AFRL-SR-AR-TR-09-0047

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 2/19/2009	3. REPORT TYPE AND DATES COVERED
		Final Technical Report 1 Jan 2006 – 30 November, 2008

4. TITLE AND SUBTITLE
From the Theory of Chemical Lasers to the Spectra of High-Energy Density Materials Higher Order Conical Intersections Play a Key Role

5. FUNDING NUMBERS
Grant:
FA9550-06-1-0065

6. AUTHOR(S)
David R. YARKONY

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
Johns Hopkins University
Baltimore, MD 21218

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Dr. Michael Berman
AFOSR/NL
875 Randolph Street
Suite 325, Rm 3112
Arlington, VA 22203

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 Words)***

Our AFOSR funded work has included both the development of new computational tools to determine photoelectron spectra within the time independent multimode vibronic coupling model, and the use of those tools, and techniques developed as part of other funded research, to determine photoelectron spectra for the selected azolides, anion precursors of the radical species, $(CH)_mN_{5-m}$, for $m = 0 - 4$. These anions have been suggested as components of ionic liquids and have been studied experimentally and computationally in Lineberger's group. Key to our ability to determine photoelectron spectra is an open-ended, fine-grained parallel algorithm for solving the nuclear Schrödinger equation using large vibronic bases. This algorithm was used to determine the negative ion photodetachment spectrum of the anion of pyrazolyl, $(CH)_mN_{5-m}$, for $m = 3$, whose determination, as recently as 2006, was declared computationally unfeasible! Work is currently finishing up on pyrrolyl, $m = 4$, is significantly in progress on triazolyl $m = 2$ and has begun on pentazolyl, $m = 0$. We have also studied a novel conical intersection topography in excited states of N_3^+ a potential photoionization probe of cyclic N_3, in which 3 symmetry equivalent seams of conical intersection are found in close proximity to a symmetry required seam. Finally, we have and will continue to do work on the role of conical intersections in the photodissociation of nitramines, which has been suggested as being relevant to the ignition process in HMX, RDX and related species.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Energetic materials, polynitrogen compounds, conical intersections Photoelectron spectra	14
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
	Unclassified	Unclassified	

From the Theory of Chemical Lasers to the Spectra of High-Energy Density Materials Higher Order Conical Intersections Play a Key Role

David. R. Yarkony
Department of Chemistry, Johns Hopkins University
Baltimore, MD 21218

Grant/Contract Number: FA9550-06-1-0065

Final Technical Report
1 Jan 2006 – 30 November, 2008

TABLE OF CONTENTS

A. Overview

A key aspect of the captioned grant has been the simulation of photoelectron spectra of molecules that are relevant to the high energy density materials program and involve states strongly coupled by conical intersections. Our AFOSR funded work has included both the development of new computational tools to determine photoelectron spectra within the time independent multimode vibronic coupling model, and the use of those tools, and techniques developed as part of other funded research, to determine photoelectron spectra for the selected azolides, anion precursors of the heterocycle radicals, $(CH)_mN_{5-m}$, for m = 0 - 4. These anions have been suggested as components of ionic liquids and have been studied experimentally and computationally in Lineberger's group.[1,2,3,4] Key to our ability to determine photoelectron spectra is an open-ended, fine-grained parallel algorithm for solving the nuclear Schrödinger equation using large vibronic bases.[5] This algorithm (see Sec. B below) was used to determine the negative ion photodetachment spectrum of the anion of pyrazolyl,[6] $(CH)_mN_{5-m}$, for m = 3, whose determination, as recently as 2006, was declared computationally unfeasible![4] Work is currently finishing up on pyrrolyl, m = 4, is significantly in progress on triazolyl m = 2 and has begun on pentazolyl, m = 0. We have also studied[7] a novel conical intersection topography in excited states of N_3^+ a potential photoionization probe of cyclic N_3, in which 3 symmetry equivalent seams of conical intersection are found in close proximity to a symmetry required seam. Finally, we have and will continue to do work on the role of conical intersections in the photodissociation of nitramines, which has been suggested as being relevant to the ignition process in HMX, RDX and related species.[8,9]

B. Computational Tools

(i) Parallel Lanczos Algorithm
M. S. Schuurman, R. A. Young, and D. R. Yarkony, Chem. Phys. **347**, 57 (2008).

We developed a fine-grained parallel algorithm to solve the secular equation that arises in the time independent multimode expansion of the vibronic coupling problem.[10] The implementation, which defines the state of the art in this area, can handle expansions of arbitrary length, with the open-ended character of the algorithm achieved through the use of fine grained parallelism to partition the trial vectors. The algorithm has been used to treat vibronic expansions comprised of over 1 billion basis functions.[5]

C. Photoelectron Spectroscopy of the Azolyls $(CH)_mN_{5-m}$: States Strongly Coupled by Conical Intersection

These studies were motivated by the photoelectron spectra measured in Carl Lineberger's laboratory, which we initially learned about at an AFOSR contractor's meeting in 2003. We originally showed that these radicals exhibited low-lying seams of conical intersections of two and three electronic states.[11] The goal of the captioned research effort was to understand what the effect of this complicated series of conical intersection seams has on the photoelectron spectra. The primary challenges arise from the strong coupling of (at least) three low-lying electronic states, and the consequent low-lying seams of two and three state conical intersections, as well as the significant number of internal degrees of freedom that must be treated. Our recent methodological advances have made the study of this difficult problem tractable using the time-independent multimode vibronic coupling method.

(i) The photoelectron spectrum of Pyrazolyl
M. S. Schuurman and D. R. Yarkony, J. Chem. Phys 127, 064304 (2008).

The spectrum of the pyrazolyl radical, $(CH)_3N_2$, obtained from negative ion photodetachment of an electron from the pyrazolide anion, proved to be a particularly demanding

computational problem. Indeed, as recently as 2006 the determination of this spectrum was declared computationally unfeasible![4]

The first step in the determination of the photoelectron spectrum was the development a quasi-diabatic Hamiltonian, $\mathbf{H}^d$, which accurately describes the electronic structure aspects of the problem as determined by *ab initio* multireference configuration interaction wave functions. Not only must the equilibrium geometries and harmonic frequencies of the nominal $\tilde{X}^2A_2$ ground state and low-lying $\tilde{A}^2B_1$ excited state, be well described but so must the minimum energy points on the lowest two-state ($\tilde{X}^2A_2$, $\tilde{A}^2B_1$) and three-state ($\tilde{X}^2A_2$, $\tilde{A}^2B_1$, $\tilde{B}^2B_2$) seams of conical intersection. $\mathbf{H}^d$ is then used to form a vibronic Hamiltonian in the multimode vibronic coupling approximation in a basis designed to limit the size of the vibronic expansion. The vibronic Hamiltonian, of dimension greater than 500 million, was diagonalized to obtain the negative-ion photoelectron spectra for pyrazolide-h_3. Our predicted spectrum, compares quite favorably with the measured photoelectron spectrum.[4] See Fig. 1 below.

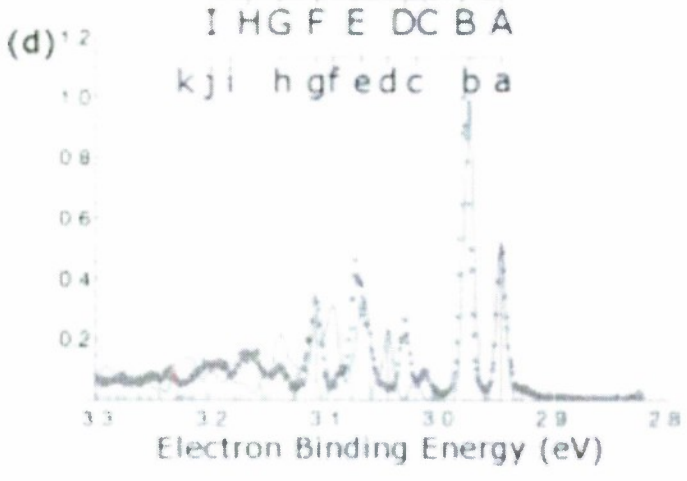

Figure 1:Experimental(dots) and calculated (solid lines) photoelectron spectrum of pyrazolide-h_3

(ii) The photoelectron spectrum of Triazolyl

The photoelectron spectrum of the anion of triazolyl, triazolide, is quite challenging to determine computationally. In triazolyl, the combination of 3 nitrogen lone pairs and a half filled 5 electron, 5 orbital orbital conjugated π–system, requires that four low-lying electronic states be considered. The proper description of these four states and their interactions, which is essential for the determination of the photoelectron spectrum, is made difficult by the significant differences in the equilibrium geometries of the four states. To accommodate this situation we are employing an extension of the procedure used to construct the $\mathbf{H}^d$ for pyrazolyl, a procedure based on a unique normal equations approach.[12] The normal equations approach allows us to incorporate data averaging over a range of nuclear geometries while assuring quasi-diabaticity.

Our treatment of the electronic structure of triazolyl is quite ambitious being an 11 electrons in 8 orbitals active space. The second order configuration interaction wave functions, with only 5 core orbitals kept doubly occupied, comprised more than 200 million configuration state functions.

At present we are in the process of determining an $\mathbf{H}^d$ which is converged with respect to the normal equations averaging procedure. In our normal equations approach for triazolyl, $\mathbf{H}^d$ is constructed using data from both the region of the ground state minimum and that of minimum energy crossing point. Figure 2 below compares the experimental[3] photoelectron spectrum (upper panel) to our simulations (lower panels), which currently employ over 200 million vibronic basis functions. The two lower panels juxtapose spectra obtained with the minimum energy crossing (lower left) and ground state energy minimum (lower right) as the origin for $\mathbf{H}^d$, respectively.

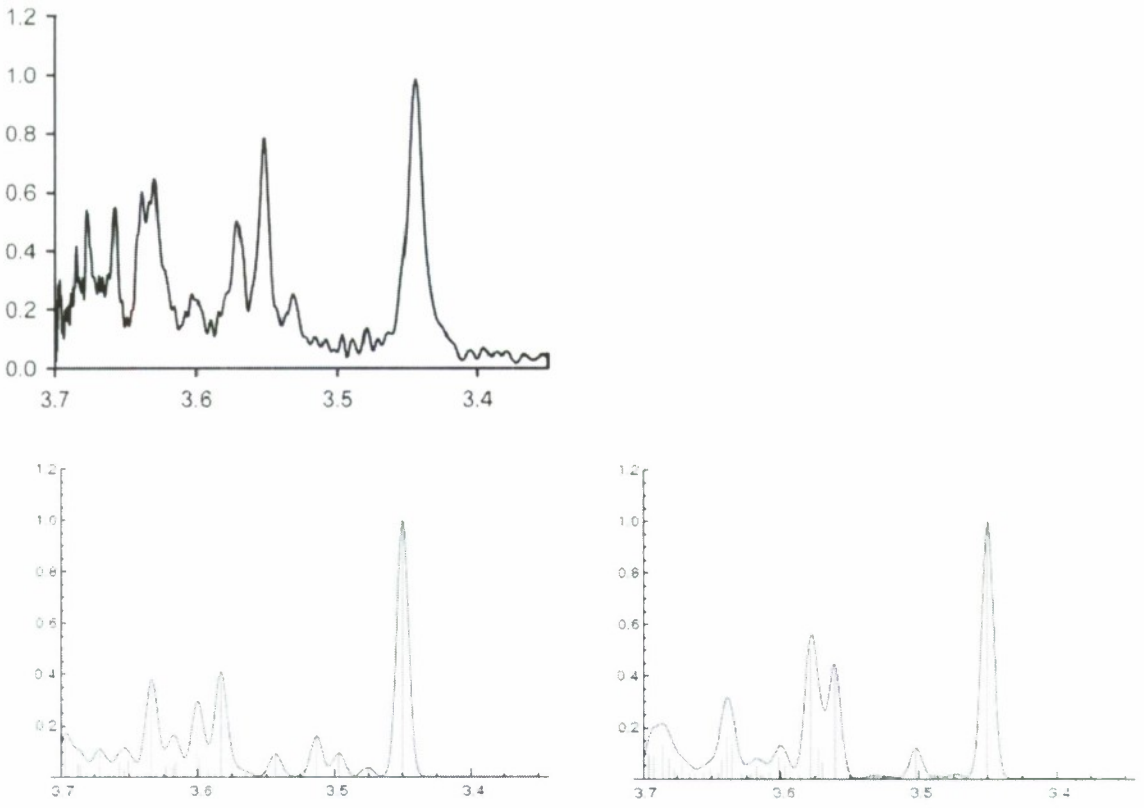

Figure 2: Photoelectron spectrum of triazolyl: upper panel experimental spectrum and lower panels computed spectrum, left panel minimum energy crossing point as the origin of H^d, right panel ground state minimum as origin of H^d.

While additional work on the representation of $\mathbf{H}^d$ is required, the improvement when the minimum energy conical intersection point is used as the origin is palpable and reflects positively on the weighted normal equations approach we developed in the course of our study of pyrrolyl described below.

(iii) The photoelectron spectrum of pyrrolide

The photoelectron detachment spectrum of pyrrolide, the anion of pyrrolyl $(CH)_4N$, has been the object of recent experimental[2] and theoretical studies.[13] The photodetachment of an electron from the ground state of pyrrolide, produces a neutral in either its nominal ground $^2A_2$ state or its excited $^2B_1$ state. Here the attribute nominal is meant to indicate that both the $^2A_2$ state and the $^2B_1$ state are actually on the ground state potential energy surface as the result of

coupling via a conical intersection. Interestingly, the experimental photoelectron spectrum is devoid of features attributable to the $^2B_1$ state and those features resulting from the nominal $^2A_2$ state are perturbed. There are two potential sources for the absence of spectral features attributable to the $^2B_1$ state, strong nonadiabatic effects or small transition moments (technically small photodetachment cross sections). This diminution of the intensity of peaks in an adiabatic states spectrum by nonadiabatic and transition moment effects is a problem of enduring interest.[14,12] This issue was the principal concern of our study.

Attempts to describe this photoelectron spectrum using an adiabatic state model were largely unsuccessful.[2] The only existing theoretical nonadiabatic simulation of this spectrum used a simple computational model, only linear as opposed to fully quadratic vibronic coupling was included and only a limited number of normal modes were explicitly treated.[13] While that analysis did demonstrate the importance of nonadiabatic effects in the diminution of the $^2B_1$ contribution to this spectrum, questions concerning the origin of the diminution still remained.

We have completed our computational study of the photoelectron spectrum of pyrrolide and are preparing the results for publication. A very reliable $\mathbf{H}^d$ based on the fully quadratic vibronic coupling model developed using weighted data averaging, has enabled more quantitative assessment of the role of nonadiabatic effects in this photoelectron spectrum than was possible in the previous[13] study. This $\mathbf{H}^d$, which has as its origin at the minimum energy point of conical intersection of the $^2A_2$ and the $^2B_1$ states, describes both this crossing region and the minimum energy structures of these two states very accurately.

The simulated and experimental photoelectron spectra are presented below. The agreement is seen to be excellent.

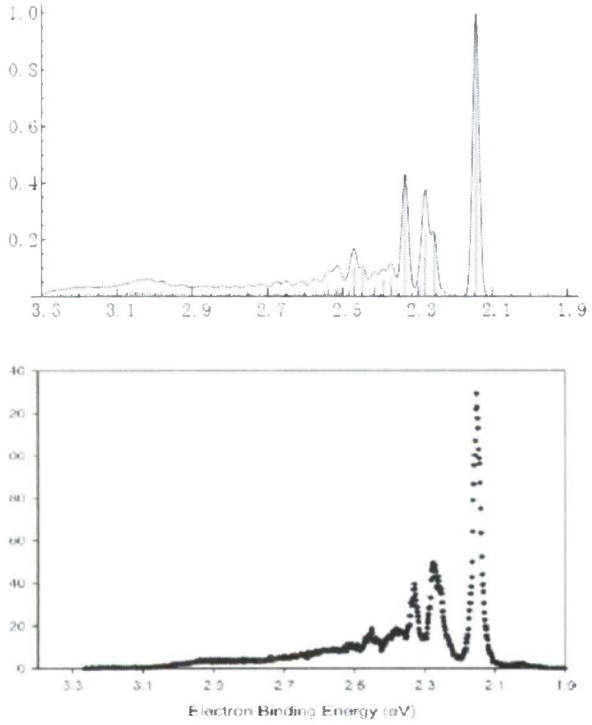

Figure 3: Simulated (upper) and experimental[2] (lower) photoelectron spectrum of pyrrolide.

The quality of the simulated spectrum allows us to reach reliable conclusions concerning the relative importance of the two factors, nonadiabatic interactions and photodetachment cross sections, in the diminution of the $^2B_1$ state contribution of the photoelectron spectrum. From our study it emerged that the intensities of the simulated spectrum reflect both the influence nonadiabatic interactions and the intrinsic photodetachment cross sections for the states involved. There are currently no direct measurements or calculations of these photodetachment cross sections. However our careful treatment of nonadiabatic effects allowed us to draw conclusions about the size of these cross sections which will serve as invaluable benchmarks when, in the future, calculations of the photodetachment cross sections become available.

D. Photodissociation of nitramide $H_2N\text{-}NO_2$.

The mechanism the photodissociation of high energy materials such as HMX and RDX is a significant issue because of the potential role of excited electronic states in the detonation process.[8,9] Experimental measurements have established[8] that the initial step in the photodissociation of these and related nitramines including $(CH_3)_2N\text{-}NO_2$ is the production of NO following a nitro-nitrite rearrangement. Previous computational efforts to explain NO production did not focus on the potential role of conical intersections in this process.[9] We believe, that based on other research,[15] this neglect is not justified.

As a first step in a systematic study of the initial step of the photodissociation of nitramines we are investigating the topography of the S_0 and S_1 potential energy surfaces of nitramide. The results of our first order configuration interaction treatment based on a DZP basis are summarized in Figure 4, below.

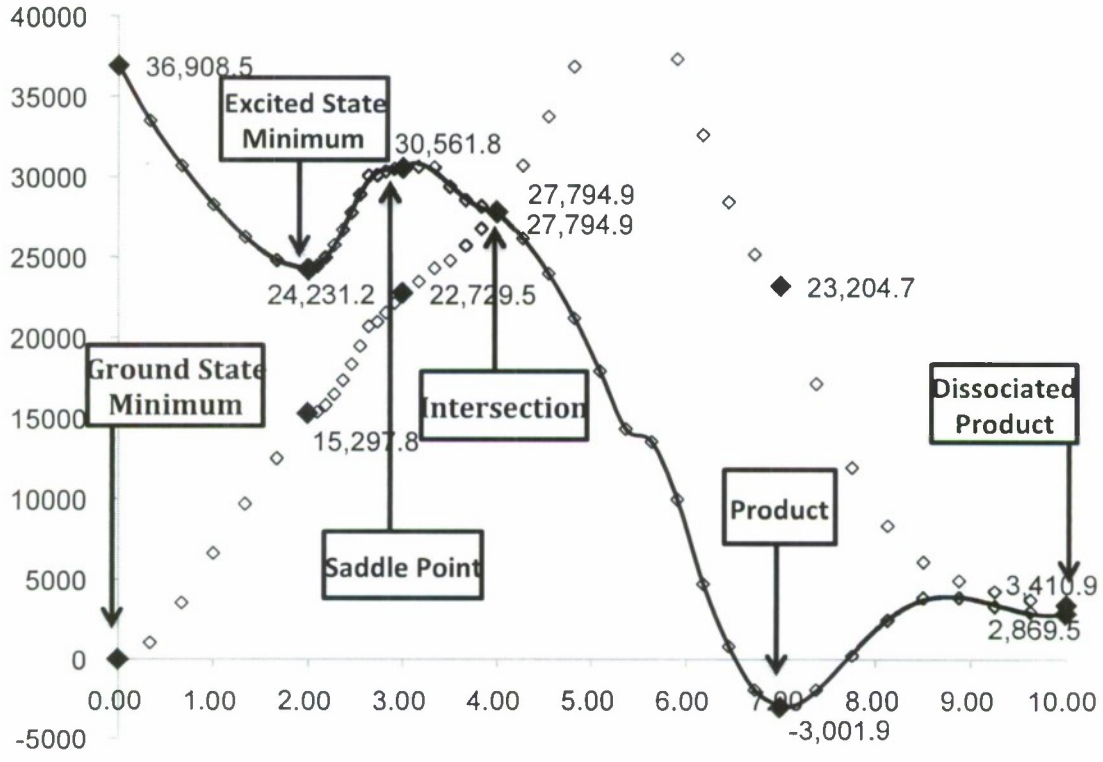

Figure 4. Key points on the S_0 and S_1 potential energy surfaces of nitramide (filled diamonds) connected by linear synchronous transit paths (open diamonds) on S_1 before the conical

intersection (labeled Intersection) and S_0 after conical intersection. The abscissa scale is arbitrary. Product = rearranged structure H_2N-ONO. Dissociated product = H_2NO + NO.

This figure shows that following excitation to S_1 from the equilibrium geometry of H_2N-NO_2 on S_0, the molecule can evolve through the region of a minimum on S_1 and over a barrier, to an $S_0 - S_1$ conical intersection. To consider the impact of passage through this conical intersection on the photodissociation we examined "routing", the motions favored by the branching[16] or g-h[17] plane as the wave packet emerges on the ground state surface. By following the gradient from distinct points in the *g-h* plane, we found that after going through the intersection to ground state, the molecule is either routed back to the ground state minimum, or to the rearranged product H_2N-ONO which subsequently dissociates into NO and H_2NO. See Figure 4. This analysis supports our conjecture that the $S_0 - S_1$ conical intersection seam plays a key role in the photochemical production of NO.

However this analysis may be too simplistic. Although only a single point of conical intersection (the minimum energy crossing point) is noted on Fig. 4, an extended seam of conical intersection near the nitro-nitrite rearrangement path was found. This continuous seam includes both geometries that are close to the S_1 minimum and those that are more similar to the rearranged product H_2N-ONO. We are currently analyzing the effect of routing at different points on the $S_0 - S_1$ seam. In the future we will extent of our electronic structure treatment to the more reliable second order configuration interaction level. Subsequently more complicated derivatives of H_2N-NO_2 will be considered.

E. Future Directions

In the renewal of this grant we intend to pursue the following research directions described in detail in our renewal proposal. Determine the photoelectron spectra of the azolides, including triazolide ($(CH)_2N_3^-$ - work in progress) and pentazolide (N_5^- work just started). In

order to efficiently perform the electronic structure calculations required to determine the quasi-diabatic Hamiltonian $\mathbf{H}^d$ for penazolyl, algorithms previously developed to efficiently handle the C_{3v} point group will be extended to arbitrary nonabelian point groups. We anticipate introducing $\mathbf{H}^d$ with higher order (that is beyond quadratic) terms and *ab initio* calculated transition dipole moments into our simulations of photoelectron spectra. Finally we will consider the role of conical intersections in decomposition of electronically excited nitramines and other energetic species including diazirine H_2CN_2. This later project will be performed in collaboration with Hanna Reisler at the University of Southern California.

Literature Cited

1 A. J. Gianola, T. Ichino, S. Kato, V. M. Bierbaum, and W. C. Lineberger, J. Phys. Chem. A 110, 8457 (2006).

2 A. J. Gianola, T. Ichino, R. L. Hoenigman, S. Kato, V. M. Bierbaum, and W. C. Lineberger, J. Phys. Chem. A 108, 10326 (2004).

3 T. Ichino, D. H. Andrews, G. J. Rathbone, F. Misaiozu, R. M. D. Calvi, S. W. Wren, S. Kato, V. M. Bierbaum, and W. C. Lineberger, J. Phys. CHem. B 112, 545 (2008).

4 T. Ichino, A. J. Gianola, W. C. Lineberger, and J. F. Stanton, J. Chem. Phys. 125, 084312 (2006).

5 M. S. Schuurman, R. A. Young, and D. R. Yarkony, Chem. Phys. 347, 57 (2008).

6 M. S. Schuurman and D. R. Yarkony, J. Chem. Phys 127, 064304(11 pages) (2008).

7 J. J. Dillon and D. R. Yarkony, J. Chem. Phys. 126, 124113(7 pages) (2007).

8 Y. Q. Guo, M. Greenfield, and E. R. Bernstein, J. Chem. Phys. 122, 244310 (2005).

9 Y. Q. Guo, M. Greenfield, A. Bhattacharya, and E. R. Bernstein, J. Chem. Phys. 127, 154301 (2007).

10 H. Köppel, W. Domcke, and L. S. Cederbaum, in Conical Intersections, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, New Jersey, 2004), Vol. 15, pp. 323.

11 S. Matsika and D. R. Yarkony, J. Amer. Chem. Soc. 125, 12428 (2003).

12 B. N. Papas, M. S. Schuurman, and D. R. Yarkony, J. Chem. Phys. **129**,124104 (2009).

13 A. Motzke, Z. Lan, C. Woywod, and W. Domcke, Chem. Phys. 329, 50 (2006).

14 J. Zhou, E. Garand, W. Eisfeld, and D. M. Neumark, J. Chem. Phys. 127, 034304(7 pages) (2007).

15 J. Soto, J. F. Arenas, J. C. Otero, and D. Pelaez, J. Phys. Chem. A. 110, 8221 (2006).

16 G. J. Atchity, S. S. Xantheas, and K. Ruedenberg, J. Chem. Phys. 95, 1862 (1991).

17 D. R. Yarkony, Acc. Chem. Res. 31, 511 (1998).

PUBLICATIONS since January 2006

1. *On the Characterization of Three State Conical Intersections using a Group Homomorphism Approach: Mapping the Full N- 5 Dimensional Seam Space*
Michael S. Schuurman and David R. Yarkony, J. Chem. Phys. **124**, 244103 (11 pages)(2006)

2. *Seam near Seams: The Jahn-Teller Effect in the $^1E''$ State of N_3^+*
Joseph J. Dillon and David R. Yarkony, J. Chem. Phys. **126** 124113(7 pages) (2007)

3. *On the Multimode Quadratic Vibronic Coupling Model. An Open-ended Solution to the Secular Problem Using a Parallel Lanczos Algorithm*
Michael S. Schuurman, Richard A. Young and David R. Yarkony, Chem. Phys. **347**, 57-64 (2008)

4. *A simulation of the photoelectron spectrum of pyrazolide,*
Michael S. Schuurman and David R. Yarkony, J. Chem. Phys, **129** 064304(10 pages)(2008).

PERSONNEL

The following scientists in my research group have contributed to work reported herein.

Postdoctoral Research Associates	**Principal Investigator(PI)**
Dr. Michael Schuurman (Jan. 2006 – Jan. 2009)	Professor David R. Yarkony

Graduate Students

Mr. Xiaolei Zhu(Jan, 2008-

Mr. Joseph Dillon (Jan. 2006-

Mr. Richard A. Young (Jan. 2006-Ph. D awarded June 2007)

INTERACTIONS

Invited Presentations

Below are listed invited talks given by the PI based on work performed as part of this grant

1 *Nonadiabatic Effect in Photoelectron Spectroscopy*
American Physical Society Meeting, Denver, CO, March 2007

2. *Photoelectron spectra of involving coupled electronic states*
at MARM, Ursinus College, May 2007

3. *Theoretical Determination of Photoelectron Spectra involving Strongly Coupled Electronic States*
at *Excited Electronic States in Chemistry and Biology: Theory and Experiment* at the 234th National Meeting of the American Chemical Society in Boston, MA on August 19-23, 2007.

4. *Photoelectron Spectra of States Strongly Coupled by Conical Intersections,*
at 235th National ACS Meeting, New Orleans , LA; 6-10 April 2008

5. *Photoelectron Spectra of States Strongly Coupled by Conical Intersections,*
at 2008 Atomic and Molecular Interactions Gordon Research Conference, July 2008

6. XIX International Symposium on the Jahn-Teller Effect:Vibronic Interactions and Orbital Physics in Molecules and in the Condensed Phase; Heidelberg, Germany August 2008;the *US Member of the Meetings Scientific Committee*

7. *Conical Intersections and Photoelectron Spectra*
at 2009 Gordon Research Conference on Molecular Energy Transfer (GRCOMET); Ventura, CA January 2009