DYNAMIC PHASE AND POPULATION CONTROL OF STATE SELECTED WAVE PACKETS IN Li_2

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This thesis for the Doctor of Philosophy degree by

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

Ballard, Joshua (Ph.D., Physical Chemistry)

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Thesis directed by Professor Stephen R. Leone

Pulse shaping of ultrafast pulses with a Liquid Crystal Spatial Light Modulator (SLM) is used to control both transient and non-transient state-resolved wave packet dynamics in Li_2. In almost all of the experiments, a single launch state (generally $A^1\Sigma_u^+$ v_A=11, J_A=28) is prepared via excitation with a cw laser, from which a pump pulse excites a superposition of states on an excited electronic potential energy curve followed by a photoionizing ultrafast probe pulse. Using feedback and an Evolutionary Algorithm (EA), the weak field pump-probe photoionization signal at a single time delay is optimized in Li_2 for the state $E\,^1\Sigma_g^+$ (v_E=9, J_E=27 & 29). First order time dependent perturbation theory is used to explain the mechanism by which the photoionization is maximized. Following this, the transient dynamics of excitation of wave packets is studied in detail. A clear separation is made between resonant and nonresonant effects. Both population and resultant phase in the molecule are transiently manipulated. By varying the polarization of the probe light, population dynamics can be separated from interfering wave packet dynamics, allowing precise determination of the instantaneous population and wave packet dynamics. A pulse shaping scheme is described that implements a sign inversion for one state of a two state superposition, and all sign inversion matrix elements are quantified. Elements of strong field coherent control are also explored in Li_2. From the launch state, the strong optical field couples the A and E electronic states,

inducing sequential $\Delta J=\pm 1$ transitions to populate states up to $\Delta J=\pm 4$. Taking advantage of Rapid Adiabatic Passage, state selectivity is controlled by manipulating chirp parameters on the excitation pulse, achieving selectivity of either Stokes or anti-Stokes quantum beats of nearly unity. Finally, wave packet dynamics on highly excited electronic states is examined. Electronic wave packets consisting of beating between bound states on the $F^1\Sigma_g^+$ and $G^1\Pi_g$ electronic states are observed.

“I thought of that while riding my bike.”

-Albert Einstein on the theory of relativity

Acknowledgements

To fully describe the degree to which I feel indebted to my wife for her support in this endeavor of studying graduate chemistry, a little background is in order. By 1997, after my wife and I had lived in San Francisco for a few years, we had a very comfortable existence. The internet and multimedia industries were blooming in The City, and jobs were plentiful and high paying. Even though I was enjoying a well paying position in high-tech, I had time to direct and produce my own movies for personal expression while my wife Rebecca and I were living in the most quaint neighborhood just two blocks from Golden Gate Park. From our front door, we could walk to any of sixty restaurants within five minutes. Even in this very urban environment, our house was surrounded by gardens, and we would wake to the sound of birds chirping without the usual din expected of the city. It was quite peaceful spending the morning in our mature garden sipping coffee and collecting our thoughts for the day.

On one particular trip home to visit the parents, I had a conversation with my father-in-law Garth Gillan, who at the time was a Professor of philosophy at the local university. I was telling him about how cool a life we were living, and he asked me if I felt like I was getting anything out of it, or if I was just whoring myself out to the highest bidder. Try to guess my answer…. Shortly after that, I quit my job to study chemistry. Within three months, I was taking some undergraduate chemistry courses, and we had moved to one of the roughest neighborhoods in San Francisco. It was typical to have to wade through a group of thugs clad in ski-masks to get up the stoop to our front door (actually, we'd just go to our back door). Now, instead of being

surrounded by birds chirping and gardens, we were in the midst of what would be considered a war zone anywhere but in America. One night, as Rebecca and I were on our way to BART, we passed by a bleeding stabbing victim. There were police there, so we kept on walking. One block later, we passed a gunshot victim. Hey, I wanted to go to graduate school. Rebecca knew that I needed to study to get to graduate school, so she endured this extreme change in situation—for me.

It is especially comforting to know that I have someone like Rebecca behind me. As might be expected, her support has not wavered since entering graduate school.

One particularly large series of events in graduate school revolved around relocating our lives and labs back to California. It would have been impossible to deal with if not for the collective impetus of everybody in the group. Laurie and Jodi were especially nice to have around. We started graduate school together and spent countless hours in the same room in lab. Seeing them in California is an important constant, helping make the personal adjustments bearable.

In lab, it has been a pleasure to share so many conversations with Hans Stauffer. He tends to get worked up when talking about science, and that can be very motivating during the long haul of graduate school. On a personal level, it has been very nice to have Hans and the rest of his family around for so many important events.

Through my five years of graduate school, there have been many others who have helped me develop or endure. First of all, my advisor Steve has been quite a source of motivation, that is in addition to taking all of the responsibilities of the role

of advisor that needs not be explained to anybody reading this text. It seems like almost every conversation I had with him resulted in me wanting to do some of the best science ever. There were several times I would go into a meeting with him feeling like Dave Stoler [from *Breaking Away*] working in his father's used car lot, and leave feeling like Dave on the last lap of the Little 500.

I have to give a shout out to JILA, where it is very easy to do science. There are so many people there whose main goal is to make the pursuit of knowledge seamless. I particularly enjoyed participating in OSEP, where I got to follow the progress of people in so many different groups. I can hardly imagine getting through grad school with nearly the perspective I have if it were not for everybody involved in OSEP. It has truly been an enriching experience to be involved in such an interdisciplinary group.

There are many others that deserve acknowledgement from me. We have to keep perspective though: this isn't the Oscars.

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