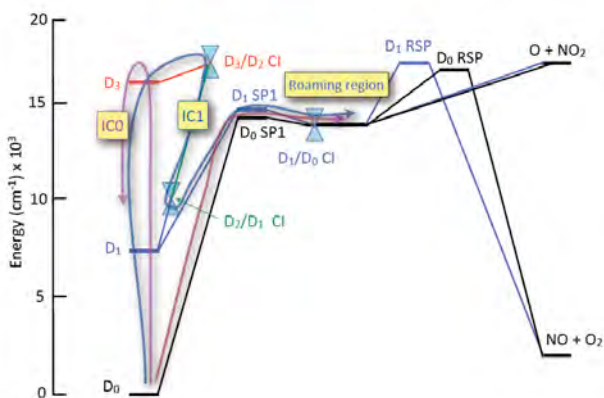


Fig. 1. Relevant features of the potential energy surfaces of the nitrate radical.

vibronically coupled<sup>13</sup>, so the ground state need not be accessed primarily via  $D_1$ . In this scenario, after IC to  $D_0$ , the system may proceed to the roaming region, then “roam upstairs” via the  $D_0/D_1$  CI, which is located in the roaming region. From there it may roam on  $D_1$  or simply dissociate. If the energy is above the O atom loss threshold, decay via that path is strongly preferred both for  $D_1$  and  $D_0$ , based on both experiment<sup>16</sup> and on the trajectory calculations.<sup>24</sup>

Taking all these points into consideration, we believe the evidence supports the second alternative relaxation pathway mentioned above, i.e., direct IC from the bright state to  $D_0$ , with  $D_1$  subsequently accessed from the ground state, probably via mixing in the roaming region where these surfaces are strongly coupled as shown in Fig. 5. The points in support of this view are as follows: The  $D_3$  and  $D_0$  surfaces possess strong vibronic coupling, directly impacting both the ground state vibrational level structure and the bright state fluorescence lifetimes, while that between the bright state and  $D_1$  is very weak.<sup>14</sup> Moreover, the fluorescence lifetimes suggest a dilution of the bright state that can only be accounted for by the ground state density of states.<sup>26,27</sup> The fact that our translational energy distributions are essentially identical whether we use electronic excitation with probe on a 10 ns timescale, or coupled with IR excitation 0.7 microseconds later, suggests that this relaxation is complete on the 10 ns timescale.

### 2.3 IRMPD imaging of nitroalkanes and alkyl nitrites

The advent of infrared multiphoton dissociation (IRMPD) in the early 70’s has been highly instrumental in the study of nascent photofragments originating from dissociation of small molecules on the ground electronic state.<sup>28</sup> With the introduction of powerful TEA-CO<sub>2</sub> lasers, IRMPD became a unique tool for studying unimolecular dissociation. It has been used extensively to study reactions that involve concerted pathways as well as tight transition states and simple bond rupture. IRMPD has more recently been exploited for mass spectrometric applications. However, roaming dynamics are likely to occur from the ground state near threshold, so IRMPD offers a powerful way to probe these processes. Roaming-mediated isomerization has been invoked in dissociation of nitrobenzene<sup>15</sup> and nitromethane<sup>14,16</sup> to account for the significant yield of

the NO loss channel in these systems. To-date, however, in primary photodissociation studies of roaming dynamics, only UV excitation has been used to prepare excited molecules for subsequent investigation. Since reactions involving roaming mechanisms largely arise from the ground electronic state, IRMPD studies can be very helpful in providing unambiguous information about such processes. In our recent studies, we have applied IRMPD with powerful state-resolved ion imaging methods for the first time.

We have recently performed an IRMPD/DC slice imaging study of nitroethane, nitropropane, nitrobutane, butylnitrite, and isobutyl nitrite with state-resolved probing of the NO product. Infrared multiphoton dissociation (IRMPD), is used to dissociate the molecules on the ground electronic state, which is a significant advantage in that we can be confident we are studying ground state processes, unlike the case of electronic excitation. The channels that produced NO as a product were studied and compared with each other to gain insight into the isomerization mechanism and the dissociation. We show preliminary results for nitrobutane and butyl nitrite, and we are in the process of analyzing the rich datasets we have obtained for all of these systems.

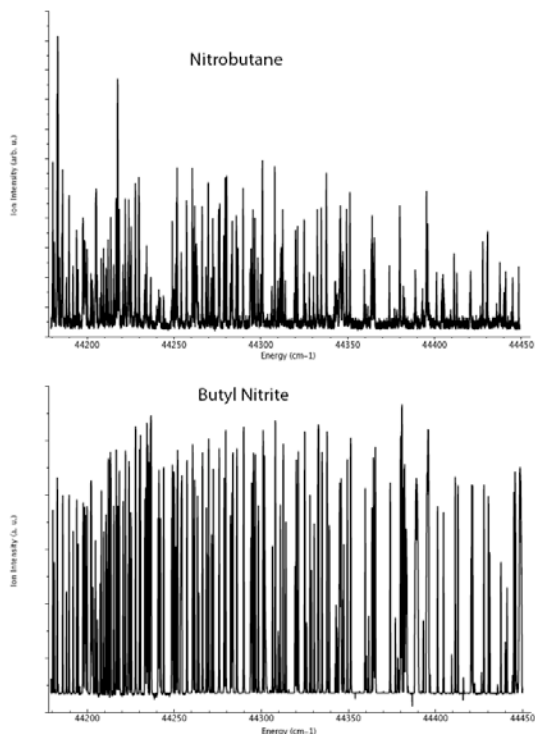


Fig. 2. REMPI spectra for NO from nitrobutane and butyl nitrite

Resonant multiphoton ionization (REMPI) spectra were recorded for the NO product of each system following IRMPD on the 0-0 band for the  $A(^2\Sigma^+) \leftarrow X(^2\Pi_r)$  transition in the range of 44180 – 44450  $\text{cm}^{-1}$ . The peaks are assigned to each rotational level by comparing to a simulated NO spectrum obtained using LIFBASE. We show the results for butyl nitrite and nitrobutane in Fig. 2 by way of example. It is immediately apparent that the butyl nitrite has a much hotter rotational distribution than nitrobutane.

The total translational energy distributions were also obtained from the DC slice images of the NO product from the IRMPD of these nitroalkanes and alkyl nitrites. The images were recorded for the nascent NO products for different J values from the dissociation. Total translational energy distributions were obtained by using the conservation of mass and momentum. In figure 3 the images are shown alongside the total translational energy distribution for a single NO quantum state for IRMPD of 1-nitrobutane and butyl nitrite. The obtained total translational energies peak at zero, which suggest barrierless dissociation of the molecules. In the images we see a significantly greater translational energy release for the butyl nitrite compared to nitrobutane, consistent with the REMPI spectra. Interestingly,

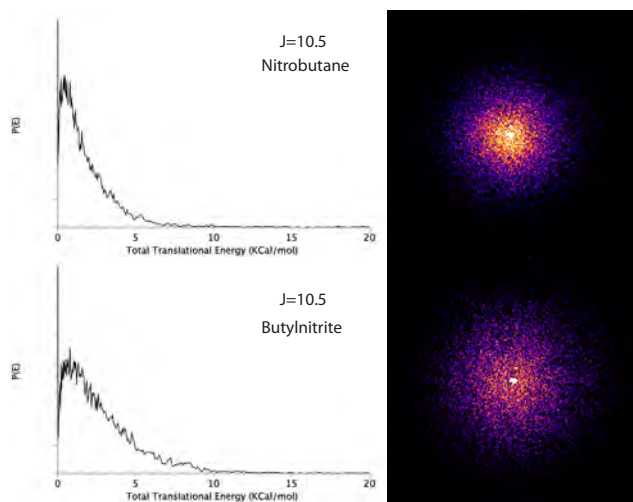


Fig. 3 DC sliced images (right) and translational energy distributions (left) for NO  $J=10.5$  from IRMPD of indicated molecule.

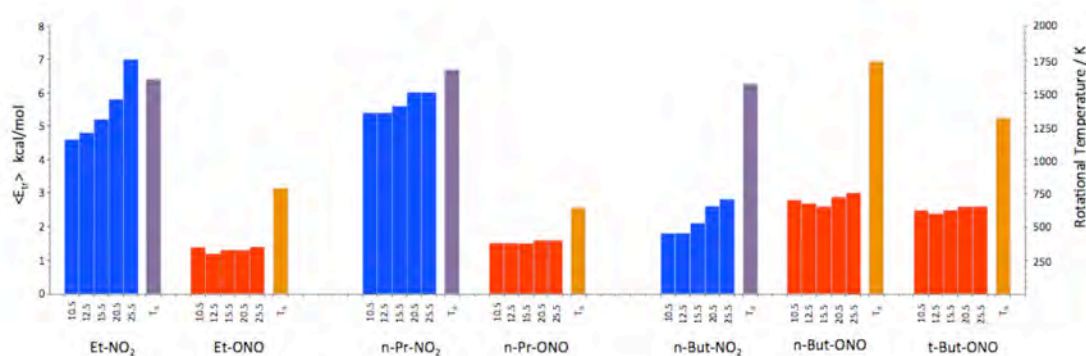
release for nitroethane ranges from 4.9 kcal/mol to 7.0 kcal/mol (low- $J$  to high- $J$ ) while for ethyl nitrite it ranges from 1.2 kcal/mol to 1.4 kcal/mol. The limiting value for the total translational energy release of nitroethane was found to be  $\sim 14$  kcal/mol and  $\sim 5$  kcal/mol for ethyl nitrite. This difference in the translational energy release is also manifested in the product rotational excitation: 1600K for nitroethane and 768 for ethyl nitrite. We note also that for nitroethane (and the other nitro systems), there is a correlation between average translational energy release and rotational excitation (Fig. 8), consistent with an impulsive origin of the rotation. Interestingly, this is not seen for the nitrites. These results show the same trends as the IRMPD results of nitromethane and methyl nitrite we reported previously, supporting the association to RMI[2].

The isomerization of nitroethane to ethyl nitrite has to compete with the direct C-N bond fission channel and an alternative pathway, concerted molecular elimination (CME) to HONO + ethylene, for which there is no analogue in nitromethane. Denis et al. reported a density functional study of the stationary points relevant to 2003. They found the barrierless simple bond fission (SBF) of the C-N bond at 53.8 kcal/mol above the nitroethane minimum, and they placed the TS for CME about 12 kcal/mol lower. They found a tight TS for isomerization to the nitrite 6 kcal/mol *above* the SBF channel and troubled over this, as they also found a similar value for nitromethane but, as noted by Lin, this high barrier would not permit effective competition between isomerization and SBF as had been seen for nitromethane in the Wodtke and Lee experiments. Denis et al. concluded in any case that the CME channel would dominate in nitroethane and nitropropane, and took solace in the fact that Wodtke and Lee did not see a measurable yield of NO in the nitroethane case. However, our results clearly show that isomerization to the nitrite does occur, as this is the only feasible means of producing NO from the nitroethane. Furthermore, the likely mechanism is RMI, just as in the nitromethane case. However, although the branching to isomerization is substantial for nitromethane, our results give no

these results are exactly counter to the trends we observed in nitromethane and methyl nitrite.

The average translational energy release for each system and each rotational level was obtained from the translational energy distributions and these are given for all systems studied and all rotational levels, along with the rotational temperatures, in Fig. 4. The average translational energy

indication as to the branching here: it could be and likely is relatively small. Indeed, Wodtke et al. reported no evidence for isomerization in IRMPD of nitroethane or 2-nitropropane; However they did not report an upper bound for this channel. Given mass spectrometric interference from both  $\text{NO}_2$  and  $\text{HONO}$  at  $m/z=30$  in their study, and the challenge of identifying ions associated with  $\text{C}_2\text{H}_5\text{O}$ , it is reasonable to imagine that branching up to 15% could easily be overlooked in those experiments. In any case, our results suggest that there is a loose roaming transition state analogous to that found by Zhu and Lin for the nitromethane case, or else isomerization would be very unlikely, as suggested by Denis et al. Nitroethane and the other systems studied here all have the vicinal carbon that allows for the five-membered transition state leading to CME. In a sense these systems have aspects in common with the formaldehyde potential surface in which roaming was first recognized. In formaldehyde, the SBF threshold and the roaming TS are also above a CME transition state, about 7 kcal/mol higher in that case. The extent to which



**Fig. 4.** Average translational energy distribution change with rotational level and rotational temperature.

roaming persists above the SBF threshold is strongly system-dependent, and a subject of considerable interest. In formaldehyde, branching to the roaming pathway remains significant even at energies 10 kcal/mol or more above the roaming threshold[35]. In the nitrate radical, RMI shuts down almost immediately above threshold. In nitromethane, there is some disagreement among the theoretical treatments. Homayoon and Bowman used full-dimensional quasiclassical trajectory calculations and saw RMI persist more than 5 kcal/mol above the SBF threshold. Annesley et al. used a reduced dimensionality “rigid-body” trajectory treatment and concluded that RMI is operative only up to 2 kcal/mol or so above threshold. They also reported the pressure dependence and concluded that SBF will dominate at high pressures (120 torr). We should note that, following isomerization to the nitrite, pathways leading to  $\text{HNO}$  + acetaldehyde are also accessible, either via a four-center transition state, or by  $\text{NO}$  roaming. A recent report of ethyl nitrite pyrolysis using chirped-pulse mm-Wave spectroscopy and kinetic modeling has concluded that roaming dynamics are responsible for  $\text{HNO}$  formation in that case. Future studies to determine the branching accurately for these systems would be of considerable interest.

#### 2.4 Chirped-pulse probing of ethyl nitrite flash pyrolysis

In collaboration with the Field group at MIT, we have begun application of the powerful technique of chirped-pulse (CP) spectroscopy to reaction dynamics. We illustrate this with recent results obtained at MIT using CP millimeter-wave spectroscopy coupled to flash pyrolysis of ethyl nitrite. This approach was used to measure product branching and extract information about the reaction mechanism, guided by kinetic modeling. Pyrolysis of ethyl nitrite,  $\text{CH}_3\text{CH}_2\text{ONO}$ , was studied in a Chen type flash pyrolysis reactor at temperatures of 1000–1800 K. The branching ratios of HNO,  $\text{CH}_2\text{O}$ , and  $\text{CH}_3\text{CHO}$  products are measured and compared to the kinetic models generated by the Reaction Mechanism Generator software. We find that roaming  $\text{CH}_3\text{CH}_2\text{ONO} \rightarrow \text{CH}_3\text{CHO} + \text{HNO}$  plays an important role in the thermal decomposition of ethyl nitrite, with its rate, at 1000 K, comparable to that of the radical elimination channel  $\text{CH}_3\text{CH}_2\text{ONO} \rightarrow \text{CH}_3\text{CH}_2\text{O} + \text{NO}$ . HNO is a signature of roaming in this system.

### *2.5 IRMPD of vinyl chloride yields cold vinylidene*

Velocity map imaging of the infrared multiphoton dissociation of vinyl chloride shows the formation of HCl in rotational levels below  $J=10$  that are associated with the 3-center elimination pathway. The total translational energy release was observed to peak at 3-5 kcal/mol, which is consistent with the low reverse barrier predicted for the formation of HCl with vinylidene co-products. Direct dynamics trajectory studies from the 3-center transition state reproduce the observed distributions and show the associated vinylidene is formed with only modest rotational excitation, precluding Coriolis-induced mixing among the excited vibrational levels of acetylene that would lead to distribution of vinylidene character into many vibrationally mixed acetylene vibrational levels. The results suggest that infrared multiphoton dissociation of vinyl chloride is an efficient route to synthesis of stable, cold vinylidene.

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