Annual Report for Period: 08/2007 - 07/2008
Submitted on: 07/31/2008
Principal Investigator: Drucker, Stephen .
Award ID: 0420928
Organization: U of Wisconsin Eau Claire
Submitted By:
Drucker, Stephen - Principal Investigator
Title:
MRI: Acquisition of a Transportable Pulsed Laser System to Enhance Undergraduate Research Programs

Project Participants

Senior Personnel

Name: Drucker, Stephen
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Muyskens, Mark
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Polik, William
Worked for more than 160 Hours: No
Contribution to Project:

Name: Zwier, Timothy
Worked for more than 160 Hours: No
Contribution to Project:

Name: Muyskens, Karen
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Bartz, Jeffrey
Worked for more than 160 Hours: Yes
Contribution to Project:
Dr. Bartz used the Nd:YAG-pumped dye laser system in his research laboratory at Kalamazoo College for chemical dynamics experiments.

Post-doc

Graduate Student

Undergraduate Student

Name: Hoffelt, Laura
Worked for more than 160 Hours: Yes
Contribution to Project:
As an undergraduate student, Laura Hoffelt conducted collaborative research with PI Stephen Drucker. Laura used the MRI-funded laser equipment in Drucker's lab during the period November 2005-August 2006.

Name: Springer, Mitchell
Worked for more than 160 Hours: Yes

Contribution to Project:

As an undergraduate student, Mitchell Springer conducted collaborative research with PI Stephen Drucker. Mitchell used the MRI-funded laser equipment in Drucker's lab during the period November 2005-August 2006.

Name: Heslinga, Michael

Worked for more than 160 Hours: Yes

Contribution to Project:

As an undergraduate student, Michael Heslinga conducted collaborative research with PIs Karen and Mark Muyskens. Michael used the MRI-funded laser equipment in the Muyskens lab during summer 2005.

Name: Newcomb, Eric

Worked for more than 160 Hours: No

Contribution to Project:

Name: Kieda, Ryan

Worked for more than 160 Hours: Yes

Contribution to Project:

Ryan Kieda undertook an undergraduate research project on the photodissociation of Co(CO)3NO in a velocity-mapping time-of-flight mass spectrometer.

Name: Alsum, Joel

Worked for more than 160 Hours: Yes

Contribution to Project:

As an undergraduate student, Mr. Alsum conducted research collaboratively with Profs. Mark and Karen Muyskens at Calvin College.

Name: Breck, Kelsey

Worked for more than 160 Hours: Yes

Contribution to Project:

Kelsey Breck undertook an undergraduate research project on the photodissociation of methyl nitrite at 335 nm.

Name: Peden, Amber

Worked for more than 160 Hours: Yes

Contribution to Project:

Amber Peden undertook an undergraduate research project on the photodissociation of CpNiNO near 225 nm.

Technician, Programmer

Name: Hedderich, Hartmut

Worked for more than 160 Hours: Yes

Contribution to Project:

Dr. Hedderich is the manager of the Purdue Laser Facility and provides technical support for the maintenance and transportation of the laser system acquired via the MRI grant.

Other Participant

Research Experience for Undergraduates

Organizational Partners

Other Collaborators or Contacts

Prof. Jaebum Choo (Hanyang University, Korea) collaborated with PI Stephen Drucker in the analysis of spectroscopic data. The data set consisted of the phosphorescence excitation spectrum of the 4H-pyran-1-one. The spectrum was recorded using the MRI-funded laser system. It included a portion of the the T1 <-- S0 (singlet-triplet) vibronic band system. Prof. Choo used density functional theory to calculate fundamental vibrational frequencies in the excited state. These predictions were used to guide the assignment of vibronic bands.

Prof. Richard Judge (University of Wisconsin-Parkside) also collaborated with PI Stephen Drucker in the analysis of the 4H-pyran-1-one data. This data set motivated Prof. Judge to enhance the capabilities of a program previously written for simulating band contours of singlet-triplet electronic absorption spectra. The enhanced program enabled PI Drucker and his students to confirm the assignment of the T1 <-- S0 origin band.

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)
See attached file.

Findings: (See PDF version submitted by PI at the end of the report)
See attached file.

Training and Development:
Grant Year 1:

Calvin College undergraduate Michael Heslinga had the opportunity to do research using the laser system as part of a 10-week, full-time, summer undergraduate research project with K. Muyskens and M. Muyskens (co-PI's) in the summer of 2005. Michael was involved with the installation and testing of the laser system as well as using the laser in the research described above. He gained considerable experience in using lasers and made significant contributions to the research project. Michael is currently a senior at Calvin majoring in chemical engineering and physics. He has been accepted to several graduate programs in chemical engineering and will be starting graduate school in the fall of 2006 at the University of Michigan.

Grant Year 2:

Two undergraduate students, Mitch Springer and Laura Hoffelt, conducted research using the new laser system installed in PI S. Drucker's laboratory. As a result of the projects made possible with the new laser, both of the students received extensive training in laser technology, electronics, optics, computer programming, and chemical synthesis. Each of these students has become proficient in recording and analyzing spectroscopic data, and in designing and troubleshooting experimental protocols for obtaining such data.

Both of the students received B.S. degrees in May 2007 and are bound for postgraduate study. In fall 2007, Mitch will enter a Ph.D. program in genetics at the University of Pittsburgh. Laura will attend medical school at Michigan State.

Grant Year 3:

Calvin College undergraduate Joel Alsum handled all aspects of the experimental research in the Muyskens' lab: sample preparation, gas handling on vacuum manifold, laser operation to carry out photochemical reaction, sample analysis using ultraviolet and infrared spectroscopy, data analysis, technique development. He received training in all of these areas, and he received training in chemical safety.

Kalamazoo College sophomore undergraduate Eric Newcomb was involved in the set-up and operation of the Nd:YAG-pumped dye laser system. In the course of assisting in the laboratory, he learned about lasers, optics, and vacuum. Eric will be applying to graduate school for organic chemistry in Fall 2008 and will earn his bachelor's degree in Chemistry in June 2009.

Grant Year 4:
Kalamazoo College senior undergraduate Ryan Kieda was involved in an undergraduate research project on the photodissociation of $Co(CO)_3NO$ near 225 nm that will be the basis of his senior thesis. Ryan operated all of the lasers and instrumentation in the laboratory. Ryan will graduate with a bachelor's degree in Chemistry in June 2009. He plans to apply to graduate school in chemistry.

Kalamazoo College junior undergraduate Kelsey Breck was involved in an undergraduate research project on the photodissociation of CH_3ONO at 355 nm. Kelsey operated all of the instrumentation in the laboratory and synthesized her molecule based on literature methods.

She will graduate in 2010 and is currently interested in pursuing graduate school in molecular and cellular biology.

Kalamazoo College sophomore undergraduate Amber Peden was involved in an undergraduate research project on the photodissociation of CpNiNO near 225 nm. Amber operated all of the instruments in the laboratory and synthesized her compound based on literature methods. She will graduate in 2011 and is currently considering medical school.

Outreach Activities:

Grant Year 1:

The Calvin College Science Division hosted a visit of about 200 students from Central High School in Grand Rapids, Michigan on September 21, 2006. This high school serves primarily inner-city youth. As part of the Chemistry Department tour, we demonstrated the power of the Nd:YAG laser and tuneability of the dye laser to small groups that visited our laser lab. Students are surprised at the power and intrigued by being able to change the wavelength. The coumarin dye we use for our experiments dramatically shows a color change from green to blue. The Chemistry Department involved most of our faculty and students to engage our visitors, make the tour interesting, and encourage them to consider science in their career planning.

Journal Publications

Laura M. Hoffelt, Mitchell G. Springer, and Stephen Drucker, "Phosphorescence excitation spectrum of the T1 - S0 transition of 4H-pyran-4-one", The Journal of Chemical Physics, p. 104312, vol. 128, (2008). Published, 10.1063/1.2834922

Books or Other One-time Publications

Mark Muyskens, Karen Muyskens, Matthew Schmitz, Michael J. Heslinga, "Ultraviolet-laser photodissociation of trifluoroacetylacetone using HF-chemical laser IR detection", (2006). Conference Proceeding, Published
Bibliography: Poster presented at the 231st ACS National Meeting

Michael J. Heslinga, "Laser photochemistry: Creation of hydrogen fluoride from fluorine-containing organic molecules", (2006). Conference Proceeding, Published
Bibliography: Presentation at the Calvin College Science Division Summer Research Poster Session

Laura M. Hoffelt
Mitchell G. Springer
Stephen Drucker, "Triplet Excited States of Cyclic Enones Characterized by Vibronically Resolved Spectroscopy", (2007). conference proceeding, Published
Bibliography: Proceedings of the 233rd National Meeting of the Americal Chemical Society

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

Grant Year 1:

The photoelimination studies of M. and K. Muyskens contribute to the general field of photochemistry by increasing the understanding of how the presence of fluorine atoms in molecules influences the photochemistry. The Muyskens' specific work on TFAA gives more information on the photochemistry of a molecule that has until recently received little attention.

Grant Year 2:

Triplet excited states often play a central role in molecular photochemistry. The T_1 or T_2 excitation energy, as well as the shape of the triplet potential surfaces, can strongly influence product formation. In such cases, characterization of the lowest-energy triplet surfaces is an important step toward understanding or predicting photochemical outcomes.

S. Drucker and student collaborators are characterizing triplet excited states through vibronicallly resolved spectroscopy. The spectra provide a rigorous test of computed potential surfaces, via comparison of experimental vs. calculated vibrational frequencies, electronic excitation energies, and geometry changes associated with electronic excitation. Comparisons with experiment are critical for refining the computational methods used to treat excited states.

Beyond the testing of computational results, Drucker's experimental work probes the intrinsic differences between singlet and triplet excited-state species, and offers insights about the unique roles that the triplet species can play in photochemical processes.

Historically it has been possible to obtain spectroscopic data routinely for singlet excited states, but the experimental database for triplet states is far less well developed. This is essentially because singlet-triplet transitions originating from the ground state are nominally spin-forbidden. To meet this challenge, Drucker has employed the highly sensitive cavity ringdown (CRD) spectroscopic technique in prior studies. The new MRI-funded laser system has enabled Drucker to add phosphorescence excitation (PE) spectroscopy to his experimental repertoire.

Drucker's group has used the PE technique to record the first spectrum of the T1 <-- S0 band system in the 4H-pyran-4-one molecule.

Grant Years 3 & 4:
Senior personnel J. Bartz's group studies the photodissociation of volatile metal nitrosyls. Specifically, the vector correlations between and among the transition dipole, ý, velocity, v, and angular momentum, J, in the NO product reveal information on the potential energy surfaces involved in NO production.

Bartz's group has recently completed a study on the gas-phase photodissociation of cyclopentadienyl nickel nitrosyl, .eta.5-(C5H5)NiNO, a pseudo-linear molecule, in an ion imaging time-of-flight mass spectrometer. They have shown that excitation of .eta.5-(C5H5)NiNO at 450 and 280 nm, in the gas phase, produces isotropic NO velocity distributions. Photodissociation near 225 nm, however, yields two NO speed distributions, an isotropic one with a maximum at zero and a second, anisotropic, distribution with an average speed around 1300 m/s.

The MRI-funded laser system added a second tunable laser in the range of 224-227 nm and allowed more a detailed investigation of the 225-nm photodissociation of .eta.5-(C5H5)NiNO. With the MRI-funded laser, Bartz's group has found that the aniosotropic speed distribution of the NO product, with an average speed of 1200 m/s, has strong u-v, v-J, and u-v-J correlations. The high correlation in v-J and u-v-J reveals that the Ni-NO bond must dissociate through a bent configuration as is predicted by electronic structure calculations. The experimental method has been extended to the study of Co(CO)3NO, a molecule with a linear metal-NO bond.

Further studies have probed the 355 nm photodissociation of methyl nitrite, CH3ONO, a molecule with a bent CH3O - NO bond. Initial experiments find a smaller translational energy release than previously reported.

Contributions to Other Disciplines:

Contributions to Human Resource Development:

Grant Year 1:

Through his summer undergraduate research experience in the Muyskens' laboratory, Michael Heslinga received an excellent exposure to the rigors of research, including the underlying tasks of technical instrumentation: installation, programming, operation and repair. He is seeking to further develop his skills in research through an advanced degree in chemical engineering; Michael will be starting a Ph.D. program in Chemical Engineering at the University of Michigan in the fall of 2006.

Grant Year 2:

The project has enabled two undergraduate students, Laura Hoffelt and Mitch Springer, to conduct research collaboratively in Drucker's group. These two students received B.S. degrees in May 2007 and then pursued postgraduate studies -- one in an M.D. program and the other in a genetics Ph.D. program. Their admission applications to these programs were strengthened significantly by their participation in the

MRI-supported research.

Grant Year 3:
The project has enabled one undergraduate, Eric Newcomb, to learn about physical chemistry research. Eric will be applying to graduate school for a Ph.D. in organic chemistry and will graduate with a B.A. in Chemistry in June 2009.

Grant Year 4:
The project has enabled one undergraduate, junior Ryan Kieda, to participate in physical chemistry research. Ryan has continued his work in Summer 2008 and was joined by two other undergraduate students, sophomore Kelsey Breck and freshman Amber Peden. All three undergraduates performed full-time research in Summmer 2008.

Contributions to Resources for Research and Education:

Grant Year 1:

This grant tests a model for collaborative equipment sharing among primarily undergraduate institutions (PUIs) û particularly with expensive equipment that is not normally viewed as being easily shared. We have already successfully transported the entire laser system from Michigan to Wisconsin, and had the system up and running with only about two weeks' down time for transport.

That the laser system will be used well during the prime summer research period is not in question. But well beyond the time constraints of summer research, we are showing very efficient use of the laser system during the academic year, when the PUI faculty members typically have heavy teaching schedules. For 2005-06 we arranged for the system to reside at UW-Eau Claire, where PI Stephen Drucker is on sabbatical and freed from all formal teaching responsibilities. In the spring semester of 2007, the system will return to Calvin College, where co-PIs Karen and Mark Muyskens have gained teaching time release through an internal fellowship program.

An innovation in the grant project is the involvement of resources from Purdue, a research university, to support the PUIs in the project. Dr. Hartmut Hedderich, manager of the Purdue Laser facility, has been extremely helpful as an advisor and information resource in the process of procuring and installing the laser system.

Grant Year 2:

The present grant, in supporting collaborative research with scientists at Purdue University, has enabled PI S. Drucker to identify new spectroscopic approaches (for example, jet-cooled phosphorescence excitation) that can be imported to his own laboratory in Eau Claire. With proof of concept in hand, Drucker was able to propose the new approaches as part of his application to the Camille and Henry Dreyfus Foundation for a Henry Dreyfus Teacher-Scholar award. These awards are made annually to support research and teaching at primarily undergraduate institutions. The application was successful and resulted in a $60,000 award made to UW-Eau Claire in October 2006.

The Henry Dreyfus Teacher-Scholar award will certainly improve the instrumentation infrastructure in Drucker's research lab, but is also enhancing institutional resources for instruction. A $5000 allotment from the award was matched 3:1 by UW-Eau Claire, and has allowed Drucker to acquire $20,000 worth of instrumentation that will be put to dedicated use in the senior-level physical analysis laboratory course at UW-Eau Claire.

Grant Year 3:
As in many scientific disciplines, the laboratory portion of an undergraduate physical chemistry course is often years or even decades away from being state of the art. With the Nd:YAG system supported by this MRI award, senior personnel Jeff Bartz set up a simple two-laser experiment in his Physical Chemistry II class at Kalamazoo College. Students saw how the polarization of the excitation laser affected the velocity distribution of NO from the 355-nm photodissociation of NO2 in an ion imaging mass spectrometer. Further, they saw how the polarization of the probe beam, from a Nd:YAG-pumped dye laser, affected the intensity of the signal--revealing a strongly aligned NO photoproduct.

Contributions Beyond Science and Engineering:

Grant year 1:

The tuneable laser system was demonstrated to inner-city youth from Central High School in Grand Rapids, Mich. It is hoped that this demonstration will inspire the students to go to college and perhaps even find a career in science.

Special Requirements

Special reporting requirements: None

Change in Objectives or Scope: None

Animal, Human Subjects, Biohazards: None

Categories for which nothing is reported:

Organizational Partners

Any Web/Internet Site

Any Product

Contributions: To Any Other Disciplines

Research Findings under Award CHE-0420928

Grant Year 1: August 2004-July 2005

Calvin College: Trifluoroacetic acid (TFAA) photolysis. The data show significantly decreasing signal (HF formation) with increasing pressure, following 266-nm excitation. Figure 1(a) shows the experimental signals, and Figure 1(b) shows the signal amplitude as a function of pressure. The key result is that the signal is reduced to one half of its largest amplitude at around 400 mTorr. This is a lower pressure than what is observed for the higher energy 248-nm photolysis, suggesting that it is easier to collisionally deactivate the energized TFAA molecule when it has less total energy. This represents an interesting preliminary result that warrants further investigation to determine the quenching pressure as a function of excitation wavelength. An additional experimental result from the summer clearly demonstrated the linear 266-nm power dependence of our experimental signal.

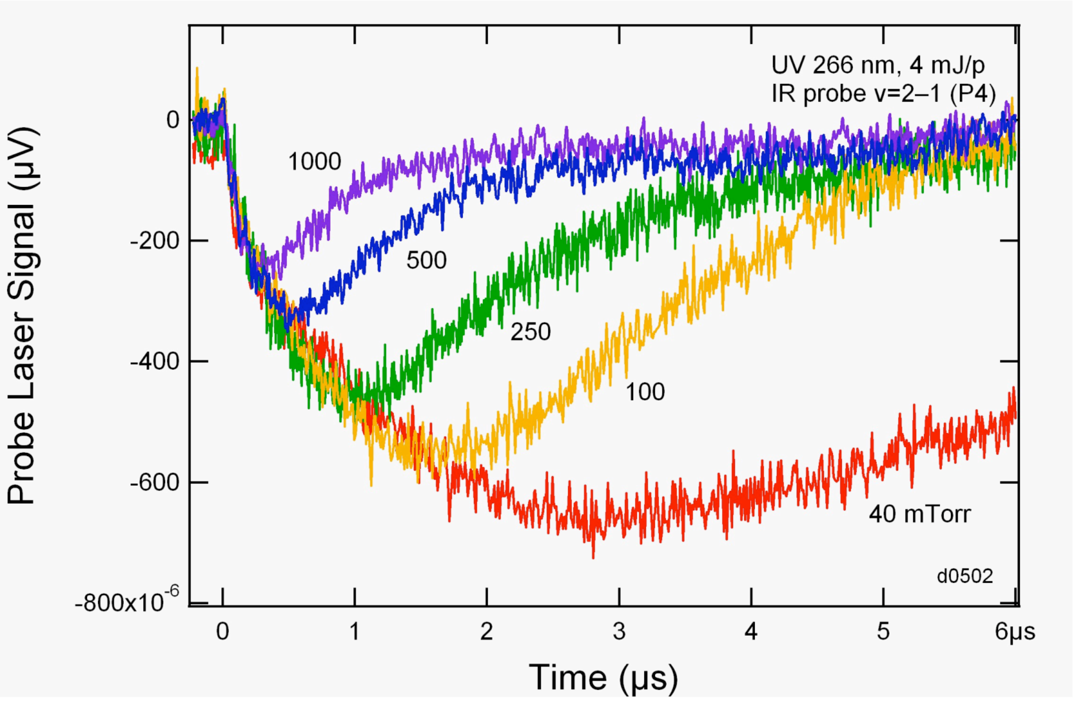

Figure 1(a)

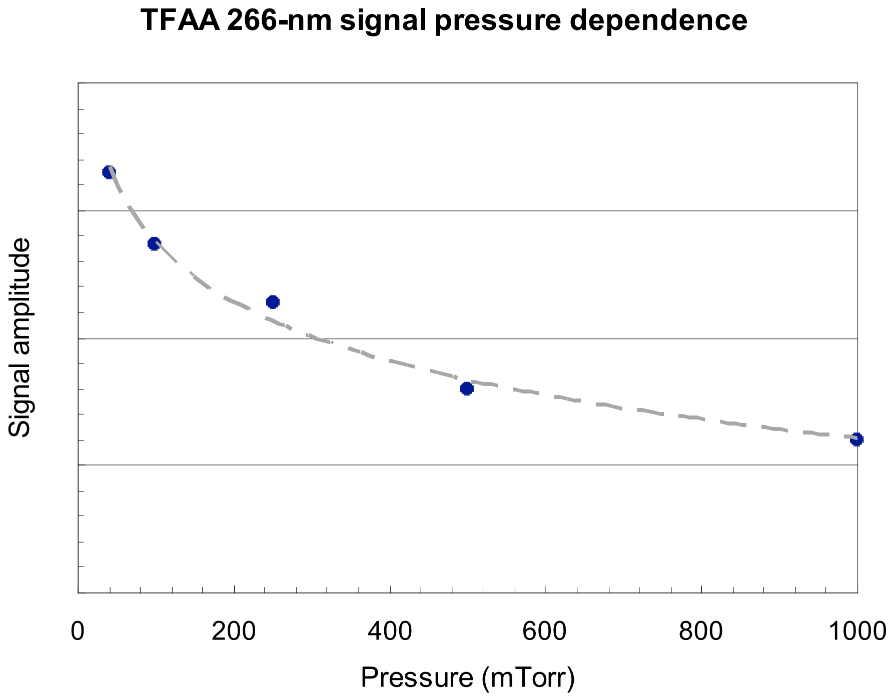

Figure 1(b)

Grant Year 2: August 2005-July 2006

UW-Eau Claire: Phosphorescence excitation spectroscopy of 4*H*-Pyran-4-one (4PN).

We have used phosphorescence excitation at 50 °C to record the first $T_1(n,\pi^*) \leftarrow S_0$ spectrum of 4PN. The spectrum is shown in Figure 2. The most prominent feature is the origin band. Attached to it are $\Delta v=0$ sequences involving the lowest-frequency (ring torsion) modes, ν_{18} and ν_{13}.

Transitions of the type Δv =odd are not observed in the low-frequency region of the $T_1 \leftarrow S_0$ spectrum. The low-frequency out-of-plane modes have a_2 or b_1 symmetry (C_{2v} point group), so that their Δv=odd transitions in the PE spectrum have a vanishing vibrational overlap integral. The origin band and other Δv =even transitions are observed with relatively high intensity in the $T_1 \leftarrow S_0$ spectrum, in contrast to the $S_1 \leftarrow S_0$ spectrum that was reported by Gordon and Park[1] in 1993. An origin band was not observed in the latter, indicative of an orbitally forbidden ${}^1A_2(n,\pi^*) \leftarrow {}^1A_1$ transition. For the present triplet band system, the ${}^3A_2(n,\pi^*) \leftarrow {}^1A_1$ transition evidently borrows oscillator strength from an orbitally allowed $\pi^* \leftarrow \pi$ transition.

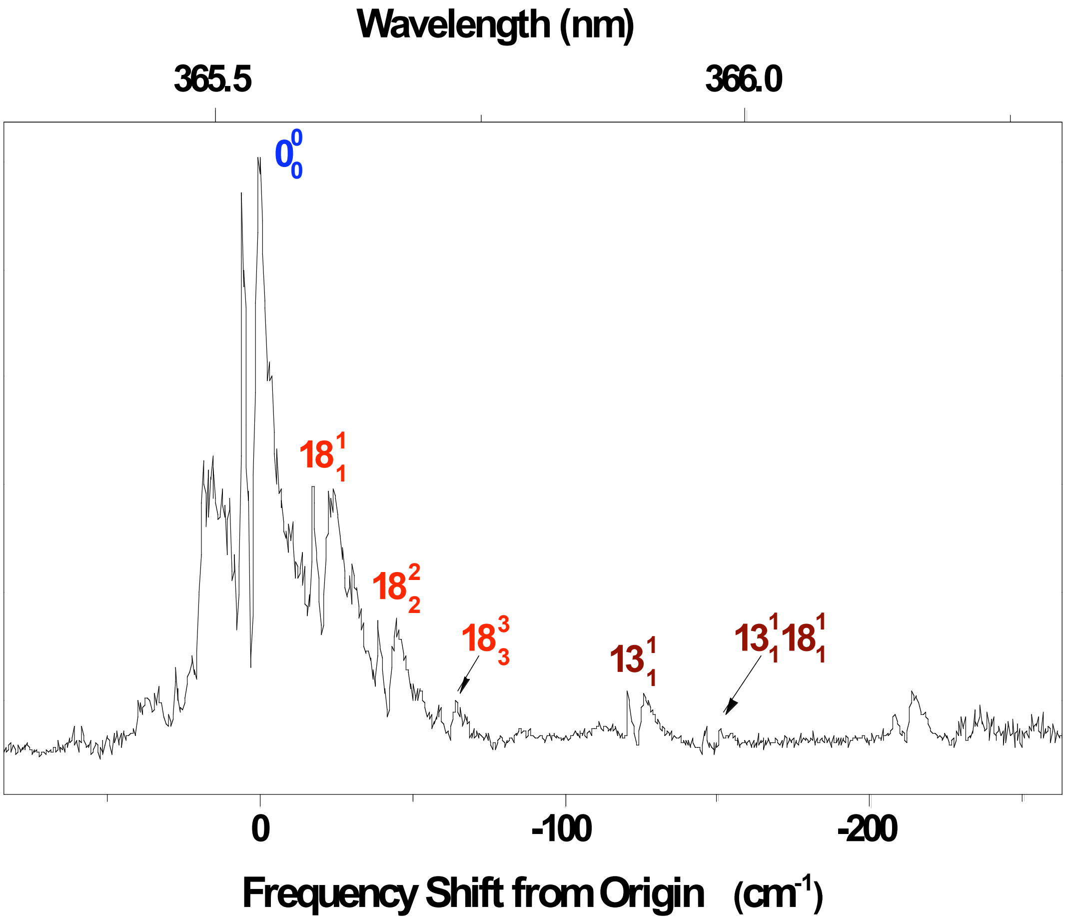

Figure 2: Phosphorescence excitation spectrum of 4PN recorded in a static sample cell at 50 °C. Assignments are indicated for symmetry-allowed hot bands within the $T_1(n,\pi^*) \leftarrow S_0$ system.

A significant finding is that the ν_{18} fundamental frequency drops from 145 cm^{-1} in the S_1 state to 122 cm^{-1} in the T_1 state. This suggests that the $\pi^* \leftarrow n$ chromophore is more delocalized to include the ring atoms in the case of triplet compared to singlet excitation. We reached the same conclusion in analyzing the $T_1 \leftarrow S_0$ spectrum of 2-cyclopenent-1-one (2CP).[2] We found that the $T_1(n,\pi^*)$ state of 2CP has a slightly bent equilibrium geometry, in contrast to the planar structures of the ground and $S_1(n,\pi^*)$ states; this indicates a more severe disruption of conjugation in the triplet, compared to the singlet $\pi^* \leftarrow n$ excited state of 2CP. With this observation for both the 2CP and 4PN molecules in mind, we are analyzing the singlet-singlet and singlet triplet spectra of 2-cyclohexen-1-one. (We recorded these spectra previously via CRD spectroscopy.) We are investigating whether the more extensive ring delocalization observed for the triplet states of 2CP and 4PN is a general property of cyclic enones.

The 4PN spectrum in Figure 2 was presented at the National ACS meeting in March 2007. A manuscript on this work, to be submitted to the *Journal of Chemical Physics*, is in preparation.

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1 Gordon, R. D.; Park, W. K. C. *Can. J. Chem.* **1993**, *71*, 1672.
2 Pillsbury, N. R.; Choo, J.; Laane, J.; Drucker, S. *J. Phys. Chem. A* **2003**, *107*, 10648.

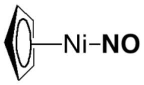
Grant Years 3&4: August 2006-May 2008

Kalamazoo College: Photodissociation of Organometallic Nitrosyls and Vector Correlations in the Products

Jeffrey Bartz used the Nd:YAG-pumped dye laser from this award to sort out some chemical dynamics that his laboratory could not do with its instrumentation alone. Bartz's group studies the photodissociation of organometallic nitrosyls and NO-containing aromatics. In the photochemistry of η^5-CpNiNO (**I**) excitation by visible or near-UV light, in a metal-to-nitrosyl CT region, creates a long-lived charge transfer state that lowers the NO stretching frequency significantly and causes the Ni-NO bond to bend. Using one Nd:YAG and two dye lasers in Bartz's lab, his students have shown that the photodissociation of **I** at 450 and 280 nm produces isotropic NO velocity distributions. However, photodissociation near 225 nm populates a doubly degenerate state and yields two NO speed distributions, an isotropic one with a maximum at zero and a second, anisotropic, distribution with an average speed around 1300 m/s. (Figure 3) The anisotropic velocity distribution has a high correlation between the NO velocity (**v**) and the transition dipole (**μ**). The traditional measure of **μ**-**v** correlation, ß is greater than 1.9 (range -0.5 to 2.0), indicating a vertical transition with a lifetime of less than 800 fs.

In the 225 nm experiment with Bartz's laser system, the frequency-doubled dye laser output (225 nm light) does both the photodissociation of the parent molecule and the probe of the NO photoproduct. To reveal more subtle aspects of nascent NO product, a second Nd:YAG-pumped dye laser was needed. The NSF-funded laser system arrived at Kalamazoo in December 2007. By January 2008, Bartz and his students were able to independently control the linear polarizations of the dissociation and probe lasers. They have found that the NO photoproduct has strong correlations between velocity (**v**) and angular momentum (**J**) and among **μ**-**v**-**J**. In Figure 3, the intensity (yellow color) of the high-speed NO products with a horizontally-polarized probe beam shows alignment of that the angular momentum of NO products in the laboratory frame with **v** perpendicular to **J**. Simply, after 225-nm photodissociation of **I** with vertially-polarized light, the NO products are flying like Frisbees up and down in the laboratory frame.

Bartz and co-workers are preparing a manuscript based on these results as they continue to study the photodissociation of **I**. Open questions include the vector correlation in NO products in the v"=1 state. A second open question is whether the speed distribution of the NO products depends on the rotational state.



I

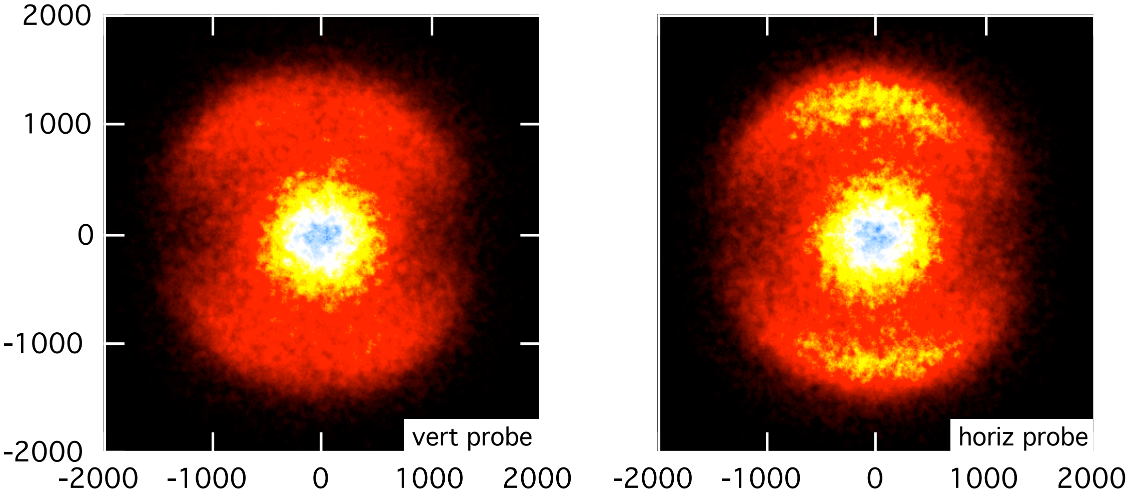


Figure 3. Ion images of the NO [Q_{22}(35.5)] photoproduct from the photodissociation of η^5-CpNiNO at 225 nm. The 225 nm dissociation beam was vertically polarized in the laboratory frame. The fact that the fast distribution only appears on the top and the bottom of the image indicates that the molecule falls apart fast relative to the rotational period of the molecule. The probe polarization is as indicated. The higher intensity of the fast distribution with a horizontal probe indicates that the NO rotation is aligned in the lab frame with $\mathbf{v} \perp \mathbf{J}$ in a Frisbee-like orientation.

Grant Year 4: May 2008 – July 2008

Kalamazoo College: Photodissociation of NO-Containing Molecules and Vector Correlations in the Products

Jeffrey Bartz used the Nd:YAG-pumped dye laser from this award to continue photodissociation experiments. Bartz's group studies the photodissociation of organometallic nitrosyls and NO-containing molecules.

Velocity Distributions in the Photodissociation of η^5-CpNiNO

In the 225-nm photodissociation of η^5-CpNiNO, Bartz and co-workers found that at higher NO rotational quantum numbers, the velocity distribution has a fast component not seen at lower J" levels. Figure 3 shows the velocity distribution of NO in the J"=33.5 state. Figure 4 is for a similar experiment that probed the J"=46.5 state. A significant difference between the two images is that the NO products have a higher velocity in Figure 4, where a higher J" state of NO was probed. The NO product with higher translational energies only occurs above a threshold J" that is currently under investigation. What the results may reveal is a curve crossing to a dissociation surface that results in less energy remaining in the CpNi fragment. The internal motion that aids the curve crossing is bending the Ni-NO bond, resulting in some NO products exiting with more translational energy and a higher rotational energy.

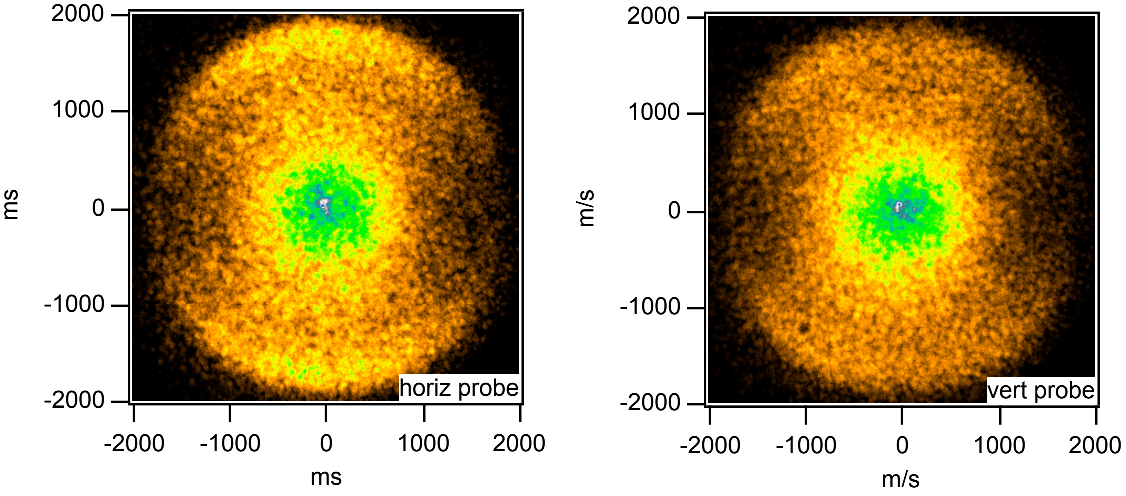


Figure 4. Ion images of the NO [$Q_{22}(46.5)$] photoproduct from the photodissociation of η^5-CpNiNO at 225 nm. The 225 nm dissociation beam was vertically polarized in the laboratory frame.

Vector Correlations in the Photodissociation of Methyl Nitrite, CH_3ONO

Methyl nitrite, CH_3ONO, is a molecule with a bent CH_3O – NO bond. Bartz and co-workers have studied the photodissociation of CH_3ONO at 355 nm to study the vector correlation (transition dipole, velocity, and/or angular momentum) in the NO photoproduct. Because the molecule has roughly a 120° CH_3O – NO bond, breaking that bond should result in a Frisbee-like motion, which they have found in the laboratory. They have measured the **μ-v** (transition dipole – velocity) correlation in the NO product. The traditional measure of this correlation is the anisotropy parameter, β, according to equation 1,

$$I(\theta) \propto \frac{1}{4\pi}\left[1+\beta P_2(\cos\theta)\right] \qquad (1)$$

where I(θ) is the angular distribution of the photoproducts and P_2 is the second Legendre polynomial, $(3x^2/2 - 1/2)$. The anisotropy parameter, β, has values from +2 when $\mathbf{\mu} \parallel \mathbf{v}$ to -1 when $\mathbf{\mu} \perp \mathbf{v}$. Bartz and co-workers have measured β as -0.62 (Figure 5), indicating that the electronic transition at 355 nm is perpendicular to the CH_3O – NO bond. Further experiments will determine the magnitude of the **v-J** correlation and how the rotational energy of the NO product affects the translational energy release.

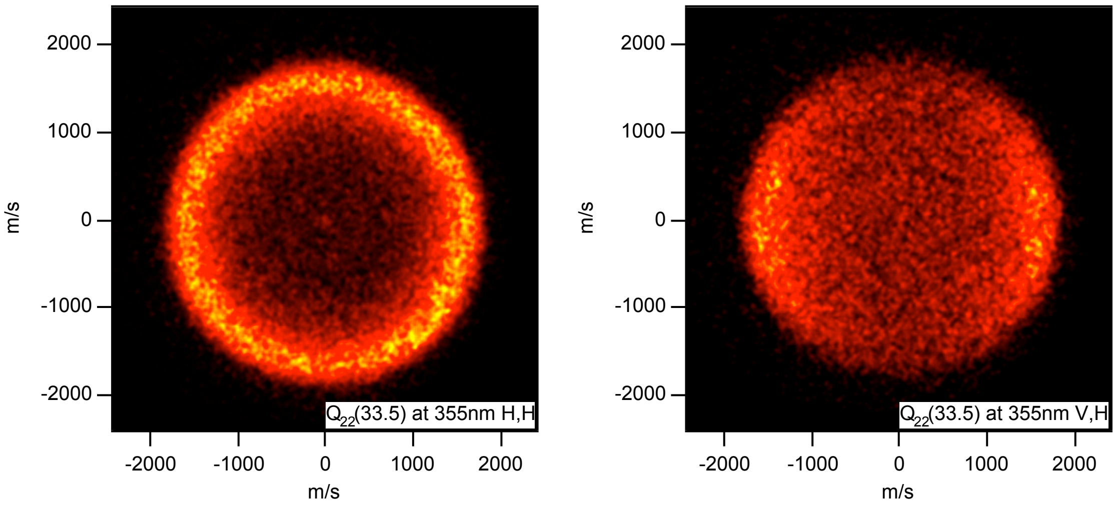


Figure 5. Ion images of the NO [Q_{22}(335.5)] photoproduct from the photodissociation of CH_3ONO at 355 nm. The 355 nm dissociation beam was horizontally polarized in the left image and vertically polarized in the right image. The 225 nm probe beam was horizontally polarized in the laboratory frame in both images. The measured anisotropy parameter, β, was -0.62 in these experiments.

Vector Correlations in the Photodissociation of $Co(CO)_3NO$

There are both electronic structure calculations and spectroscopic evidence that electronically-excited $Co(CO)_3NO$ undergoes a Jahn-Teller distortion, bending the Co-NO bond. Bartz and co-workers have phoodissociated $Co(CO)_3NO$ at 225 nm to look for dynamical evidence that the $Co(CO)_3NO$ dissociates through a bent excited state. The ground state of $Co(CO)_3NO$ has a linear Co-NO bond. The process of bending and breaking the Co-NO bond should result in a Frisbee-like motion in the NO, with $\mathbf{v} \perp \mathbf{J}$.

Figure 6 shows two ion images of the velocity distributions of NO from the 225-nm photodissociation of $Co(CO)_3NO$. Two things are evident in the images. First, the NO product with a speed peaked around 1600 m/s is aligned in the laboratory frame. The dissociation is prompt relative to the rotational period of the molecule. Second, the intensity differences in the same 1600 m/s NO product upon changing the probe polarization indicates that the NO shows Frisbee-like **v-J** correlation. Experiments to further investigate the vector correlations are ongoing.

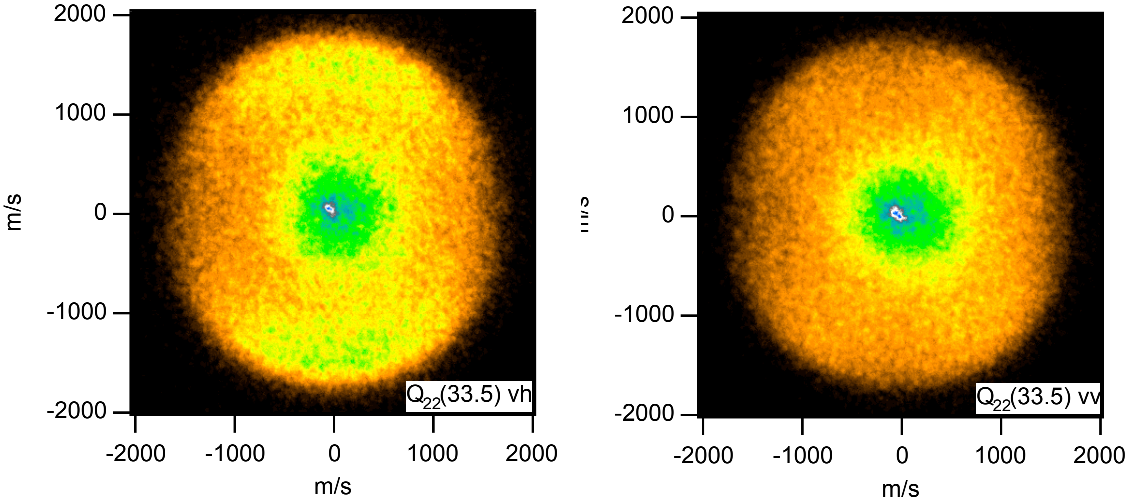


Figure 6. Ion images of the NO [Q_{22}(33.5)] photoproduct from the photodissociation of $Co(CO)_3NO$ at 225 nm. The 225 nm dissociation beam was vertically polarized in the laboratory frame. The probe beam is in horizontally polarized in the left image and vertically polarized in the right image. Differences in intensity at ±1600 m/s indicate that the NO products are aligned in the laboratory frame, with $\mathbf{v} \perp \mathbf{J}$.

Research Activities under Award CHE-0420928

Grant Year 1: August 2004-July 2005

Formulation of a Shared Usage Plan. As was emphasized in the original proposal, this grant represents a unique model for improving the research infrastructure at undergraduate institutions. At the core of this project is the opportunity for researchers to have access to state-of-the art instrumentation periodically *at their home institutions*. Thus it was important for us to formulate a reliable plan for logistics and shared usage of the laser system. We took an appropriate amount of time and care to develop this plan, and so we feel it is worthwhile to present a chronology of this crucial stage of our work, before detailing the specific scientific activities:

The senior personnel assigned to grant convened at Purdue University in July 2004 to formulate the sharing plan and to meet with Hartmut Hedderich, the manager of the Purdue Laser Facility. Dr. Hedderich's role in the project is to assist with installations, as well as to provide maintenance and other technical services to ensure that the laser system is performing optimally during the period of the grant.

At the Purdue meeting, the participants outlined the performance requirements for the new laser system, identified vendors, and set up a usage schedule that would lead to maximal productivity. It was decided that the new laser system would be delivered to Calvin College, to be used by co-PIs Mark and Karen Muyskens and their research group from the period June 1 - November 1, 2005. The laser system would then be transported to UW-Eau Claire, to be used by PI Stephen Drucker from November 1, 2005 - July 1, 2006, in conjunction with his academic-year sabbatical. After this period, the senior personnel at the Michigan colleges, within 100 miles of each other, would retain the laser system for the duration of the 3-year grant.

Following the meeting at Purdue, the individual investigators assembled performance comparisons and bids for the candidate laser systems. By late fall 2004 we made the decision to obtain a Nd:YAG laser manufactured by InnoLas. This instrument is used to pump a dye laser manufactured by Radiant Dyes. Both of the laser vendors are German companies with excellent reputations in Europe. These companies have been eager to penetrate the US market and have provided us significant price and service incentives to buy their systems.

The laser system was installed at Calvin College in July 2005. Although the delivery and installation schedule did not quite meet our expectations, the system has been performing admirably since the original installation, by continuously meeting manufacturers' specifications and requiring minimal daily maintenance.

Research Activities at Calvin College. M. and K. Muyskens used the laser system to investigate the wavelength dependence of trifluoracetylacetone (TFAA) photodissociation. Prior work by the Muyskens on the 248-nm photoelimination reaction of TFAA to produce hydrogen fluoride (HF) shows evidence of collisional quenching of the photochemistry. The goal of the work using the NSF-funded laser system is to investigate the dependence of the quenching in TFAA on excitation wavelength, and then to extend the HF-elimination wavelength-dependence experiments to the small molecule formyl fluoride (HFCO), which shows much vibrational structure in its UV absorption spectrum.

The laser installation process occurred at Calvin College over the course of the summer 2005 research period, but the Muyskens were able to take advantage of both the 266-nm output of the Nd:YAG laser and the UV output of the dye laser to accomplish some preliminary experiments. The 266-nm output of the Nd:YAG laser was used to investigate the degree of collisional quenching in TFAA at this photolysis energy. The quenching was monitored by observing the pressure dependence of HF formation.

Once the dye laser was installed and optimal operating conditions established, the Muyskens were able to do one experiment to test the complete *wavelength-tuneable* laser system and demonstrate the type of study that will be conducted when the laser system next returns to Calvin College. This experiment examined the HF signal from TFAA photodissociation as a function of excitation laser wavelength over the wavelength range 263 to 247 nm. This used the full capabilities of the laser system by doubling the output of the dye laser and tuning the wavelength. Future work will investigate the full pressure-dependence of the HF signal at each excitation wavelength for a better comparison of the effect of using different photolysis energies on the quenching.

Grant Year 2: August 2005-July 2006

Update on Shared Usage Plan

The laser instrumentation purchased by this grant has enhanced research opportunities at our undergraduate institutions, as described in this report. We have found, however, that the optimal time for having the laser at a given institution is longer than the two to ten weeks scheduled in our original proposal. We have found the most efficient use of the instrumentation occurs when it can reside at a given institution for a minimum of either two semesters (a full academic year), or a summer plus an academic semester. This allows the laser to be used more fully to complete a project within the time and resource constraints of being at a primarily undergraduate institution. Thus, our rotation schedule for use of the laser has stretched into a longer timescale as shown in the table below, with significant use of the laser at Hope College in the fourth year and UW-Eau Claire and Kalamazoo College in the fifth year. We requested a one-year, no cost extension to allow the laser equipment to be used by the PI at Hope College (William Polik) during the time when the grant is still active.

Time period	Institution using the laser equipment
AY 2004-05	• Equipment specified and ordered
Summer 2005	• Calvin College (June – Sept.)
AY 2005-06 Summer 2006	• UW-Eau Claire (November- August)
Fall 2006	• Kalamazoo College (September - December)
Spring 2007 Summer 2007	• Calvin College (January - August)
AY 2007-2008 Summer 2008	• Hope College (Sept - August)
AY 2008-09	• UW Eau Claire
Summer 2009 Fall 2009	• Kalamazoo College

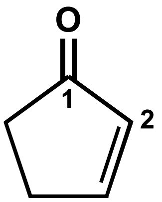
Note on Schedule of Annual Reports

The present documents ("Activities" and "Findings") provide detail through the end of grant year 2, which is August 2005-July 2006. These documents are part of the second annual report, submitted in July 2007 during grant year 3. For unknown reasons, grant year 2 is not listed in the annual report schedule on FastLane. According to FastLane, grant year 3 (August 2006-July 2007) reporting is due in July 2007. Instead of omitting grant year 2 information, we are including it in the present report. Grant year 3 is not included. The next report submission (third annual report) will include grant year 3 information. We would welcome advice regarding the submission date for the third annual report.

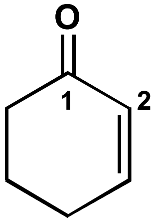
Research Activities at UW-Eau Claire

On November 1, 2005, the entire laser system was sent via rented truck to Stephen Drucker's laboratory at UW-Eau Claire. Only two days were spent at Calvin College preparing the laser system for shipment. By November 15, 2005, the system was up and running at UW-Eau Claire, and meeting performance specifications measured just prior to the shipment from Calvin.

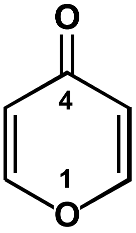
The laser system was used at UW-Eau Claire to advance S. Drucker's research program in molecular spectroscopy. Drucker's research goal is to characterize the structure and dynamics of low-lying triplet excited states of monocyclic enones. Drucker's group has focused on the molecules 2-cyclopenten-1-one (2CP), 2-cyclohexen-1-one (2CH), and 4*H*-pyran-4-one (4PN), shown below.



2CP



2CH



4PN

When the laser system was installed in November 2005, the group had completed (and published) a study of the $T_1(n,\pi^*) \leftarrow S_0$ band system of 2CP using cavity ringdown (CRD) absorption spectroscopy. A CRD investigation of the $T_2(n,\pi^*) \leftarrow S_0$ band system of 2CH was also under way at the time. The existing laser system in Drucker's lab, with modest power output in the UV region, was well matched to the CRD absorption studies.

The new laser has a higher power output in the UV region and was used to test the feasibility of phosphorescence excitation (PE) studies of the triplet species. With the new laser, Drucker's group found that it was possible to record a $T_1(n,\pi^*) \leftarrow S_0$ spectrum 2CP, with comparable signal-to-noise ratio to that of the CRD spectrum. These pilot studies, conducted in a room-temperature sample cell, led Drucker to pursue collaborative work with Timothy Zwier (co-PI on the grant) at Purdue, focused on the PE spectroscopy of 2CP in a jet-cooled environment.

With the laser system tuned up for maximal power, Drucker's group at UW-Eau Claire initiated PE experiments of the $T_1(n,\pi^*) \leftarrow S_0$ band system of 4PN. The experiment required spectral coverage in the 370-350 nm region. The new laser system readily met this requirement through its capability for frequency doubling of the 700-nm fundamental output. The previously existing laser in Drucker's lab lacks the doubling capability and is restricted to use in the visible region of the spectrum. Hence the new laser system singularly permitted Drucker to conduct experiments integral to his research goals. The results of the 4PN $T_1(n,\pi^*) \leftarrow S_0$ investigation are presented in the Findings section of this report.

The frequency doubling component of the new laser system provided a working model for the development of a similar doubling system to operate in conjunction with Drucker's existing tuneable dye laser. Construction of the new doubling system, now permanently integrated into Drucker's experimental setup, was accomplished by the time the MRI-funded laser was moved to Kalamazoo College in August 2006.

Grant Years 3 and 4: August 2006-May 2008

Update on Shared Usage Plan

The shared laser system supported by this award has continued to enhance the research opportunities at our undergraduate institutions. Our current schedule for sharing the laser system is below.

Time period	Institution using the laser equipment
AY 2004-05	• Equipment specified and ordered
Summer 2005	• Calvin College (June – Sept.)
AY 2005-06 Summer 2006	• UW-Eau Claire (November- August)
Fall 2006	• Kalamazoo College (September - December)
Spring 2007 - Fall 2007	• Calvin College (January - November)
Winter 2007 - Summer 2008	• Kalamazoo College (December - August)
AY 2008-09	• UW Eau Claire
Summer 2009 Fall 2009	• Hope College

Jeffrey Bartz at Kalamazoo College was able to jump ahead in the queue because of three factors: (1) the previous schedule, listed in Grant Year 2 above, was out of sync with when the laser was needed at Hope College; (2) the laser system was within an hour's driving distance from Kalamazoo; and, (3) it was an optimal time for his research program to have a second tunable dye laser system in the range of 448 – 454 nm.

Research Activities, at Kalamazoo College, August 2006 – January 2007

Associate Professor Jeffrey Bartz at Kalamazoo College, used the Nd:YAG-pumped dye for a speculative venture into detecting OH radical in his ion imaging time-of-flight mass spectrometer. The detection scheme was to generate a OH radicals, excite OH in the $X \rightarrow A$ region, and ionize the excited OH radicals with 125-nm vacuum ultraviolet light created in a Hg heat pipe through resonant four-wave mixing. The MRI-funded laser generated the 625 and 312.5 nm light needed to pump the Hg heat pipe. No OH signal was detected.

Research Activities, at Calvin College, January 2007 – December 2007

M. and K. Muyskens used the laser system to investigate the wavelength dependence of trifluoracetylacetone (TFAA) photodissociation.

Research Activities at Kalamazoo College

Associate Professor Jeffrey Bartz at Kalamazoo College used the Nd:YAG-pumped dye laser from this award to dissociate an organometallic compound. The products were detected in his existing laser and mass spectrometer. Having two laser systems with tunable light in the region of 224-227 nm was invaluable for Bartz's current research.

Bartz and co-workers found that setting the laser up for a second stint was easy. For his group, the biggest challenge was to learn how to maximize the laser power out of the 20 Hz Innolas Nd:YAG-pumped dye laser system and time the firing of the lab's existing 10 Hz Nd:YAG-pumped dye laser system with the Innolas. Bartz found that the Innolas gave more pulse energy if the flashlamps were fired at 20 Hz, even though the Q-switch only fired at 10 Hz, the same rate as the existing laser. The Innolas has some shot-to-shot jitter, ca. 50 ns, which is acceptable in his current experiments.

Grant Year 4: May-July 2008

Update on Shared Usage Plan

The shared laser system supported by this award has continued to enhance the research opportunities at our undergraduate institutions. Our current schedule for sharing the laser system is below.

Time period	**Institution using the laser equipment**
AY 2004-05	• Equipment specified and ordered
Summer 2005	• Calvin College (June – Sept.)
AY 2005-06 Summer 2006	• UW-Eau Claire (November- August)
Fall 2006	• Kalamazoo College (September - December)
Spring 2007 - Fall 2007	• Calvin College (January - November)
Winter 2007 - Summer 2008	• Kalamazoo College (December - August)
AY 2008-09	• Calvin College
Summer 2009 Fall 2009	• Hope College

Research Activities at Kalamazoo College

Associate Professor Jeffrey Bartz at Kalamazoo College has used the Nd:YAG-pumped dye laser from this award as the dissociation laser in ion imaging experiments. The products were detected in his existing laser and mass spectrometer. Having two laser systems with tunable light in the region of 224-227 nm was invaluable for Bartz's current research.

In the first series of experiments, Bartz and co-workers have studied the photodissociation of η^5-(C_5H_5)NiNO in a velocity-mapping time-of-flight mass spectrometer. The laser system funded through this award has allowed Bartz to independently control the polarization of the 225 nm dissociation beam and the tunable 224-227 nm probe beam to detect free NO. The pump-probe method has been extended to a second molecule, $Co(CO)_3NO$.

In a second set of experiments, Bartz and co-workers have studied the 335 nm photodissociation of CH_3ONO by velocity mapping of the NO photoproduct. The third harmonic of the Nd:YAG laser funded through this MRI award is used to generate the dissociation beam. The probe and ionization beams are generated with the lab's permanent Nd:YAG and dye laser.