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14. ABSTRACT
This project is a theoretical and computational investigation of a novel and general mechanism for chemical reactions of importance for the development of energetic materials. The mechanism, termed "roaming", was discovered recently in joint theoretical/experimental studies of the photodissociation of the formaldehyde and acetaldehyde molecules. This mechanism, although now firmly established, is not understood quantitatively using a statistical theory known as Transition State Theory. This theory is widely used to obtain the rates of chemical reactions which are the input for large scale computer models of combustion, atmospheric chemistry, etc.

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Report Title

Final Report: Theoretical Chemistry: Theoretical Studies of "Roaming" Reactions

ABSTRACT

This project is a theoretical and computational investigation of a novel and general mechanism for chemical reactions of importance for the development of energetic materials. The mechanism, termed "roaming", was discovered recently in joint theoretical/experimental studies of the photodissociation of the formaldehyde and acetaldehyde molecules. This mechanism, although now firmly established, is not understood quantitatively using a statistical theory known as Transition State Theory. This theory is widely used to obtain the rates of chemical reactions which are the input for large-scale computer models of combustion, atmospheric chemistry, etc. Roaming can significantly affect models of chemical reactions that lead to release of large amounts of chemical energy and so it is important to develop quantitative approaches that can account for the extent of roaming and also the internal energy distributions of reaction projects. The proposed research will use demanding but rigorous dynamical theory to elucidate the quantitative aspects of roaming. These methods will be applied to the formaldehyde and acetaldehyde reactions for diagnostic purposes and also to the energetic material methylnitrite. The outcome of this research, which will be done in close collaboration with experiment, will be new, predictive and quantitative ways to model the roaming mechanism in chemical reactions.

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)

Received		Paper
08/23/2013	1.00	Zahra Homayoon, Pablo G. Jambrina, F. Javier Aoiz, Joel M. Bowman. Communication: Rate coefficients from quasiclassical trajectory calculations from the reverse reaction: The Mu?+?H2 reaction re-visited, The Journal of Chemical Physics, (09 2012): 0. doi: 10.1063/1.4734316
08/23/2013	2.00	Joel M Bowman, Zahra Homayoon. Quasiclassical Trajectory Study of CHCH3NO2 Decomposition via Roaming Mediated Isomerization Using a Global Potential EnergySurface, The Journal of Physical Chemistry A, (02 2013): 1. doi: 10.1021/jp312076z
08/23/2013	3.00	Bina Fu, Joel M. Bowman, Hongyan Xiao, Satoshi Maeda, Keiji Morokuma. Quasiclassical Trajectory Studies of the Photodissociation Dynamics of NO, Journal of Chemical Theory and Computation, (02 2013): 893. doi: 10.1021/ct3009792
08/23/2013	4.00	Bina Fu, Dong H. Zhang, Joel M. Bowman. Quasiclassical trajectory studies of 18O(3P) + NO2 isotope exchange and reaction to O2 + NO on D0 and D1 potentials, The Journal of Chemical Physics, (2013): 0. doi: 10.1063/1.4812802
08/23/2013	5.00	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, Zeitschrift für Physikalische Chemie, (07 2013): 0. doi: 10.1524/zpch.2013.0409
TOTAL:	**5**	

Number of Papers published in peer-reviewed journals:

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

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

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

Received Paper

TOTAL:

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

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

Received Paper

TOTAL:

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

(d) Manuscripts

Received		Paper
11/14/2016	10.00	Zahra Homayoon. MULTIMODE quantum calculations of vibrational energies and IR spectrum of the NO+ (H2O) cluster using accuratepotential energy and dipole moment surfaces, J. Chem. Phys. (08 2014)
11/14/2016	8.00	Arghya Dey, Ravin Fernando, Chamara Abeysekera, Zahra Homayoon, Joel M. Bowman, Arthur G. Suits. Photodissociation dynamics of nitromethane and methyl nitrite by infrared multiphoton dissociation imaging with quasiclassical trajectory calculations: Signatures of the roaming pathway, The Journal of Chemical Physics (02 2014)
11/14/2016	9.00	Zahra Homayoon, Joel M. Bowman, Francesco A. Evangelista. Calculations of Mode-Specific Tunneling of Double-Hydrogen Transfer in Porphycene Agree with and Illuminate Experiment, The Journal of Physical Chemistry Letters (08 2014)
11/14/2016	7.00	Zahra Homayoon, Joel M. Bowman. A Global Potential Energy Surface Describing the N(, The Journal of Physical Chemistry A (01 2014)
11/14/2016	11.00	Ravin Fernando , Arghya Dey , Bernadette M. Broderick, Bina Fu , Zahra Homayoon, Joel M. Bowman , Arthur G. Suits. Visible/Infrared Dissociation of NO3: Roaming in the Dark or Roaming on the Ground?, J. Phys. Chem. A (10 2014)
TOTAL:		**5**

Number of Manuscripts:

Books

Received	Book
TOTAL:	

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
John Mancini	0.30	
Hank Liu	0.20	
FTE Equivalent:	**0.50**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Yimin Wang	0.20
Zahra Homayoon	1.00
FTE Equivalent:	**1.20**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

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: .....

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

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:.....

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

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

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense .....

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: .....

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

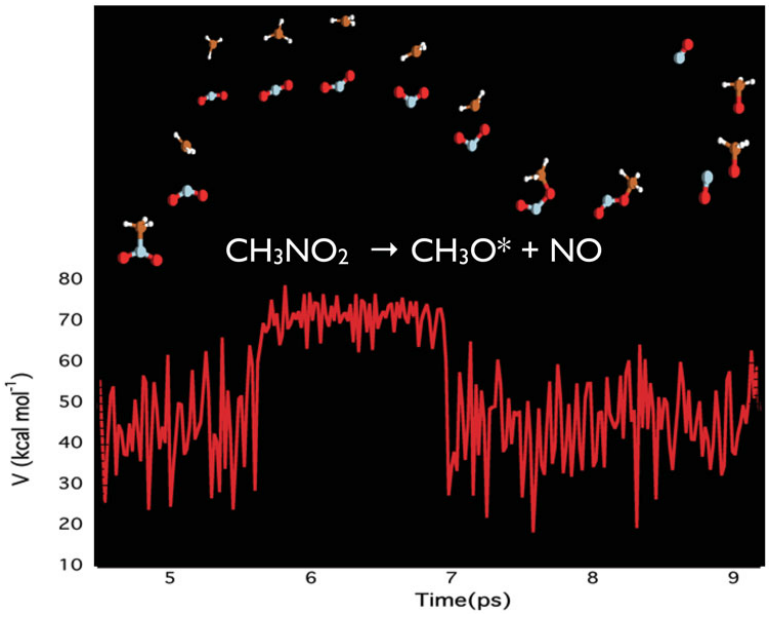
Substantial progress was made in the study of reaction dynamics with an emphasis on "roaming". This work was reported in 10 peer-reviewed publications and so a detailed summary of all this work in not feasible here. I do however note the major work on CH3NO2 and NO3. New global potential energy surfaces were obtained and detailed calculations of the reaction dynamics were performed. This work was done in part in collaboration with the experimental group of Arthur Suits, and a several joint publications resulted from this. The work on NO3 was also done in part in collaboration with Suits with again several joint publications resulting from this. Roaming plays a major role in these reaction systems and our work has provided the most detailed and definitive study of this unusual reaction pathway.

Technology Transfer

Final Report Narrative for Theoretical Studies of Roaming Reactions

(W911NF-11-1-0477)

Research funded by this grant resulted in eleven publications.[1-11] Most of these focused on roaming in the isomerization reaction CH_3NO_2 to a variety of products, but with a focus on the CH_3O+ NO produces. These calculations made use of a new global potential energy surface (PES) and then performing tens of thousands of quasiclassical trajectory calculations, most of which were initiated from the methylnitrate minimum. In some studies trajectories were initiated from the *cis* and *trans* isomers CH_3ONO to investigate the extent of non-statistical behavior in the reaction. A representative roaming trajectory is shown to the left. As seen, the incipient radical products CH_3+NO_2 appear to be formed. However, after a period of "roaming", (the near horizontal potential at round 75 kcal/mol), a self-abstraction occurs to form CH3O + NO, with significant vibrational excitation of methoxy. This work was done in collaboration with Prof. Arthur Suits and resulted in several joint publications.[5,7]



A major effort was undertaken to study roaming in the photodissociation of NO_3. This resulted in development of two global PESs based on permutationally invariant fitting of roughly 100 000 CASPT2 electronic energies.[3] These surfaces were used in quasiclassical trajectory calculations of the O_2+NO products considering both the ground and first excited doublet states. Agreement with experiment from North and earlier from Suits is excellent. These PESs were also used in studies of isotope scrambling in the bimolecular reactions of O_2 with NO.[4] Again agreement with molecular beam experiments of Lee and co-workers is very good.

Finally, in collaboration with the experimental group of Cassavechia, we developed a global PES for the N(^{2}D)+H2O reaction.[9] The detailed dynamics

calculations and comparisons with experiment were reported in a subsequent ARO grant period.

References to papers supported by the grant.

1. Z. Homayoon, P. G. Jambrina, F. Javier Aoiz, J. M. Bowman. Communication: Rate coefficients from quasiclassical trajectory calculations from the reverse reaction: The Mu+H2 reaction re-visited, J. Chem. Phys. **137**, 021102 (2012).
2. J. M Bowman, Z. Homayoon, Quasiclassical Trajectory Study of CH_3NO_2 Decomposition via Roaming Mediated Isomerization Using a Global Potential Energy Surface, J. Phys. Chem. *A*, **117**, 11665-11672 (2013).
3. B. Fu, J. M. Bowman, H. Xiao, S. Maeda, K. Morokuma. Quasiclassical Trajectory Studies of the Photodissociation Dynamics of NO_3 from the D_0 and D_1 Potential Energy Surfaces, J. Chem. Theory Comput. **9**, 893-900 (2013).
4. , B. Fu, D. H. Zhang, and J. M. Bowman, Quasiclassical Trajectory Studies of $^{18}O(^3P)$ + NO_2 Isotope Exchange and Reaction to O_2 + NO on D_0 and D_1 Potentials J. Chem. Phys. **139**, 024303 (2013).
5. Z. Homayoon, J. M. Bowman, A. Dey, C. Abeysekera, R. Fernando, A. G. Suits. Experimental and Theoretical Studies of Roaming Dynamics in the Unimolecular Dissociation of CH_3NO_2 to CH_3O+ NO, Zeits. für Physik. Chemie **227**, 1267-1280 (2013).
6. Z. Homayoon. MULTIMODE quantum calculations of vibrational energies and IR spectrum of the NO^+ (H_2O) cluster using accurate potential energy and dipole moment surfaces, J. Chem. Phys. **141**, 124311 (2014).
7. A. Dey, R. Fernando, C. Abeysekera, Z. Homayoon, J. M. Bowman, A. G. Suits. Photodissociation dynamics of nitromethane and methyl nitrite by infrared multiphoton dissociation imaging with quasiclassical trajectory calculations: Signatures of the roaming pathway, J Chem Phys **140**, 054305 (2014).
8. Z. Homayoon, J. M. Bowman, F. A. Evangelista. Calculations of Mode-Specific Tunneling of Double-Hydrogen Transfer in Porphycene Agree with and Illuminate Experiment, J. Phys. Chem. Lett. **5**, 2723-2727 (2014).
9. Z. Homayoon and J. M. Bowman A Global Potential Energy Surface Describing the $N(^2D)$ + H_2O Reaction and a Quasiclassical Trajectory Study of the Reaction to NH + OH, J. Phys. Chem. A **118**, 545-553 (2014).
10. Z. Homayoon and J. M. Bowman, Communication: MULTIMODE calculations of low-lying vibrational states of NO_3 using an adiabatic potential energy surface, J. Chem. Phys. **141**, 161104 (2014).
11. J. M. Bowman, Roaming, Mol. Phys. **112**, 2516-2528 (2014).