QUANTUM COHERENT CONTROL OF H₃⁺ FORMATION IN STRONG FIELDS

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ABSTRACT

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The goal of this dissertation work was to better understand laser-matter interactions and if they are able to controlled by simple pulse shaping. Quantum coherent control (QCC) has been successfully demonstrated experimentally and theoretically for two- and three-photon optical excitation of atoms and molecules. Here, we explore QCC using spectral phase functions with a single spectral phase step for controlling the yield of H_3^+ from methanol under strong laser field

excitation. We observe a significant and systematic enhanced production of H_3^+ when a negative 3/4 π phase step is applied near the low energy region of the laser spectrum and when a positive 3/4 π phase step is applied near the high energy region of the laser spectrum. In some cases, most notably the HCO⁺ fragment, we found the enhancement exceeded the yield measured for transform limited pulses. The observation of enhanced yield is surprising and far from the QCC prediction of yield suppression. The observed QCC enhancement implies an underlying strong field process responsible for polyatomic fragmentation controllable by easy to reproduce shaped pulses.

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TABLE OF CONTENTS

LIST OF FIGURESv	
KEY TO ABBREVIATIONS	vii
Chapter 1: Introduction	1
1.1 Overview of laser-matter interactions	1
1.2 Lasers for control	
1.2 Quantum Coherent Control	
Chapter 2: Quantum Coherent Control of H ₃ ⁺	6
2.1 Introduction	6
2.2 Experimental	
2.3 Results	
2.4 Discussion	
2.5 A note on Ethane	
2.6 Conclusions	
2.7 Future Experiments	
BIBLIOGRAPHY	

LIST OF FIGURES

Figure 4. Calculated QCC for a $\pi/2$ phase step with a two-photon transition (black) and seven-

Figure 5. First and second ionization energies of methanol (black) with intermediate excited states

Figure 11. The time-dependent intensity (black line) I(t), phase (dashed red line) $\Phi(t)$, and the instantaneous frequency of the pulse (blue line) $\omega(t)$ for the two cases where enhancement was

observed, (a) $(-3/4\pi \omega_r)$ and (b) $(+3/4\pi \omega_b)$ and where suppression was observed (c) $(+3/4\pi \omega_b)$.)
and (d) ($-3/4\pi \omega_b$). When the phase step causes enhancement, a downchirp is observed in the most	t
intense feature of the pulse and is indicated by a dotted line. When there is yield suppression, ther	e
is an up-chirp in the frequency1	5

KEY TO ABBREVIATIONS

QCC	Quantum Coherent Control
MPI	Multiphoton Ionization
HHG	High Harmonic Radiation
TL	Transform Limited
FWHM	Full width at half maximum
TOF	Time of Flight
MIIPS	Multiphoton Intrapulse Interference Phase Scan
SLM	Spatial Light Modulator
CCD	Charged Coupled Device
CCSD(T)	Coupled Cluster Single Double (Triple)
cc-pVDZ	correlation consistent - polarized Valence Double Zeta
EOM	Equations of Motion
CEP	Carrier Envelope Phase
SDI	Sequential Double Ionization
LDI	Localized Double Ionization
CE	Coulomb Explosion

Chapter 1: Introduction

1.1 Overview of laser-matter interactions

The study of laser-matter interactions using intense ultrashort laser pulses has been an active area of research since the early 1990's. It is now understood how atoms respond in strong laser fields; however, this understanding falls short with polyatomic molecules. There have been some pioneering studies that have greatly increased our understanding of the behavior of molecules in strong field by investigation of phenomena such as field induced alignment^{1–3}, enhanced ionization^{4,5} and Coulomb explosion.^{6,7}

As pulses became shorter and more intense, unexpected chemical reactions were observed; the formation of H_3^+ being one of them. The trihydrogen cation, H_3^+ , was first discovered by J.J Thompson in the early 20th century and are considered the simplest and most abundant triatomic cations in the universe.⁸ The formation of H_3^+ from small organic molecules is unique as it requires the breaking and subsequent formation of three chemical bonds. This type of reaction has significant implications in photochemistry and molecular physics as it provides understanding of intramolecular processes including hydrogen migration.

Experimental and theoretical studies on H_3^+ have uncovered the mechanisms and timescales of formation from small chain alcohols and thiols.^{9–11} There are two general pathways for the production of H_3^+ ; (i) where all three hydrogens originate from the same carbon and (ii) where association of two hydrogen atoms from one carbon and the third hydrogen from a neighboring chemical group. In each pathway, double ionization of the precursor molecule is required, followed by the production of a neutral H_2 moiety which roams and abstracts a third hydrogen atom from the remaining ion. Roaming implies that the neutral fragment explores relatively flat regions of

the potential energy surface far from the minimum energy path.^{12–15} A schematic of this process can be seen in Figure 1.



Figure 1. Primary H₃⁺ formation pathway from methanol. Pathway with green arrows shows mechanism where all hydrogens originate from the same carbon. The orange arrows show the mechanism where only two hydrogens originate from the same carbon.

1.2 Lasers for control

Not only does ultrafast spectroscopy allow the observation of these exotic chemical reactions, but there is potential for control through shaping of the laser pulses. Inspiration for control over excitation processes came from Brumer and Shapiro. They realized that quantum interference between exciting molecular transitions can be manipulated by changing the phase of one or more pathways,¹⁶ as well as using pulse shaping to control chemical reactions.^{17,18} Quantum coherent control (QCC) was made to differentiate the use of a well-defined phase function as opposed to an experimental search for a feedback optimized field, which adopts the more generic term, coherent control.

To understand QCC, one must first understand mechanisms of excitation and ionization of molecules within laser fields. At intensities below 10^{12} W/cm², atoms and molecules absorb one or more photons to reach an excited state, this is known as multiphoton ionization (MPI) (Figure 2a). Here molecules are aligned along the laser polarization direction through interaction with the induced dipole moment of the molecule. Above 10^{12} W/cm² the interaction with the laser field becomes Coulombic. Here, the atoms and molecules interact with electric field component of the pulses and field ionization can occur. Field ionization is where the intense electric field of the laser, bends the potential barrier to which an electron can tunnel through and escape (Figure 2b). At intensities close to the limit of MPI and approaching field ionization, distinction between MPI and field ionization can be difficult. The Keldysh parameter is a quantitative indicator to what ionization regime will take place. The Keldysh parameter, γ , is dependent on the ionization potential of the molecule or atom, the intensity of the electric field and frequency of the pulse (Eq. 1) Where ω is the laser frequency, I_{p_2} , is the ionization potential of the atom or molecule and E_A is the amplitude of the electric field. If $0 < \gamma < 0.5$, then field ionization is the dominant regime of

ionization; if $0.5 < \gamma$, the dominant regime is MPI. As can be seen in the Eq. 1, the Keldysh parameter has a dependence on the ionization potential; meaning, different molecules will have different Keldysh parameters for the same laser intensity.



Figure 2. A (left) Multiphoton ionization, the red arrows represent photons that are absorbed to reached excited states. B (right) Tunnel ionization, where the electric field bends the potential barrier, allowing the electron to tunnel through.

$$\gamma = \frac{\omega \sqrt{2I_p}}{E_A}$$

Equation 1. The Keldysh parameter, γ , where ω is the laser frequency, I_{p} , is the ionization potential of the atom or molecule and E_A is the amplitude of the electric field

At peak intensities between 10¹²-10¹⁴ W/cm², mixing of the electronic states and structural deformation can occur.³ For even more intense fields, 10¹⁴ W/cm² and above, there can be further ionization events for the same atom or molecule through a process known as electron rescattering. This process was described quantum mechanically by Kulander and Di Mauro and was semiclassically by Corkum and by is known as the 'three step model'.¹⁹ First an electron is removed from the molecule through tunnel ionization. Since the electric field is oscillatory, the removed electron is accelerated back into the ion. Upon rescattering, there can either be loss of further electrons, causing multiple ionizations at once or the electron can be absorbed and the additional energy can be released as light, known as high harmonic generation (HHG).^{2,20,21}

1.3 Quantum Coherent Control

QCC of two-photon transitions in atoms was elegantly demonstrated by the use of a π -step spectral phase function. When the frequency at which the π step coincides with a two-photon resonance, a constructive quantum interference was predicted and observed in the transition probability; whereas, when the π -step was detuned from the resonance, the transition probability approached zero.²² The reason for the observed QCC feature was explained by Meshulach and Silberberg using perturbation theory. In their formulation, all quantum mechanical paths leading to the two-photon resonance are integrated (Equation 2),

$$\left|\int_{-\infty}^{\infty} A(\omega_0/2+\Omega)A(\omega_0/2-\Omega)\exp[i\{\phi(\omega_0/2+\Omega)+\phi(\omega_0/2-\Omega)\}]d\Omega\right|^2$$

Equation 2. Equation to describe the probability of excitation; where $A(\omega)$ and $\phi(\omega)$ are the frequency dependent amplitude of the field and the spectral phase of the pulse, respectively

where $A(\omega)$ and $\phi(\omega)$ are the frequency dependent amplitude of the field and the spectral phase of the pulse, respectively. The formula sums the phase for the high- and low-energy detuned photons, for every path. The trivial case being transform limited (TL) pulses, when all photons have a phase of 0 or π , the exponential term for each path becomes e^{i0} or $e^{i2\pi}$, which equals 1. The non-trivial QCC interference occurs when the phase step coincides with a two-photon resonant transition, such that one-half of the frequencies have a phase of 0 and the corresponding half of the frequencies have a phase of π . In that case, the phase dependent term is $e^{i\pi} = -1$ for all of the excitation paths. The absolute value squared makes the result independent of the sign of the phase step. Destructive interference occurs when half of the paths have a phase of 0 and the other half a phase of π . In that case, the two-photon excitation probability approaches 0.

Chapter 2: Quantum Coherent Control of H₃+

2.1 Introduction

QCC of laser-matter interactions is well known for two- and three-photon resonant transitions but not understood for higher order transitions. We explore the simplest approach, in this case a π spectral phase step (Figure 3a), to QCC on a chemical process requiring strong-field double ionization with the goal to determine if it is possible to have control of laser-matter interactions involving high order, 7- to 20-photon, excitation. A positive or negative π -step at the central frequency of the pulse causes the pulse to break into two parts of equal intensity, with a temporal phase change of π between the two. Interestingly, for the case of a $\pi/2$ spectral phase modulation applied in the center of the spectrum, there is a clear difference between a positive and negative step, as shown in Figure. 3b.



Figure 3. A (left) The spectrum of a pulse (solid) with a $\pi/2$ phase step (dashed). B (right) The effect of a positive (dashed) and negative (solid) $\pi/2$ phase step at its carrier frequency in the time domain.

QCC has been used to control two- and three-photon transitions in atoms and molecules in the gas phase²³ and in the condensed phase.²⁴ The transition probability dramatically decreases as the π phase step detuned from the central frequency of the pulse; furthermore, the higher the order transition, the less likely it is to occur (Figure 4). In the case of a two-photon transition, when the

phase step coincides with the two-photon resonance, a maximum in transition probability occurs. This is not present in the case of a seven-photon transition. It is clear to see that any transition to an excited state is almost non-existent, based on this perturbative approach to the process, for a seven-photon process when a phase step is applied.



Figure 4. Calculated QCC for a $\pi/2$ phase step with a two-photon transition (black) and seven-photon transition (red)

In the single ionization intensity regime, the resulting molecular ion has relatively low internal energy of excitation.^{25,26} Subsequent fragmentation of the resulting ion is dominated by stability and the probability of the ion to absorb one or more additional photons to reach dissociative states.²⁷ Under the conditions of double ionization, polyatomic organic molecules dissociate into a variety of fragments that range from the molecular ion to hydrogen and carbon atoms. This regime results in a large number of fragment ions, and their relative yield has defied a satisfactory explanation. On one hand, one may consider a molecule under such strong-field to behave as a "bag of atoms" for which there is little or no control and all statistically possible fragment ions are produced. On the other hand, the molecular structure and properties of the laser field may determine the dissociation into multiple fragments, implying that one can shape the field in order to exert control over the yield of different fragment ions.

The aforementioned studies concentrate on control of multiphoton processes; here we explore the effect of a phase step on the field ionization regime. Peak intensities up to $4 \times 10^{14} \text{ W/cm}^2$ will be used, resulting in a Keldysh parameter of 0.45. This means that tunnel ionization will be the dominant mechanism for ionization, followed by rescattering to higher ionization states. Assuming QCC is applicable, the ion yields will be suppressed. In the rescattering regime, transform-limited pulses should produce the highest ion yield and any phase step should suppress.

2.2 Experimental

The setup consists of a Titanium:Sapphire chirped pulse amplification laser system (800 nm, 25 nm FWHM, 1 mJ/pulse, 1 KHz) and a Wiley-McLaren time-of-flight (TOF) mass spectrometer. Pulses were measured to be at 800 nm with a 42 ± 2 fs duration at FWHM. Residual high-order dispersion was corrected for using the multiphoton intrapulse interference phase scan (MIIPS) technique.²⁸ The laser intensity was calibrated by measuring Ar^{2+}/Ar^{+} and N_{2}^{2+}/N_{2}^{+} ion yields^{29,30}. The purpose of the intensity calibration is to standardize the intensities used. The ratio of a doubly charged ion to its singly charged ion is independent to experimental errors and variations in equipment. The yield of Ar^{2+}/Ar^{+} was measured on our setup and compared to that of literature values to obtain the true intensities of our laser. Experiments were carried out at a pressure of 2 x 10⁻⁶ Torr and samples were outgassed, using multiple iterations of freeze-pump-thaw cycles, prior to introduction into the TOF chamber. The pulses were shaped using a dual-mask, two-dimensional (600x800 pixels), spatial light modulator (SLM). A typical π -step scan consisted of 200 masks, applied sequentially across the entire SLM range. At each mask, a TOF spectrum was obtained by integrating over 128 laser shots. Each ion-yield plot is an average of 10 scans and each set of scans were repeated 3 times to ensure reproducibility. The uncertainty in the measured signal is less than 5%. This uncertainty originates from the high non-linearity of the process, resulting in amplitude variation in the pulses.

To ensure that the induced phase step did not affect the laser focus (position and diameter of the beam waist), the focus of the beam was observed whilst applying phase steps across the pulse using a CCD (LaserCam HR, Coherent, Inc.). It was found that the maximum deviation recorded was 0.8 μ m. Considering that the 1/e² diameter for the focused beam is 66 ± 3.3 μ m, measured by the same CCD, the deviation measured can be attributed to the error of the measurement. Thus, it can be concluded that the phase step does not spatially move the focus point or affect the beam waist diameter.

QCC assumes resonant multiphoton transitions to excited states. We performed *ab initio* calculations to determine the states that would be accessible via multiphoton resonance for the given laser photon energy (1.550 eV) and bandwidth (0.0485 eV). The first and second ionization energies of methanol were obtained at the Coupled Cluster Single Double (Triple)/correlation consistent polarized Valence Double Zeta (CCSD(T)/cc-pVDZ) while using the ground state neutral structure geometry as obtained with CCSD/cc-pVDZ level of theory, this entitles our method as CCSD(T)/cc-pVDZ//CCSD/cc-pVDZ. Using the same geometry, excited states that would facilitate multiphoton resonance transitions were calculated at the equation-of-motion (EOM)-CCSD/cc-pVDZ level of theory. The results from these calculations are given in Figure 5 and indicate a resonance at seven photons which coincides with the first ionization. Double ionization requires 20 or 21 photons; both values are possible because of the laser pulse bandwidth.



Figure 5. First and second ionization energies of methanol (black) with intermediate excited states (red)

2.3 Results

The results obtained by scanning a π phase step across the spectrum of the laser whilst detecting different ions is shown in Figure 6. The yields of C²⁺ and H₃⁺ behave a theory predicts; namely, their yields decrease as the phase step is swept across the spectrum, reaching a minimum near ω_0 . However, the yield of CHO⁺ (or COH⁺, indistinguishable by TOF mass spectrum) did not follow this trend as yield enhancement above the transform-limit was observed. This significant deviation from theory occurs near the FWHM points in the spectrum.



Figure 6. Ion yield dependence as a function of phase step position. The spectra are normalized to the value when TL pulses are used. CHO^+ *in blue,* H_3^+ *in red and* C^{2+} *in grey.*

Since the significant deviation occurs near the FWHM of the spectrum. We scanned the magnitude of the phase step, increasing from 0 to 2π while keeping the step positions at each of the FWHM. The relative difference in the H₃⁺ yield, defined as the difference between the maximum yield in

each region of the spectrum $I(\omega_b) - I(\omega_r)$ (where ω_r is the maximum yield in the red region and ω_b is the maximum yield in the blue region) divided by the average $((I(\omega_b) + I(\omega_r))/2)$ where $\omega_r = -0.012$ eV and $\omega_b = 0.018$ eV relative to ω_0 , highlights that the ion yield is dependent on the position that the phase step is applied. We find that a π step makes little or no difference, but a positive or negative $\frac{3}{4}$ - π step across the spectrum results in the greatest relative difference (Figure



Figure 7. Relative difference in the yield of H_{3^+} ions $(I(\omega_b) - I(\omega_r))/((I(\omega_b) + I(\omega_r))/2)$ at three different laser intensities; 5.5 (dashed line), 4.3 (solid line) and 3.8 (dotted line) $\times 10^{14}$ W/cm². Notice that significant changes are observed for non-integer values of π .

After realizing that a $\frac{3}{4}\pi$ step scan show the greatest differences; we decided to scan this phase across the spectrum. Subsequently, large deviations in the ion yields were observed when the step is close to the FWHM of the pulse spectrum. CHO⁺ and H₃⁺ ion yield enhanced occurs when a negative phase step is located in the low energy region of the spectrum and when a positive phase step is located in the high energy region of the spectrum (Figure 8).



Figure 8. The yield of selected ions, H_{3^+} (red) and CHO⁺ (blue), detected as a function of scanning $a \pm 3/4 \pi$ step phase, $-3/4 \pi$ (hollow dots) and $+3/4 \pi$ (filled dots), across the spectrum normalized to their value when TL pulses. In addition to the experimental points, the solid line is from 5-point smoothing.

We measured the yield of all ions as a function of linear and circular polarized light. In the rescattering regime, the light is required to be linearly polarized. Following single ionization, the oscillating electron field returns the electron back to where it originated, causing further ionization events. When the light is circularly polarized, this does not happen. It can be seen in Figure 9, that the yield of ions C^{2+} and H_{3^+} decreases when the polarization of light is changed from linear to circular. Since the molecular ion only requires single ionization, it does not depend on the returning electron; thus, the yield CH_3OH^+ shows no dependence on the polarization of the light.



Figure 9. Ion yield dependence on the angle of polarization of the light at 4.8×10^{14} W/cm². At 0°, the light is circularly polarized, and at $\pm 45^{\circ}$, it is linear (parallel to the ToF axis).

In order to rule out that the observed changes in ion yields shown in Figure 8 depend only on peak intensity, measurements as a function of linear chirp (second order dispersion) were carried out. The results, shown in Figure 10, indicate that while the yield of the different ions depends on peak intensity, the ion yield decreases symmetrically, with H_3^+ decreasing more significantly than CHO⁺. At 1000 fs², the effective chirp introduced by the phase step, there is almost no difference, ~0.75%, between the positive and negative chirp ion yields.



Figure 10. Ion yield dependence on the amount of 2nd order dispersion (chirp) applied at a laser intensity of 4.8×10^{14} W/cm². H_3^+ is in red with square symbols, CHO⁺ is in blue with circular symbols, and the black dashed line is the second-harmonic intensity dependence, included as a reference.

2.4 Discussion

The first and second ionization energies for methanol require the absorption of 7 and 20 (~1.55 eV) photons respectively, based on our calculations, under the experimental conditions (Fig. 2). At the peak laser intensity, when the pulses are TL, the Keldysh parameter is 0.45;³¹ implying single ionization occurs predominantly through a tunneling mechanism. Subsequently, double-ionization likely occurs through rescattering ^{19,32}, as confirmed by the observed H₃⁺ yield decreasing when the polarization of the laser was changed from linear to circular (Figure 5).²⁰ Following strong-field ionization, some electrons remain in a coherent superposition of excited states (or Rydberg states), which oscillates with frequencies that closely correspond to the harmonics of the laser.^{33,34} These excited states are highly susceptible to further ionization, depending on the properties of the pulse.

One would expect that if a π phase step was applied to a 20-photon absorption process, the peak intensity reduction alone would cause a major reduction in ion yield. This would result in a significant depletion of all ion yields that require a doubly charged parent ion, such as H₃⁺. However, an overall depletion is not observed. Depending on the sign of π phase step we observe either depletion or enhancement. This is in contrast to the prediction by QCC theory, of an overall depletion that is symmetric about the center of the spectrum (see Figure 4).

The reader should note that a $\pm \frac{3}{4} \pi$ phase step has an asymmetric effect on the electric field similar to that shown a $\pm \frac{\pi}{2}$ phase step (Figure 3b). When the step is positive, the pulse breaks into a weaker portion that is followed by a more intense pulse, and vice versa. Analysis of our data showed that enhancement is observed for negative phase steps in the red region (ω_t) and positive phase steps in the blue region (ω_b). This indicates the temporal shape of the pulse I(t), i.e. the order of these sub-pulses, cannot be responsible for the observed enhancement. Therefore, a more complete description of the pulses that includes the time-dependent phase $\phi(t)$, and the instantaneous frequency of the pulse $\omega(t)$ were carried out and are shown in Fig. 11. From the analysis, we note that pulses that result in enhancement (Figures 11a and b) are associated with a downchirp during the more intense part of the pulse, indicated by a straight line. Pulses that resulted in yield depletion (Figures 11c and d) show an up-chirp in the portion of the pulse with greater intensity. Down-chirped pulses have been shown to increase vibrational excitation via intrapulse pump-dump processes similar to stimulated Raman scattering, increasing the ground state vibrational energy.³⁵⁻³⁷ However, recall that we found no difference in the ion yields between

positive or negative chirp (Figure 10). This implies that the abrupt change in phase following the downchirp is essential for the observed strong-field QCC effects being reported here.



Figure 11. The time-dependent intensity (black line) I(t), phase (dashed red line) $\Phi(t)$, and the instantaneous frequency of the pulse (blue line) $\omega(t)$ for the two cases where enhancement was observed, (a) $(-3/4\pi \omega_r)$ and (b) $(+3/4\pi \omega_b)$ and where suppression was observed (c) $(+3/4\pi \omega_r)$ and (d) $(-3/4\pi \omega_b)$. When the phase step causes enhancement, a downchirp is observed in the most intense feature of the pulse and is indicated by a dotted line. When there is yield suppression, there is an up-chirp in the frequency

At this moment, it is unclear if the shaped pulses are controlling the rescattering process leading to double ionization, or if the additional vibrational energy from the pump-dump process controls the fragmentation. If we are controlling the rescattering process, then we would predict that phase step pulses should exert similar control over atomic double ionization, as well as the multiple processes associated with rescattering such as high harmonic generation¹⁹. Proton migration has been recently controlled by the carrier envelope phase (CEP) of the incident strong field.³⁸ In that work, the vibrational wave packet formed by the pulse and double ionization were shown to depend CEP. Based on those observations, one would expect the downchirp in our experiments to induce molecular vibrations and the sudden change in phase to control the phase-dependent rescattering process. In future studies, we will investigate how the phase step pulses used here affect

rescattering by looking at much simpler molecules which can be supported by theory. Furthermore, we are planning to investigate if our observations are partly due to multiphoton resonances. In our experimental conditions, seven photons are required to singly ionize methanol. Experiments with different laser pulse wavelengths and on different compounds will help identify if electronic resonances are consistent with our experimental and theoretical observations.

2.5 A note on Ethane

More recent phase step experiments have been conducted on ethane. Ethane has the potential to shed light on the different ionization pathways due to its simple mass spectrum upon fragmentation. For a given molecular system double ionization is more likely to occur from two different atoms, hereafter sequential double ionization (SDI), than from a specific atom, hereafter referred to as localized double ionization (LDI). This assertion is made purely on energetic grounds following consideration of the Coulombic repulsion between two positive charges residing in a single atom. Therefore, understanding and controlling the behavior of molecules in strong fields requires the ability to discriminate between SDI and LDI processes, which has been accomplished via laser polarization³⁹. The purpose of this study was to identify fragment ions that can only be produced via SDI or LDI; essentially, SDI primarily leads to Coulomb explosion (CE) whereas, LDI does not. It was found that a phase step in a pulse can dramatically change the yield of ionization from LDI. This effect is due to a phenomena known as attochirp. Attochirp stems from the path taken by the recolliding electron in the '3-step model', which is dependent on the phase of the pulse and at what point during the laser-matter interaction single ionization occurs. Here, reducing attochirp enhances LDI while greater attochirp suppresses LDI.

This study was not completed at the time this thesis was written.

2.6 Conclusions

To conclude, we have applied shaped pulses with π , and non-integer values of π , phase steps to explore quantum coherent control of H₃⁺ yield following the strong laser field excitation of methanol. Our results show an unexpected seven-fold enhancement in the ion yield that at times exceeds that for transform-limited pulses. The enhancement is not predicted by perturbative QCC as derived for two- and three-photon excitation. Our experimental observation indicates strong field QCC on molecules that require multiphoton (>7) excitation is possible. However, it is clear that there are several complex processes occurring and the observed effects are not simply caused by a single variable such as the excitation frequency, the temporal intensity shape of the pulse, or the chirp. Therefore, we conclude the observed control results from a combination of temporal, spectral, and phase effects. We are carrying out experiments on small molecules and in isolated atoms in order to determine the generality of our findings, and the dependence on molecular parameters. Future experiments and theory are planned to determine the physical process leading to our observations.

2.7 Future Experiments

Completion of the study as to how a phase step affects attochirp would lead greater to control of LDI and SDI. This would open the door for further experiments on phase control; specifically, how phase control affects high harmonic generation.

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