Final Technical Report for
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Isomer-specific spectroscopy of aromatics and their resonance-stabilized radical intermediates

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I. Program Definition and Scope

There are many circumstances in which complex gas-phase reaction mixtures must be interrogated and understood, including combustion, plasmas, atmospheres, and molecular clouds. Spectroscopic tools are essential to selective detection and characterization of the widening array of precursors and the reactive intermediates they generate. This research program has focused on the development and implementation of sensitive spectroscopic detection schemes that are isomer-specific and even conformation-specific. In particular, we used an array of laser-based and broadband microwave methods to carry out isomer-specific and conformation-specific spectroscopy on large flexible molecules and reactive intermediates formed by photolysis, pyrolysis, combustion, or electron-driven chemistry.

II. Research Accomplishments and Research Publications

In what follows, I provide a brief overview of this research program, breaking up the discussion into seven themes that have guided the work.

A. Spectroscopy and Photochemical Reactions of C4 hydrocarbons

While we tend to think of free radical formation as the primary means of increasing the chemical reactivity of hydrocarbons, electronic excitation can also do so in its own right. Diacetylene, C_4H_2, is a notable example. Following excitation of the ground state molecule by ultraviolet light, efficient intersystem crossing occurs to the triplet manifold, forming a long-lived triplet state that reacts efficiently with a wide-range of hydrocarbons and nitriles. Early in this research program, we explored this chemistry following UV excitation by affixing to the end of our pulsed gas valve a short reaction tube. When a mixture of C_4H_2 with co-reactant C_mH_n was pulsed into this tube, photoexcitation initiated reaction, with primary products being interrogated after supersonic expansion using VUV single-photon photoionization at 118 nm. When products were formed that themselves have well-defined UV spectra, resonant two-photon ionization provided isomer-specific detection. With DOE funding, we studied the reactions of metastable C_4H_2 with short alkynes and alkenes, 1,3-butadiene, benzene, toluene, and styrene. We also directly interrogated the triplet states of 1,3-butadiene and 2-cyclopentenone using cavity ring-down and phosphorescence excitation, respectively.

1. C.A. Arrington, C. Ramos, A.D. Robinson, and T.S. Zwier, "Aromatic Ring-Forming Reactions of Metastable Diacetylene with 1,3-butadiene", J. Phys. Chem. A **102**, 3315-3322 (1998).
2. C.A. Arrington, C. Ramos, A.D. Robinson, and T.S. Zwier, "The ultraviolet photochemistry of diacetylene with alkynes and alkenes: Spectroscopic characterization of the products", J. Phys. Chem. **103**, 1294-1299 (1999).
3. Allison G. Robinson, Paul R. Winter, Christopher Ramos, and Timothy S. Zwier, "Ultraviolet Photochemistry of Diacetylene: Reactions with Benzene and Toluene", *J. Phys. Chem. A* **104**, 10312-10320 (2000).
4. Charles S. McEnally, Allison G. Robinson, Lisa D. Pfefferle, and Timothy S. Zwier, "Aromatic Hydrocarbon Formation in Nonpremixed Flames Doped with Diacetylene, Vinylacetylene, and Other Hydrocarbons: Evidence for Pathways Involving C4 Species", Combustion and Flame **123**, 344-357 (2000).

5. Christopher Ramos, Paul R. Winter, Timothy S. Zwier, and Stephen T. Pratt, "Photoelectron Spectroscopy via the $1^1\Delta_u$ state of Diacetylene", J. Chem. Phys. **116**, 4011 (2002).
6. Allison G. Robinson, Paul R. Winter, and Timothy S. Zwier, "The singlet-triplet spectroscopy of 1,3-butadiene using cavity ring-down spectroscopy", J Chem. Phys. 116 (18): 7918-7925 (2002).
7. Allison G. Robinson, Paul R. Winter, and Timothy S. Zwier, "The Ultraviolet Photochemistry of Diacetylene with Styrene", J. Phys. Chem. A **106** (24): 4789-4796 (2002).
8. Nathan R. Pillsbury, Timothy S. Zwier, Richard H. Judge, Stephen Drucker, "Jet-cooled phosphorescence excitation spectrum of the $T_1(n,\pi^*) \leftarrow S_0$ transition of 2-cyclopenten-1-one", J. Phys. Chem. A **111**, 8357-8366 (2007).

B. Single Isomer Spectroscopy of Aromatic Derivatives

As the chemical structures of substituted aromatics become more complex, the number of structural isomers grows quickly, and conformational isomers also become increasingly prevalent. We applied a variety of double-resonance methods to characterize the single-isomer vibrational and electronic spectroscopy of a large number of such molecules, many of which are important components of petroleum fuels and/or are anticipated as prevalent intermediates on pathways toward soot formation. The interrogation methods include resonant two-photon ionization (R2PI), laser-induced fluorescence (LIF), single vibronic-level fluorescence (SVLF), UV-UV hole-burning, resonant ion-dip infared spectroscopy (RIDIRS), and stimulated emission pumping (SEP). Furthermore, we applied SEP population transfer spectroscopy to determine the barriers to conformational isomerization in the ground electronic state.

9. Jaime A. Stearns and Timothy S. Zwier, "The infrared and ultraviolet spectroscopy of jet-cooled *ortho*-, *meta*-, and *para*-diethynylbenzene", J. Phys. Chem. A 107, 10717-10724 (2003).
10. Talitha M. Selby and Timothy S. Zwier, "Conformation-specific spectroscopy of 4-phenyl-1-butyne and 5-phenyl-1-pentyne, J. Phys. Chem. A **109**, 8487-8496 (2005).
11. Talitha M. Selby, Aloke Das, T. Bekele, H.Daniel Lee, and Timothy S. Zwier, Conformation-specific spectroscopy of 3-benzyl-1,5-hexadiyne, J. Phys. Chem. A **109**, 8497-8506 (2005).
12. Talitha M. Selby, Jasper R. Clarkson, Diane Mitchell, James A.J. Fitzpatrick, and Timothy S. Zwier, "Isomer-specific spectroscopy and conformational isomerization energetics of o-, m-, and p-ethynylstyrenes", J. Phys. Chem. A **109**, 4484-96 (2005).
13. Timothy S. Zwier, "Laser probes of Conformational Isomerization in Flexible Molecules and Complexes", J. Phys. Chem. A **110**(12) 4133-4150 (2006).
14. Talitha M. Selby, W. Leo Meerts, and Timothy S. Zwier, "Isomer-specific Ultraviolet Spectroscopy of *meta*- and *para*-divinylbenzene", J. Phys. Chem. A **111**, 3697-3709 (2007).
15. Talitha M. Selby and Timothy S. Zwier, "Flexing the muscles of Divinylbenzene: Direct measurement of the barriers to conformational isomerization", J. Phys. Chem. A **111**, 3710-3718 (2007).

16. Nathan R. Pillsbury and Timothy S. Zwier, "Conformation-specific spectroscopy and excited state photophysics of 5-phenyl-1-pentene", J. Phys. Chem. A **113**, 118-125 (2009).
17. Nathan R. Pillsbury and Timothy S. Zwier, "Conformational isomerization of 5-phenyl-1-pentene probed by SEP-population transfer spectroscopy", J. Phys. Chem. A **113**, 126-134 (2009).

C. Vibronic Coupling in near-degenerate excitonic states

Vibronic coupling is a common phenomenon that mixes two excited electronic states through nuclear vibrational motion. When the two excited states are well-separated from one another in energy, perturbation theory approaches work well to describe this mixing, which is dictated primarily by $\Delta v=\pm 1$ in vibrations of the right symmetry to couple the two states. However, such perturbative theory approaches break down completely as the gap between the two excited states shrinks towards zero, leading to fascinating and challenging spectroscopy. We have studied the state-to-state mixing present in flexible bichromophores composed of two identical or nearly-identical electronic chromophores. Here the flexible linkage between the two chromophores can lead to conformational isomers that change the distance and orientation of the two UV chromophores and also modulate the low-frequency vibrations involving them. The spectroscopy has led to the development of a powerful multi-mode vibronic coupling model by Lyudmila Slipchenko and her co-workers.

18. Nathan R. Pillsbury, Jaime A. Stearns, Aloke Das, Talitha M. Selby, David F. Plusquellic, and Timothy S. Zwier, "State-specific studies of Internal Mixing in a Prototypical Flexible Bichromophore: Diphenylmethane", J. Chem. Phys. **129** 114301 (2008).
19. Jaime A. Stearns, Nathan R. Pillsbury, Christian W. Müller, Kevin O. Douglass, Timothy S. Zwier, and David F. Plusquellic, "Rotationally resolved studies of S_0 and the exciton coupled S_1/S_2 origin regions of diphenylmethane and its d_{12} isotopologue", J. Chem. Phys. **129**, 224305 (2009).
20. Nathan R. Pillsbury, Christian W. Müller, and Timothy S. Zwier, "Conformational Effects on Excitonic Interactions in a Prototypical H-bonded Bichromophore: Bis(2-hydroxyphenyl) methane", J. Phys. Chem. A **113**, 5000-5012 (2009).
21. Nathan R. Pillsbury and Timothy S. Zwier, "The Conformational Isomerization and Collisional Cooling Dynamics of Bis-(2-hydroxyphenyl)methane", J. Phys. Chem. A **113**, 5013-5021 (2009).
22. Chirantha P. Rodrigo, Christian W. Müller, Nathan R. Pillsbury, William H. James III, Timothy S. Zwier, and David F. Plusquellic, "Conformer-specific vibronic spectroscopy and vibronic coupling in a flexible bichromophore: bis-(4-hydroxyphenyl)methane", J. Chem. Phys. **134**, 164312 (2011).
23. Shin G. Chou, Chirantha P. Rodrigo, Christian W. Müller, Kevin O. Douglass, Timothy S. Zwier, and David F. Plusquellic, "Rotationally resolved C_2 symmetric conformers of bis-(4-hydroxyphenyl)-methane: Prototypical examples of Excitonic coupling in the S_1 and S_2 Electronic States, J. Phys. Chem. A **115**, 9643-9652 (2011).
24. Evan G. Buchanan, David F. Plusquellic, and Timothy S. Zwier, "Excitonic splitting and vibronic coupling in 1,2-diphenoxyethane: Conformation-specific effects in the weak coupling limit", J. Chem. Phys. **138** 204313 (2013).

25. Nathanael M. Kidwell, Benjamin Nebgen, Lyudmila Slipchenko, and Timothy S. Zwier, "The Effects of Site Asymmetry on Near-Degenerate State-to-State Vibronic Mixing in Flexible Bichromophores", J. Chem. Phys. **151**, 084313 (2019).

D. Electronic and Vibrational Spectra of Resonance-stabilized Radicals

One of the major influences on the reactivity of gas-phase free radicals is whether the radical sites are conjugated with other orbitals, leading to resonance stabilization. This additional stability causes these free radicals to be preferentially formed, and slows their reactivity once formed. They thus build up in concentration and play key roles in dictating the chemical processes present in reactive mixtures. We have studied the electronic and vibrational spectroscopy of a number of such resonance-stabilized radicals, including 1-phenylallyl, benzylallenyl, 5-methyl-2-furanylmethyl, and the alkylated benzylic radicals α–methyl, α–ethyl, and α–propyl benzyl.

26. Joshua A. Sebree, Nathan Kidwell, Evan G. Buchanan, Marek Zgierski, and Timothy S. Zwier, "Spectroscopy and Ionization Thresholds of π-Isoelectronic 1-Phenylallyl and Benzylallenyl Resonance Stabilized Radicals", Chemical Science, **2**, 1746-1754 (2011).
27. Nathanael M. Kidwell, Neil J. Reilly, Ben Nebgen, Deepali N. Mehta-Hurt, Ross D. Hoehn, Damian L. Kokkin, Michael C. McCarthy, Lyudmila V. Slipchenko, and Timothy S. Zwier, "Jet-cooled Spectroscopy of the α–Methylbenzyl Radical: Probing the State-Dependent Effects of Methyl Rocking against a Radical Site", *J. Phys. Chem. A*, **117**, 13465-80 (2013).
28. Nathanael M. Kidwell, Deepali N. Mehta-Hurt, Joseph A. Korn, and Timothy S. Zwier, "Infrared and Electronic Spectroscopy of Jet-cooled 5-methyl-2-furanylmethyl Radical derived from the Biofuel 2,5-Dimethylfuran", J. Phys. Chem. A **120**, 6434-43 (2016).
29. Joseph A. Korn, Khadija Jawad, Daniel P. Tabor, Edwin L. Sibert III, and Timothy S. Zwier, "Conformation-specific Spectroscopy of Alkylbenzyl Radicals: α-ethylbenzyl and α−propylbenzyl radicals", J. Chem. Phys. **145**, 124314 (2016).

E. Electronic Spectroscopy of model components of Lignin

Lignin is the second-most abundant biopolymer in nature, forming the structural framework for plants to grow and encasing the sugars that they produce. Unlike the highly regulated and complicated biopolymers found in DNA and proteins, lignin is composed of just three aromatic monomers, with the degree of its structural rigidity dictated by their relative compositions and the nature of the chemical linkages between them. We have used our tools for carrying out conformation-specific spectroscopy to study the ultraviolet and infrared spectroscopy of the monomers themselves (p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) and of their aromatic progenitors guaiacol and syringol. We have also extended our studies to dilignols with different linkages both as neutrals and as cryo-cooled protonated ions.

30. Chirantha P. Rodrigo, William H. James III, and Timothy S. Zwier, "Single-conformation ultraviolet and infrared spectra of jet-cooled monolignols: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol", J. Am. Chem. Soc. **133**, 2632-2641 (2011).
31. Jacob C. Dean, Deepali Mehta, William H. James III, and Timothy S. Zwier, "Conformation-specific spectroscopy and populations of diastereomers of a model

monolignol derivative: Chiral effects in a triol chain", J. Phys. Chem. A **115**, 8464-8478 (2011).
32. Jacob C. Dean, Polina Navotnaya, Alexander P. Parobek, Rachel M. Clayton, and Timothy S. Zwier, "Ultraviolet spectroscopy of fundamental Lignin sub-units: Guaiacol, 4-methylguaiacol, syringol, and 4-methylsyringol", **139**, 144313 (2013).
33. Jacob C. Dean, Patrick S. Walsh, Bidyut Biswas, P. V. Ramachandran, and Timothy S. Zwier, "Single-conformation UV and IR spectroscopy of model G-type lignin dilignols: the β-O-4 and β–β linkages", Chem. Sci., **5**, 1940 – 1955 (2014).
34. Jacob C. Dean, Nicole L. Burke, John R. Hopkins, James G. Redwine, P.V. Ramachandran, Scott A. McLuckey, and Timothy S. Zwier, "UV Photofragmentation and IR Spectroscopy of Cold, G-type β-O-4 and β–β Dilignol-Alkali Metal Complexes: Structure and Linkage-Dependent Photofragmentation", J. Phys. Chem. A **119,** 1917-32 (2015).
35. Natercia d.N. Rodrigues, Neil C. Cole-Filipiak, Karl N. Blodgett, Chamara Abeysekera, Timothy S. Zwier, and Vasilios G. Stavros, "Wavepacket insights into the photoprotection mechanism of the UV filter methyl anthranilate", Nature Comm. **9**, 5188 (2018).
36. Emily L. Holt, Konstantina M. Krokidi, Matthew A.P. Turner, Piyush Mishra, Timothy S. Zwier, Natercia d.N. Rodrigues, and Vasilios G. Stavros, "Insights into the Photoprotection mechanism of the UV filter Homosalate", Phys. Chem. Chem. Phys. **22**, 15509-15519 (2020).

F. Single-conformation infrared spectroscopy in the alkyl CH stretch region: Taming stretch-bend Fermi resonance

The alkyl CH stretch region of the infrared spectrum is potentially rich in information content regarding the isomeric structure of the alkyl chain; however, the closely-spaced absorptions and rampant Fermi resonance mixing between the CH stretch and bend overtones have seriously impeded progress in using these spectra for structural characterization. Working in collaboration with Ned Sibert at UW-Madison, we have provided single-conformation alkyl CH stretch infrared spectra of a series of jet-cooled molecules that could be used to test their model for anharmonic mixing. This has led to a powerful local-mode based theory that not only does a remarkable job of accounting for the detailed structure found in the alkyl CH stretch region, but also provides a means for their interpretation.

37. Evan G. Buchanan, Jacob C. Dean, Timothy S. Zwier, and Edwin L. Sibert III, "Towards a first-principles model of Fermi resonances in the alkyl CH stretch region: Application to 1,2-diphenylethane and 2,2,2-paracyclophane", J. Chem. Phys. **134**, 064308 (2013).
38. Evan G. Buchanan, Edwin L. Sibert III, and Timothy S. Zwier, Ground state Conformational Preferences and CH stretch-bend coupling in a model alkoxy chain: 1,2-diphenoxyethane", J. Phys. Chem. A **117**, 2800-2811 (2013).
39. Edwin L. Sibert III, Daniel P. Tabor, Nathanael M. Kidwell, Jacob C. Dean, and Timothy S. Zwier, "Fermi Resonance Effects in the Vibrational Spectroscopy of Methyl and Methoxy Groups", J. Phys. Chem. A **118**, 11272-81 (2014).
40. Daniel P. Tabor, Daniel M. Hewett, Sebastian Bocklitz, Joseph A. Korn, Anthony J. Tomaine, Arun K. Ghosh, Timothy S. Zwier, and Edwin L. Sibert III, "Anharmonic

modeling of the conformation-specific IR spectra of ethyl, n-propyl, and n-butylbenzene", J. Chem. Phys. **144**, 224310 (2016).
41. Daniel P. Tabor, Daniel M. Hewett, Sebastian Bocklitz, Joseph A. Korn, Anthony J. Tomaine, Arun K. Ghosh, Timothy S. Zwier, and Edwin L. Sibert III, "Anharmonic modeling of the conformation-specific IR spectra of ethyl, n-propyl, and n-butylbenzene", J. Chem. Phys. **144**, 224310 (2016).
42. Daniel M. Hewett, Sebastian Bocklitz, Daniel P. Tabor, Edwin L. Sibert III, Martin Suhm, and Timothy S. Zwier, "Identifying the First Folded Alkylbenzene via Ultraviolet, Infrared, and Raman Spectroscopy of Pentylbenzene through Decylbenzene", Chem. Sci. **8**, 5305-18 (2017).
43. Daniel M. Hewett, Daniel P. Tabor, Joshua L. Fischer, Edwin L. Sibert III, and Timothy S. Zwier, "Infrared-Enhanced Fluorescence-Gain Spectroscopy: Conformation-Specific Excited-State Infrared Spectra of Alkylbenzenes", J. Phys. Chem. Lett. **8**, 5296-5300 (2017).
44. Piyush Mishra, Daniel M. Hewett, and Timothy S. Zwier, "Conformational Explosion: Understanding the complexity of short chain *para*-dialkylbenzene potential energy surfaces", J. Chem. Phys. **148**, 184304 (2018).

G. Chirped-pulse Fourier Transform Microwave Spectroscopy

One of the more revolutionary developments in modern, gas-phase spectroscopy is the implementation of broadband methods of microwave spectroscopy built upon high-powered, chirped-pulse excitation. We have brought this technology into our laboratory and made improvements to it, most notably along two directions. First, we have developed a strong-field scheme for selectively modulating the signal due to a selective subset of microwave transitions due to a single component of a gas-phase mixture. We have applied this method of strong-field coherence breaking to provide sets of transitions that could be used to obtain preliminary fits to the spectra of conformational isomers, ^{13}C isotopologues, free radicals, and methyl rotor states. We have also pursued a deeper understanding of the physics behind such methods, which to this day is still not well understood. Second, we have built a time-of-flight mass spectrometer onto our microwave vacuum chamber, enabling a multiplexed approach in which microwave spectra and VUV photoionization mass spectra can be recorded as a function of pyrolysis temperature. This has enabled acquisition and identification of microwave transitions due to free radicals in the presence of exceedingly complex microwave spectra.

45. A.O. Hernandez, Chamara Abeysekera, Brian M. Hays, and Timothy S. Zwier, "Broadband Multi-resonant Strong Field Coherence Breaking as a Tool for Single Isomer Microwave Spectroscopy", J. Chem. Phys. **145**, 114203 (2016).
46. Alicia O. Hernandez-Castillo, Chamara Abeysekera, Brian M. Hays, Isabelle Kleiner, Ha Vinh Lam Nguyen, and Timothy S. Zwier, "Conformational Preferences and Internal Rotation of Methyl Butyrate by Microwave Spectroscopy", J. Mol. Spec. **337**, 51-58 (2017).
47. Sean M. Fritz, Brian M. Hays, Alicia O. Hernandez-Castillo, Chamara Abeysekera, and Timothy S. Zwier, "Multiplexed Characterization of Complex Gas Phase Mixtures combining Chirped-Pulse Fourier Transform Microwave Spectroscopy and VUV photoionization Time-of-Flight Mass Spectrometry", Rev. Sci. Instr. **89**, 093101 (2018).

48. Chamara Abeysekera, A.O. Hernandez-Castillo, John F. Stanton, and Timothy S. Zwier, Broadband Microwave Spectroscopy of 2-Furanyloxy Radical: Primary Pyrolysis Product of 2-Methoxyfuran, J. Phys. Chem. A **122**, 6879-85 (2018).
49. Alicia O. Hernandez-Castillo, Chamara Abeysekera, John F. Stanton, and Timothy S. Zwier, "Structural Characterization of Phenoxy Radical with Mass-Correlated Broadband Microwave Spectroscopy", J. Phys. Chem. Lett. **10**, 2919-23 (2019).
50. Sean M. Fritz, Piyush Mishra, and Timothy S. Zwier, "Strong Field Coherence Breaking as a Tool for Identifying Methyl Rotor States in Microwave Spectra: 2-Hexanone", J. Chem. Phys. **151**, 041104 (2019).
51. A.O. Hernandez-Castillo, C. Abeysekera, F. Robicheaux, and Timothy S. Zwier, "Propogating Molecular Rotational Coherences following Single-Frequency Pulse Excitation in the Strong-Field Regime", J. Chem. Phys. **151**, 084312 (2019).
52. Piyush Mishra, Sean M. Fritz, Brian M. Hays, Deepali N. Mehta-Hurt, Khadija M. Jawad, and Timothy S. Zwier, "Broadband Rotational Spectroscopy of *trans*-3-pentenenitrile and 4-pentenenitrile", Phys. Chem. Chem. Phys. **21**, 23651-62 (2019).
53. Sven Herbers, Sean M. Fritz, Piyush Mishra, H.V.L. Nguyen, and Timothy S. Zwier, "Local and Global Approaches to Treat the Torsional Barriers of 4-methylacetophenone using Microwave Spectroscopy", J. Chem. Phys. **152**, 074301 (2020).

III. Invited Lectures on topics related to DOE-supported research (2013-present, 240 total invited lectures prior to 2013)

1. Physical Chemistry Symposium on Reaction Dynamics, Spring 2013 National ACS meeting, New Orleans, LA.
2. RESOLV workshop on Solvation Science, Ruhr University, Bochum Germany, June 2013.
3. Dynamics of Molecular Collisions 2013, Lake Tahoe, CA, July 2013.
4. Telluride Summer Research Conference on Vibrational Dynamics, Telluride, CO, July 2013.
7. Chemistry Department Colloquium, University of Rochester, Rochester, NY, Oct. 2013.
8. Physical Chemistry Seminar, Ohio State University, Columbus, OH, Jan. 2014.
9. Chemistry Department Colloquium, Berea College, Berea, KY, Jan. 2014.
10. Chemistry Department Colloquium, Univ. Louisville, Louisville, KY, Jan. 2014.
11. Chemistry Department Colloquium, Calvin College, Grand Rapids, MI, Feb. 2014.
12. Chemistry Department Colloquium, Hope College, Holland, MI, Feb. 2014.
14. Atomic and Molecular Interactions Gordon Conference, Stonehill College, MA, July 2014.
16. Chemistry Department Colloquium, Oberlin College, Oberlin, OH, Oct. 2014.
17. Physical Chemistry Seminar, Wayne State University, Detroit, MI, Oct. 2014.
18. Chemistry Department Colloquium, Marquette University, Milwaukee, WI, Feb. 2015.
19. Physical Chemistry Seminar, University of Wisconsin-Madison, Madison, WI, March 2015.
20. Physical Chemistry Seminar, Seoul National University, Seoul, Korea, August 2015.
21. Chemistry Department Seminar, Yonsei University, Seoul, Korea, August 2015.
22. Keynote Speaker, Symposium on New aspects of Chemical Reaction Dynamics and Laser Spectroscopy, IUPAC 2015, Busan, Korea, August 2015.
24. Symposium on Reactive Intermediates in Combustion and Atmospheric Chemistry, Pacifichem 2015, Honolulu, Hawaii, Dec. 2015.
25. Spectroscopy and Dynamics Group Meeting, University of Warwick, Warwick, UK, Jan. 2016.

26. Department of Chemistry Colloquium, University of Arizona, Tucson, AZ, Feb. 2016.
27. Department of Chemistry Colloquium, University of Massachusetts-Amherst, Amherst, MA, Feb. 2016.
28. Symposium on "Decoding the Spectroscopic Signatures of Large-Amplitude Motions", Spring 2016 ACS Meeting, San Diego, CA, March 2016.
29. Symposium honoring Prof. Hiroshi Sekiya, "Recent Progress in Molecular Spectroscopy and Dynamics", Fukuoka, Japan, July 2016.
30. Gordon Conference on Vibrational Spectroscopy, University of New England, New Brunswick, Maine, July 2016.
31. High Resolution Molecular Spectroscopy Symposium (PRAHA 2016), Prague, Czech Republic, August 2016.
33. Chemistry and Physics Departmental Seminar, Indiana State University, Terre Haute, IN, March 2017.
34. International Conference on Advanced Vibrational Spectroscopy, Victoria, BC, June 2017.
37. JILA Visiting Fellow Seminar, JILA, University of Colorado, Boulder, CO, Sept. 2017.
38. Workshop on Spectroscopy and Dynamics,. Department of Chemistry, University of Copenhagen, Copenhagen, Denmark, October, 2017.
39. Workshop of the International Research Network on Quantitative Detection of Molecular and Radical Trace Species (QUADMARTS), University of Rennes, Rennes, France, October 2017.
40. Chemistry Departmental Colloquium, University of Pittsburgh, Pittsburgh, PA, November 2017.
41. Pacific Conference on Spectroscopy and Dynamics, San Diego, CA, January 2018.
42. Combustion Research Facility, Sandia National Laboratories, Feb. 2018.
43. Department of Chemistry, Univ. Hannover, Hannover, Germany, March 2018.
44. Molecular Physics Seminar, CFEL / DESY, Hamburg, Germany, March 2018.
46. ETH-Zurich Physical Chemistry Seminar, Zurich, Switzerland, April 2018.
47. Molecular Physics Seminar, Fritz Haber Institute, Max Planck, Berlin, Germany, April 2018.
48. 2018 Gas Phase Chemical Physics DOE Contractors' Meeting, Washington, DC, May 2018.
49. Telluride Workshop on the Spectroscopy and Dynamics on Multiple Potential Energy Surfaces, Telluride, CO, July 2018.
50. Department of Chemistry, University of Texas-Austin, Austin, TX, Nov. 2018.
51. Department of Chemistry, Baylor University, Waco, TX, Nov. 2018.
52. QUADMARTS Workshop, California Institute of Technology, Pasadena, CA, Nov. 2018.
53. Gas Phase Chemical Dynamics Group, Argonne National Laboratory, Jan. 2019.
54. Combustion Research Facility, Sandia National Laboratory, Feb. 2019.
55. Spring 2019 ACS National Meeting, Computers in Chemistry Symposium, Orlando, FL, April 2019.
56. Chemistry Dept. Seminar, Wabash College, Crawfordsville, IN, April 2019.
57. QUADMARTS Workshop, Univ. Lorraine, Nancy, France, May 2019.

IV. Students and Post-docs Supported in Full or Part by DE-FG02-96ER14656

Graduate Students: (20)
Christopher Ramos, Allison D. Robinson, Nathan R. Pillsbury, Jaime A. Stearns, Talitha M. Selby, Chirantha P. Rodrigo, Evan G. Buchanan, Nathanael M. Kidwell, Joshua A. Sebree, Joseph A. Korn, William H. James III, Jacob C. Dean, Patrick S. Walsh, Nicole L. Burke, Karl N. Blodgett, Piyush Mishra, Daniel M. Hewett, Joshua L. Fischer, Alicia O. Hernandez-Castillo, Sean M. Fritz

Post-doctoral Research Associates: (7)
Caleb Arrington, Paul R. Winter, Aloke Das, Christian W. Muller, Chamara Abeysekera, Brian M. Hays, Sven Herbers

V. Research Summary

The DOE Gas Phase Chemical Physics program has supported this single-investigator academic research program for over two decades. It has provided support 20 graduate students and 7 post-doctoral research associates, who have now taken up positions of scientific leadership in academia, federal laboratories, and high-tech industry. All twenty of the graduate students received Ph.D. degrees based on their work.

I have now transitioned to a position on the scientific staff of the Gas Phase Chemical Physics program at Sandia National Laboratories in Livermore, California. As such, I am supported in large measure by the same program at DOE BES as I work collaboratively with the excellent scientists and technical staff there. Much of the instrumentation that was used for the work summarized here has been set up at the CRF and is being improved to better position its use in that program. We are heading in new and interesting directions, and look forward to contributing significantly to the DOE BES GPCP program in the years ahead.