Detection and Characterization of Unidirectional Molecular Rotation

by

Casey Bloomquist

B.A., Hamilton College, 2010

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

(Physics)

The University Of British Columbia

(Vancouver)

August 2012

© Casey Bloomquist, 2012
Abstract

The main goal of this work is the detection of the directionality of molecular rotation and the characterization of two experimental approaches to controlling the directionality of molecular rotation with ultrashort pulses. Control of the directionality of molecular rotation is desired in order to learn more about the internal properties of molecular systems as well as for studying and controlling molecular interactions. Further, the techniques for generating unidirectional molecular rotation must be studied to understand the properties of the molecular ensembles that are generated. In order to detect the directionality of molecular rotation, we use circular polarization sensitive resonance-enhanced multiphoton ionization spectroscopy to allow state-selective directionality detection. In this work we explain this technique and demonstrate its ability to measure the directionality of individual rotational states.

The two methods for controlling the directionality of molecular rotation are based on the molecular interaction with either a pair of pulses (a “double-kick” scheme) or a larger sequence of pulses (a “chiral pulse train” scheme). In both cases, rotational control is achieved by varying the polarization of and the time delay between consecutive laser pulses. The double-kick and chiral train methods have demonstrated the ability to control the directionality of molecular rotation but have not been extensively studied. In this work, we perform experiments with both the double-kick and chiral train techniques for thorough comparison and characterization of both methods. We show that both methods produce significant rotational directionality. We also demonstrate that increasing the number of excitation pulses enables one to control the sense of molecular rotation and predominately excite a single rotational state, i.e. quantum state selectivity. To further explore the capa-
bilities of both techniques we perform experiments on selectivity in mixtures of spin isomers and molecular isotopologues. We demonstrate the ability of both techniques to generate counter-rotation of molecular nuclear spin isomers (here, ortho- and para-nitrogen) and molecular isotopologues (here, $^{14}N_2$ and $^{15}N_2$).
Preface

Section 5.1 presents the results of the published paper,


S. Zhdanovich was the lead researcher of the work, supervised by V. Milner. A.A. Milner assisted with the circularly polarized detection technique and data collection. J. Floß and I. Sh. Averbukh provided numerical calculations and valuable discussion. I helped design and build the experimental setup, was responsible for interpreting the Resonance Enhanced Multi-Photon Ionization (REMPI) spectra and assisted with data collection. I wrote the section on REMPI in the paper and produced the REMPI figure.

Section 5.2 presents the results of a paper to be submitted for publication,

Directional Spinning of Molecules with Sequences of Femtosecond Pulses. C. Bloomquist, S. Zhdanovich, A. A. Milner and V. Milner.

In this work, I built the double-kick setup, performed experimental measurements and analysis and wrote the paper with assistance from S. Zhdanovich and A. A. Milner and under the supervision of V. Milner.

Additionally, I coauthored the published paper,

Quantum Resonances in Selective Rotational Excitation of Molecules with a Sequence of Ultrashort Laser Pulses. S. Zhdanovich, C. Bloomquist, J. Floß, I. Sh. Averbukh, J. W. Hepburn and V. Milner, Phys. Rev. Lett. 109, 143003, the results of which are not included as part of this thesis.
Table of Contents

Abstract ................................................................. ii
Preface ................................................................. iv
Table of Contents ....................................................... v
List of Tables ............................................................ viii
List of Figures ........................................................... ix
Glossary ................................................................. xv
Acknowledgments ........................................................ xvi

1 Introduction ............................................................ 1
  1.1 Unidirectional Molecular Rotation ............................... 1
  1.2 Detection of Unidirectional Molecular Rotation .......... 3
  1.3 Thesis Layout ................................................... 4

2 Unidirectional Molecular Rotation .................................. 6
  2.1 Laser-molecule Interaction ...................................... 6
    2.1.1 Classical Description .................................... 6
    2.1.2 Quantum Description .................................... 7
    2.1.3 Molecular Alignment .................................... 9
  2.2 Generating Unidirectional Molecular Rotation ............. 10
    2.2.1 Double-kick Technique of Molecular Spinning ....... 10

v
A.2.2 Excited State: $a^1\Pi_g$
List of Tables

Table 3.1  Two-photon Hönl-London factors for the $a^1\Pi_g \leftrightarrow X^1\Sigma_g^+$ transition in $N_2$ [1, 25]. M(O)-M(S) are transition dipole factors that depend on the rotational branch and control the relative strength of the branches. .............................................. 31
# List of Figures

| Figure 1.1 | Example \((X + Y)\) REMPI schemes. \(X\) number of photons raise the molecule to an excited state and \(Y\) photons ionize the molecule. | 3 |
| Figure 2.1 | Schematic of the laser-molecule interaction. | 7 |
| Figure 2.2 | Laser-molecule interaction. After time \(\Delta t\), the molecular ensemble aligns along the polarization axis. Then the molecules dephase and rephase. Due to the quantized nature of the molecular rotations, the molecular distribution repeats itself after a characteristic time \(T_{\text{rev}}\). | 10 |
| Figure 2.3 | Generating unidirectional molecular rotation with the double-kick method. The first pulse produces an aligned state. The second pulse produces a torque on the aligned ensemble, generating unidirectional rotation. | 11 |
| Figure 2.4 | Selective unidirectional molecular rotation. Molecules with a rotational velocity that is faster (dark blue) or slower (light blue) than the laser polarization rotation are slowed down or sped up, respectively, by the next pulse. The effect of multiple pulses is to narrow the distribution of molecular axis around the laser polarization. | 12 |
| Figure 3.1 | Rotational energy level structure of the \(X^3\Sigma_g^-\) ground state of oxygen. Only odd \(N\) states exist due to the nuclear spin statistics and the levels within each triplet do not lie in order of \(J\) values. | 14 |
Figure 3.2 Vector coupling diagram for Hund’s case (b) for the $X^3\Sigma_g^-$ ground state of oxygen. .................................................. 15
Figure 3.3 Vector coupling diagram for Hund’s case (a) for the $C^3\Pi_g^-$ excited state of oxygen. .................................................. 19
Figure 3.4 Rotational energy level structure of the $C^3\Pi_g^-$ excited state of oxygen with the multiplets $^3\Pi_0(F_1), ^3\Pi_1(F_2)$, and $^3\Pi_2(F_2)$. .................................................. 20
Figure 3.5 Experimental REMPI spectrum of oxygen at T=300 K. The contribution from each $F$-component is labelled. .................. 21
Figure 3.6 Experimental REMPI spectrum of jet-cooled oxygen. The contributions from $F_2$ and $F_3$ are labelled. The $F_1$ component is to the left of the $F_2$ component and is not included on this plot. At the low temperature of the supersonic beam ($T = 8$ K), only the lowest rotational levels are populated and the $F$-components do not overlap. .................. 22
Figure 3.7 Allowed two-photon transitions from the $N'' = 5$ rotational level of $X^3\Sigma_g^-$ to $3\Sigma_3^-(F_3)$. Transitions occur to each $F$-component of the excited state. Here, only $F_3$ is shown for clarity. On the left, the five allowed transitions are shown for each $J''$ state in the ground state triplet. On the right the same transitions are grouped by $\Delta N$ and show the seven allowed transitions, $\Delta N = -2, -1, 0, 1, 2, 3, 4$. .................. 23
Figure 3.8 Experimental (top) and simulated (bottom) REMPI spectra of $O_2$ at 300 K. .................................................. 25
Figure 3.9 Experimental (top) and simulated (bottom) REMPI spectra of $O_2$ at 8 K. Line assignments are shown. At 8 K, only $N'' = 1, 3$ are populated. .................................................. 26
Figure 3.10 Rotational energy level structure for the $X^1\Sigma_g^+$ ground state (including $J = 0$ dashed line) and the $a^1\Pi_g$ excited state (excluding the $J = 0$ dashed line) of nitrogen. .................. 27
Figure 3.11 Vector coupling diagram for the symmetric top. .................. 28
Figure 3.12 Experimental (top) and simulated (bottom) REMPI spectra of $N_2$ at 300 K. .................................................. 32
Figure 3.13  Experimental (top) and simulated (bottom) REMPI spectra of $N_2$ at 6.3 K. Line assignments are shown. At 6.3 K, only $J'' = 0, 1, 2$ are populated. The O-branch does not appear because the first O-branch transition is from $J'' = 3$.

Figure 4.1  Cold molecule source setup.
Figure 4.2  Schematic of Time-of-Flight (TOF) apparatus.
Figure 4.3  (a) Double-kick, two ultrashort pulses are delayed by time $\tau$ and the polarization is rotated pulse-to-pulse by an angle $\delta$. (b) Chiral train, a train of ultrashort pulses are delayed by time $\tau$ and the polarization is rotated pulse-to-pulse by an angle $\delta$.
Figure 4.4  Pulse shaping used for the double-kick technique.
Figure 4.5  Pulse shaping used for the chiral train technique.
Figure 4.6  Polarization sensitive cross-correlation setup.
Figure 4.7  Polarization sensitive cross-correlation results for chiral train with $\delta = \pi/4$. Top panel shows the measured (red) and calculated (green) pulse trains with non-rotating polarization and train period $\tau = 8$ ps. Lower panel shows the results of the polarization sensitive cross-correlation measurement for the chiral pulse train. White diamonds and dashed lines mark the peak positions of the non-linear signal for the 7 pulses in the train. The half-wave plate is rotated by $\approx 22.5^\circ$ from peak to peak, indicating that the polarization is rotated by $45^\circ$ between consecutive pulses ($\delta = \pi/4$).
Figure 4.8  Dependence of directionality signal on input power for chiral train (black triangles) and double-kick (red circles).
Figure 4.9  General experimental setup.
Figure 4.10 Normalized REMPI spectra of cold oxygen: experimental results (lower solid curve) and calculations (lower dashed line). Upper solid curve shows the spectrum of rotationally excited molecules (shifted up for clarity). Dashed vertical lines indicate the frequencies of transitions originated from a certain rotational state, labeled with the corresponding $N''$ numbers. Vertical arrows point at the two peaks which correspond mostly to $N''=3$, and $N''=5$ initial rotational states.  

Figure 4.11 Normalized REMPI spectra of $^{14}\text{N}_2$. Relevant peaks of the S-branch are labeled by the corresponding $N''$ numbers. Prior to the application of a femtosecond pulse train, the distribution of rotational population is thermal and corresponds to 6.3K (lower solid blue line - experiment, dashed green line - calculations [14]). At this temperature, only $J''=0, 1$ and 2 are populated significantly. An example of the REMPI spectrum of rotationally excited molecules is shown by upper solid red line. For the total laser kick strength used in our experiments, rotational states up to $J''=7$ are populated.  

Figure 5.1 Total excitation efficiency of oxygen molecules excited to $N''=3$ (a,c) and $N''=5$ (b,d) rotational state (note the difference in time scale). (a,b) - experimental data, (c,d) - numerical calculations. Each experimental data point represents an average over 150 probe pulses. Grayscale coding: (a,b) min: $S=0$, max: $S=1$ (arb.units); (c) min $P=0.1$, max $P=0.6$; (d) min: $P=0$, max: $P=0.35$.  

Figure 5.2 Directionality of molecular rotation for $N''=3$ (a,c) and $N''=5$ (b,d) state (note the difference in time scale). Grayscale coding: (a) min: $\varepsilon = -0.2$, max: $\varepsilon = +0.2$; (b) min: $\varepsilon = -0.4$, max: $\varepsilon = +0.4$; (c) min: $\varepsilon = -0.7$, max: $\varepsilon = +0.7$; (d) min: $\varepsilon = -0.8$, max: $\varepsilon = +0.8$.  

xii
Figure 5.3 Total excitation efficiency for $J'' = 3$ (a),(c) and $J'' = 4$ (b),(d) rotational states of nitrogen. (a),(b): double-kick excitation scheme, (c),(d): excitation with the chiral pulse train. In panel (b), the drop-off in signal at higher $\delta$ is caused by a drift of probe wavelength over the course of the scan (2-3 hours). . . . 55

Figure 5.4 Directionality of molecular rotation for $J'' = 3$ (a),(c) and $J'' = 4$ (b),(d) rotational states. (a),(b): double-kick excitation scheme, (c),(d): excitation with the chiral pulse train. The maximum/minimum directionality achieved is $\varepsilon = \pm 0.7$ with the double-kick and $\varepsilon = \pm 0.4$ with the chiral train technique. . . . . . . . . . 56

Figure 5.5 Directionality of molecular rotation for $J'' = 2 - 4$ with the double-kick (upper panel) and chiral pulse train (lower panel) excitation techniques. In both cases, the relative polarization angle between consecutive pulses is $\delta = \pi/4$. Vertical dashed lines denote $1/4 T_{\text{rev}}, 1/2 T_{\text{rev}}, 3/4 T_{\text{rev}}$ and full revival time $T_{\text{rev}}$. Higher $J$’s are not shown due to the low signal-to-noise ratio. . . . . 57

Figure 5.6 Normalized excitation efficiency (upper panel) and degree of directionality (lower panel) for $J = 2 - 5$ states excited with the chiral pulse train of period $\tau$ and pulse-to-pulse polarization angle of $\delta = \pi/4$. Vertical dashed lines indicate pulse periods for selective excitation of a particular rotational state and the corresponding directionality at that time (see text for details). Solid black vertical lines mark $1/4 T_{\text{rev}}$ and $3/4 T_{\text{rev}}$. . . . . . . . . . . . 59

Figure 5.7 Degree of rotational directionality for nitrogen isotopologues, $^{14}N_2$ (upper panel) and $^{15}N_2$ (lower panel), induced with the double-kick technique at $\delta = \pi/4$. Solid (dashed) lines indicate full (half) revival time for each molecule, $T_{\text{rev}} = 8.38$ ps for $^{14}N_2$, and $T_{\text{rev}} = 8.98$ ps for $^{15}N_2$. Black squares (circles) mark the values of $\tau$ resulting in clockwise (counterclockwise) rotation for $J = 3$ and $J = 4$. . . . . . . . . . . . . 60
Figure 5.8  Directionality measurements for $J'' = 3$ and $A = 2 - 4$ (left panel). The plots for each $A$ are offset for clarity. Right panel shows the calculated electric field envelopes for values of the modulation amplitude, $A$, from 2 to 4. The train period is $\tau = 4.5$ ps. Polarization rotation that occurs from pulse to pulse in a chiral pulse train is not shown in this figure.
Glossary

**CCD**  Charge-Coupled Device

**MCP**  Micro Channel Plate

**REMPI**  Resonance Enhanced Multi-Photon Ionization

**SLM**  Spatial Light Modulator

**TOF**  Time-of-Flight
Acknowledgments

I would like to thank my supervisor Dr. Valery Milner for the opportunity to work with a fantastic research group and for all of his support and guidance.

I would like to thank Dr. Sergey Zhdanovich for his help and support. Without him, I would not have been able to accomplish what I did. I would also like to thank Guillaume Bussiere for his assistance and valuable discussions.

I would like to thank my group members for creating a stimulating and exciting research environment, in particular, Martin Bitter and Gilad Hurvitz for providing an enjoyable office environment and Thom Drane for his advice and willingness to help with anything.

Finally, I would like to thank my family and friends for their love and support.
Chapter 1

Introduction

1.1 Unidirectional Molecular Rotation

The goal of coherent control is to drive a quantum system towards particular behavior and create molecular ensembles with specific, controllable characteristics. In this work, I focus on the control of molecular rotation.

Lasers have provided a useful tool in the control of molecular rotation, in particular with strong, ultrashort laser pulses. The timescale of ultrashort laser pulses ($10^{-15}$ seconds) is much shorter than the timescale of typical molecular rotation ($10^{-12}$ seconds), enabling effective rotational control and manipulation. The established technology of femtosecond pulse shaping, which enables one to control characteristics of the laser pulses (such as time duration and temporal shape) has led to interesting schemes for the control of molecular rotation. Control of molecular rotation with strong non-resonant laser fields has led to promising applications such as control of chemical reactions [28, 31] and control of molecular collisions with atoms [34] and surfaces [13, 21, 29, 33, 43]. The use of non-resonant laser fields for the control of molecular rotation means that it is not necessary to tune the laser excitation wavelength to the molecular resonances, making the whole approach very flexible.

Much focus has been placed on creating aligned ensembles of molecules using ultrashort pulse schemes [12, 16, 26, 31]. Alignment refers to a state of order of the molecular geometry with respect to a space fixed axis, for example the alignment
of the molecular axes along the laser polarization of a strong, ultrashort pulse [31]. Increasing the degree of molecular alignment has been achieved by employing a sequence of ultrashort laser pulses (a “pulse train”) [5, 22, 44].

However, there is no circular anisotropy, or preferred sense of direction, in the aligned ensembles. Circularly anisotropic ensembles may prove useful in extracting more information about the internal properties of the molecular system as well as for studying and controlling molecular interactions. One example of a circularly anisotropic molecular ensemble is an ensemble of molecules rotating in the same direction around a certain spatial direction. An ensemble of unidirectionally rotating molecules can be produced if the polarization of the applied laser field rotates. One such technique is known as the optical centrifuge [6, 17, 37, 38, 42]. The optical centrifuge was theoretically proposed by Karczmarek et al. [17] and later demonstrated by Villeneuve et al. [37] using two oppositely chirped, circularly polarized pulses, overlapping in time and space to produce a linearly polarized pulse that rotates unidirectionally with linearly increasing rotational speed. Molecules encountering the field align along the direction of the field polarization and accelerate with it, creating a unidirectionally rotating ensemble.

Another method to generate unidirectional molecular rotation is the double-kick technique, which uses a pair of laser pulses with the polarization rotated pulse to pulse [10, 19]. The molecules align to the polarization axis of the first pulse. If the polarization of the second pulse is rotated and the pulse is applied while the ensemble is aligned, the second pulse will generate field-free unidirectional molecular rotation. An additional method of creating unidirectional molecular rotation uses a so-called “chiral pulse train” [46]. The chiral train is a pulse train in which the polarization of the excitation field rotates from pulse to pulse by a controllable angle. Using pulse shaping techniques, the time delay between pulses and the pulse to pulse polarization rotation angle can be controlled, allowing control of the direction and speed of molecular rotation. In this work we perform experiments with both the double-kick and chiral train techniques for thorough comparison and characterization of both methods.
Figure 1.1: Example \((X + Y)\) REMPI schemes. \(X\) number of photons raise the molecule to an excited state and \(Y\) photons ionize the molecule.

1.2 Detection of Unidirectional Molecular Rotation

The detection of the directionality of molecular rotation presents an interesting challenge. In order to detect directionality, there must be some sense of directionality in the probe. Additionally, we use a state-selective probe technique in order to observe individual rotational states.

The state-selective detection technique we use is called Resonance Enhanced Multi-Photon Ionization (REMPI). For REMPI, a number of probe photons excite the molecule from the ground electronic state to an intermediate excited electronic state, through virtual states. Further probe photons ionize the molecule, which allows the use of Time-of-Flight (TOF) mass spectrometry for detection. Examples of a few REMPI schemes are shown in Figure 1.1. For our experiments, we use \((2+1)\) and \((2+2)\) REMPI schemes. These multiphoton excitation techniques have different selection rules than single photon techniques, allowing transitions that are not allowed with single photon selection rules and providing spectroscopic information that is typically not seen with single photon techniques. The REMPI
The REMPI technique is also mass selective when combined with TOF mass spectrometry, as in our experiments, thus enabling one to detect one molecular species from a mixture of many.

The REMPI technique is particularly useful for observing rotational structure in molecules. The REMPI probe pulses are generated by a tunable dye laser and are narrow enough to resolve the rotational energy structure of the molecule. For the typical REMPI measurement, the wavelength of the dye laser is scanned while the ionization signal is measured. The resulting spectrum provides information about the rotational population of the ground electronic state. Further information on REMPI spectra and rotational structure can be found in Chapter 3.

To detect the directionality of molecular rotation, we use circularly polarized REMPI probe pulses. A molecular state with a certain value $M_J$ of the projection of its total angular momentum on the laser beam axis, is coupled to the ionization continuum by a left circularly polarized probe field with an equal strength to that of a right circular polarization acting on a state with an opposite projection $-M_J$. Hence, the difference in the ionization rate between left and right circularly polarized probe pulses reflects the asymmetry in the $M$-distribution, or equivalently, the directionality of the induced rotation [19]. A Pockels cell is used to alternate the probe pulse from left to right circular polarization, pulse to pulse. The polarization was alternated pulse to pulse, rather than scan-to-scan as in [19], to measure directionality with high accuracy and low susceptibility to the power fluctuations of the dye laser.

The advantage of a state-selective directionality detection technique is the ability to measure the directionality of individual rotational states. This is particularly useful because, as will be seen later, different rotational states may rotate in opposite directions.

### 1.3 Thesis Layout

The focus of this work is the detection and characterization of unidirectional molecular rotation induced by the double-kick and chiral train techniques. The thesis layout is as follows. In Chapter 2, I explain the laser-molecule interaction and how unidirectional molecular rotation is generated. In Chapter 3, I provide the back-
ground necessary for the rotational state-resolved detection. I describe the molecular structure of the molecules used in experiments and explain how to simulate and analyze the REMPI spectra. In Chapter 4, I describe the various components of the experimental setup and the experimental procedures. In Chapter 5, I present the results of experiments on the use of the chiral train to generate unidirectional molecular rotation with oxygen and the characterization and comparison of the double-kick and chiral train techniques with nitrogen. In Chapter 6, I present the conclusions of this work and comment on future work.
Chapter 2

Unidirectional Molecular Rotation

In this chapter, I explain the laser-molecule interaction and how unidirectional molecular rotation is generated.

2.1 Laser-molecule Interaction

2.1.1 Classical Description

Consider the interaction between a classical polarizable diatomic molecule and a non-resonant, linearly polarized, intense laser field [7, 10]. The molecule and the laser field interact through the induced dipole moment,

\[ \vec{\mu} = \vec{\alpha} \cdot \vec{E} \]  (2.1)

where \( \vec{\alpha} \) is the polarizability of the molecule and \( \vec{E} \) is the electric field of the laser. The timescale of the ultrashort laser pulse (10\(^{-15}\) seconds) is much shorter than timescale of molecular rotation (10\(^{-12}\) seconds) and so the ultrashort laser pulse acts as an impulsive ‘kick’. The basic scheme of the laser-molecule is illustrated in Figure 2.1.

The potential energy of the interaction between the laser field and the induced
molecular polarization is given by \( \text{[2]} \) as,

\[
V(\theta, t) \propto -E^2(t)(\Delta \alpha \cos^2(\theta) + \alpha_\perp)
\]  

(2.2)

where \( \Delta \alpha = \alpha_\parallel - \alpha_\perp \), \( \alpha_\parallel \) and \( \alpha_\perp \) are the polarizabilities of the molecule parallel and perpendicular to the internuclear axis, \( \theta \) is the angle between the internuclear axis and the polarization of the laser field, and \( E(t) \) is the electric field strength. The effect of the kick is to rotate the molecule by providing a torque on the molecule, resulting in increased angular momentum. For the molecules we work with (oxygen and nitrogen), \( \alpha_\parallel \gg \alpha_\perp \) and so \( \Delta \alpha > 0 \). Hence, the potential energy gained by a molecule at angle \( \theta \) to the laser polarization can be approximated as

\[
V \propto -\cos^2 \theta
\]  

(2.3)

and the torque on the molecule, proportional to \( dV/d\theta \), is maximized when \( \theta = \pm \pi/4 \) [7, 10].

### 2.1.2 Quantum Description

In the quantum description, rotational excitation of a molecule by an off-resonant laser pulse is described by coherent population transfer into the higher rotational
states via rotational ladder climbing. The quantum description is required to de-
scribe relatively weak laser-molecule interactions when only low rotational states
are populated \[18\]. In this context, the potential of Equation 2.2 is added to the
system Hamiltonian and the solution of the corresponding Schrödinger equation
reveals the dynamics of the system. Depending on the amplitudes and phases of
the excited rotational states, the resulting quantum wavepacket describes classi-
cally aligned or spinning molecules.

We consider here the quantum theory of non-adiabatic rotational excitation
with short laser pulses following \[22\]. The Hamiltonian of a rigid rotor driven by
a short pulse is given by

\[
H = \frac{L^2}{2I} + V
\]

where \(L\) is the angular momentum operator, \(I\) is the moment of inertia of the
molecule and \(V\) is defined by Equation 2.2. The general solution of the unper-
turbed Hamiltonian (i.e. \(V = 0\)) is a superposition of spherical harmonics, given
by

\[
\Psi = \sum c_{n,m} Y_n^m(\theta, \phi).
\]

Starting with a single, ground state spherical harmonic

\[
\Psi(\theta, \phi, t = 0) = Y_0^0(\theta, \phi),
\]

the interaction with a short pulse in the impulsive approximation, i.e. when the
pulse is much shorter than the period of molecular rotation, results in the wave-
function

\[
\Psi(\theta, \phi, t = 0^+) = e^{iP\cos^2\theta} \Psi(\theta, \phi, t = 0),
\]

where

\[
P = \frac{\Delta \alpha}{4\hbar} \int E^2(t) dt
\]

describes the rotational kick strength measured by the amount of angular momen-
tum transferred from the laser field to the molecule \[16, 22\]. The wavefunction of
Equation 2.7 can be written as a superposition of spherical harmonics by expanding
the exponent

$$\Psi(\theta, \phi, t) = \frac{1}{4\pi} \sum_{l=0}^{\infty} c_l e^{-\frac{il(2l+1)\hbar}{I\Omega} t} Y_{2l}^0(\theta, \phi)$$

(2.9)

where $c_l$ are the expansion coefficients which depend on the kick strength.

Equation 2.9 shows that a single kick results in a coherent superposition of rotational states evolving in time. All the states in the superposition have the same azimuthal quantum number which is inherited from the initial state. The time evolution results in a periodic alignment of the ensemble in space [16]. The period of this alignment is known as revival time and is equal to $T_{rev} = 1/(2Bc)$. At this time, all the exponents in Equation 2.9 acquire phases which are integer multiples of $2\pi$.

$$-il(2l+1)\hbar/2BcI = -il(2l+1)(4\pi\hbar Ic)/2\hbar Ic$$

$$= -il(2l+1)(2\pi)$$

(2.10)

where $B = \hbar/4\pi Ic$.

### 2.1.3 Molecular Alignment

Now consider the effect of an ultrashort laser pulse on an isotropic ensemble of diatomic molecules. Because the acquired angular momentum is dependent on molecular orientation, molecules with different initial orientations in the ensemble rotate at different velocities, resulting in periodic dynamics of alignment and antialignment (see Figure 2.2). Molecules at $\theta = \pm\pi/4$ to the laser polarization receive the largest amount angular momentum and begin rotating faster than molecules closer to axis, which receive a smaller amount of angular momentum. A short time ($\Delta t$) after the laser pulse, the molecular ensemble is aligned along the polarization axis. The molecules at $\theta = \pm\pi/4$ to the laser polarization are further away from the polarization axis but rotate faster than molecules with smaller $\theta$. The molecules with $\theta \leq \pm\pi/4$ reach the polarization axis in approximately the same time ($\Delta t$) after the laser pulse, producing an aligned state as illustrated in Figure 2.2. The time, $\Delta t$, is on the order of a few hundred femtoseconds. At $T_{rev}$
after the laser pulse the molecules are in the same positions as they were when the laser pulse was applied due to the quantized energy spectrum of the molecular rotations. The revival time is on the order of picoseconds ($T_{\text{rev}} = 11.6$ ps for $O_2$, $T_{\text{rev}} = 8.38$ ps for $N_2$) which provides the opportunity to use additional pulses to further manipulate the molecular rotations.

2.2 Generating Unidirectional Molecular Rotation

2.2.1 Double-kick Technique of Molecular Spinning

To generate unidirectional molecular rotation, one may use the double-kick technique, a sequence of two pulses where the polarization rotates from pulse to pulse [10]. The first pulse interacts with the molecular ensemble and generates coherent molecular rotation. A subsequent pulse with polarization rotated by an angle $\delta$ will produce an angle dependent torque on the molecules, as described by Equation 2.2. If the molecules are isotropically distributed, the second pulse will generate molecular rotation equally in both directions. However, if the molecules are in an aligned state, the second pulse produces a torque on all of the molecules aligned along the polarization axis of the first pulse, which produces a unidirectionally rotating ensemble. This effect is illustrated in Figure 2.3.
2.2.2 State-Selective Unidirectional Molecular Rotation

In the previous section I discussed how to create ensembles of unidirectionally rotating molecules. By tailoring the polarization rotation and time delay between pulses, trains of ultrashort pulses can also be used to achieve state-selective unidirectional molecular rotation, that is selectively exciting a particular rotational state as well as controlling the direction of its rotation.

Consider a sequence of laser pulses with their linear polarization rotating from pulse to pulse with a velocity \( \Omega = \delta / \tau \), where \( \delta \) is the pulse-to-pulse polarization rotation angle and \( \tau \) is the time delay between pulses. If the rotational velocity of the laser polarization, \( \Omega \), matches the rotational velocity of a particular rotational state (illustrated by a blue colored molecule in Figure 2.4), there is no angle between the molecular axis and the laser polarization. According to Equation 2.2, the laser pulse will not affect the molecule. However, molecules that have rotational velocity that is slightly slower or faster than \( \Omega \) will be affected by the laser pulse in different ways, shown in Figure 2.4. A molecule that rotates faster than \( \Omega \) after the initial pulse (dark blue) will be slowed down by the next pulse while a molecule that rotates slower than \( \Omega \) (light blue) will be sped up. Additional pulses will cause rotational velocities of the molecules to be close to the polarization rotation velocity \( \Omega \), narrowing the distribution of the molecular axes around the rotating
Figure 2.4: Selective unidirectional molecular rotation. Molecules with a rotational velocity that is faster (dark blue) or slower (light blue) than the laser polarization rotation are slowed down or sped up, respectively, by the next pulse. The effect of multiple pulses is to narrow the distribution of molecular axis around the laser polarization.

The polarization rotation velocity can be controlled, by adjusting the time delay between pulses and the pulse-to-pulse polarization rotation, to match the rotational velocity of a particular rotational state. Thus, a particular rotational state can be selectively excited in a preferential direction. However, this is a classical description and molecular rotation follows quantum mechanics. In the classical description, the laser polarization is rotating in-sync with the molecular rotation of a particular rotational state. In the quantum description, a superposition of rotational states, rather than a single rotational state, is involved. The laser polarization rotates in-sync with a particular rotational wavepacket, which still enables state-selective unidirectional molecular rotation.
Chapter 3

Rotational State-Resolved Detection

3.1 Introduction

The use of REMPI allows us to perform rotational state-resolved detection. However, we must understand the REMPI spectrum in order to distinguish particular rotational states for our detection. To simulate the REMPI spectrum, we first calculate the energy level structure of the ground and excited state. Then, using selection rules, we determine the allowed transitions that occur. With the allowed transitions and transition probabilities, we can simulate the REMPI spectrum. Oxygen and nitrogen are used in experiments because they have high polarizability anisotropy ($\Delta \alpha$) that enable a strong laser-molecule interaction (see Equation 2.2). In this section I will describe the molecular structure of oxygen and nitrogen and how to use knowledge of the molecular structure to simulate and analyze the REMPI spectrum.

3.2 Oxygen

The first molecule we used in experiments was molecular oxygen, $O_2$. The rotational distribution was probed with (2+1) REMPI using the two-photon resonant transition, $C^3\Pi_g (v' = 2) \leftrightarrow X^3\Sigma_g^- (v'' = 0)$. Transitions are denoted with the excited state first (Excited State $\leftrightarrow$ Ground State). Other multi-photon transitions
Figure 3.1: Rotational energy level structure of the $X^3\Sigma_g^-$ ground state of oxygen. Only odd $N$ states exist due to the nuclear spin statistics and the levels within each triplet do not lie in order of $J$ values.

exist in oxygen, but most exhibit diffuse rotational structure. The $C^3\Pi_g$ excited state has rotationally resolved structure for the $\nu = 2$ vibrational band as characterized by Sur et al. [32]. REMPI via the $C^3\Pi_g(\nu' = 2) \leftrightarrow X^3\Sigma_g^-(\nu'' = 0)$ transition is sensitive enough to determine rotational state populations, thus allowing state-selective detection [32, 41].

3.2.1 Rotational Structure

Ground State: $X^3\Sigma_g^-$

The basic structure of the $X^3\Sigma_g^-$ ground state of oxygen is described in [4, 14] and shown in Figure 3.1. The vector coupling diagram for the ground state is shown in Figure 3.2. Spin-orbit (LS) coupling does not occur in the ground state because of the zero orbital angular momentum, $\Lambda = 0$. As a result, the non-zero spin angular momentum ($S = 1$) is not strongly coupled to the internuclear axis and the ground state follows Hund’s case (b). Each rotational level, $N$, is split into a “$\rho$-type
Figure 3.2: Vector coupling diagram for Hund’s case (b) for the $X^3\Sigma_g^-$ ground state of oxygen.

“triplet” due to the spin-rotation interaction, as well as the spin-spin interaction. The total angular momentum, $J$, is formed by the coupling of the total angular momentum excluding electron spin, $N$, and the electronic spin angular momentum, $S$. With $S = 1$, the possible values for the resultant total angular momentum, $J = N + S$, are $J = N, N \pm 1$. Because of the spin-spin interaction, the levels do not lie in order of $J$ values but rather the $J = N \pm 1$ levels nearly coincide and are below the $J = N$ level.

Only odd $N$ levels exist for the oxygen ground state due to molecular symmetry and nuclear spin statistics. The nuclei of oxygen are two identical bosons and so, the complete eigenfunction of the system must remain unchanged with respect to an exchange of the nuclei [14]. A molecular state that remains unchanged under an exchange of nuclei is called symmetric. The complete eigenfunction of the molecule is, to first approximation, a product of the electronic, vibrational and rotational eigenfunctions,

$$
\Psi = \psi_e \frac{1}{r} \psi_o \psi_r
$$

The vibrational eigenfunction ($\psi_o$) remains unchanged under an exchange of nuclei, the electronic eigenfunction ($\psi_e$) changes sign under an exchange of nuclei because the ground state is a $\Sigma^-$ state, and the rotational eigenfunction ($\psi_r$) remains unchanged or changes sign under an exchange of nuclei, depending on whether $N$
is even or odd. The complete eigenfunction of the molecule must be symmetric to satisfy the requirements of the oxygen nuclear spin statistics. This occurs when the rotational eigenfunction changes sign under an exchange of nuclei, which for $X^3\Sigma_g^-$ only occurs when $N$ is odd. Thus, the odd rotational states are symmetric and only the odd rotational states exist.

An expression for the energy levels of the $\rho$-type triplet was first provided by Kramers [20] which included the contribution of spin-spin interactions to the splitting. Kramers showed that the spin-spin interaction is equivalent to an interaction between $S$ and the molecular axis and thus depends only slightly on $N$, unlike the spin-rotation interaction. Schlapp [27] calculated energy levels including both the spin-spin interaction as well as the magnetic spin-rotation interaction, $\mu N \cdot S$. Mizushima and Hill [24] and Miller and Townes [23] both reexamined fine-structure formulas to get better agreement with experimental data but their approaches differ slightly in how they include the effects of centrifugal distortion. Mizushima and Hill include the effects of centrifugal distortion, under adiabatic assumption, in the Hamiltonian whereas Miller and Townes include the effects of centrifugal distortion with a rotational constant, $B$, that depends on $N$. The difference between these methods is not large because the centrifugal distortion effect is small. Further improvement of the energy level formulae involved including the centrifugal distortion effects on the spin-spin interaction [35], as well as including the dependence of the spin-rotation coupling constant, $\mu$, on nuclear vibrations [36].

For our calculations, we follow the method of Mizushima and Hill [24]. The Hamiltonian of the $\rho$-type triplet is

$$H = B|\mathbf{N}|^2 + 2\lambda(S_z^2 - |\mathbf{S}|^2) + \mu \mathbf{N} \cdot \mathbf{S}$$

where $S_z$ is the component of $S$ along the molecular axis, $\lambda$ is the spin-spin coupling constant and $\mu$ is the spin-rotation coupling constant. The first term represents the general rotational energy, the second term represents the spin-spin interaction averaged over spatial coordinates [20], and the third term represents the magnetic spin-rotation interaction [27]. With $|\mathbf{S}| = 1$, the matrix elements of the Hamiltonian
where \( J = |N + S| \) and the bases are chosen to make \( |N|^2 \) diagonal.

In Equation 3.3, the constants \( B, \lambda \) and \( \mu \) are assumed independent of \( N \). However, the constants can depend on \( N \) due to centrifugal distortion. Centrifugal distortion is the deformation of the molecule due to the centrifugal force. The molecular deformation leads to different values \( B, \lambda \) and \( \mu \) and the amount of centrifugal distortion is dependent on \( N \). As a result of centrifugal distortion, the constants \( B \) and \( \lambda \) become \( N \)-dependent

\[
B(N) = B_0 + B_1 N(N + 1) + \ldots \quad (3.4)
\]

\[
\lambda(N) = \lambda_0 + \lambda_1 N(N + 1) \quad (3.5)
\]

The \( N \)-dependence of the spin-rotation coupling constant, \( \mu \), can be neglected because \( \mu \) is very small with respect to \( B \) and \( \lambda \).

Including the effects of centrifugal distortion, the matrix elements of the Hamil-
tonian become,

\[ H = \begin{pmatrix}
B_0 J(J - 1) + B_1 J^2(J - 1)^2 & 0 & 0 \\
0 & B_0(J + 1)(J + 2) + B_1(J + 1)^2(J + 2)^2 & 0 \\
0 & 0 & B_0(J + 1) + B_1 J^2(J + 1)^2
\end{pmatrix} 
+ \begin{pmatrix}
-2 J \{ \lambda_0 + J(J - 1) \lambda_1 \} \\
2 \{ \lambda_0 + (J^2 + J + 1) \lambda_1 \} \{ J(J + 1) \}^{1/2} \ \\
0
\end{pmatrix} \left( \begin{pmatrix}
J \mu & 0 & 0 \\
0 & -(J + 1) \mu & 0 \\
0 & 0 & 0
\end{pmatrix} \right) \] (3.6)

The secular equation can be solved for the energies \( F_1(N) \), \( F_2(N) \) and \( F_3(N) \) of the \( \rho \)-type triplet, where \( F_1, F_2 \) and \( F_3 \) refer to levels with \( J = N + 1, N, \) and \( N - 1 \) respectively. Using values for the constants \( B_0, B_1, \lambda_0, \lambda_1, \) and \( \mu \) from [24], the energies \( F_1(N), F_2(N) \) and \( F_3(N) \) can be calculated. The details of the ground state energy level calculations are included in Appendix A.

**Excited State: \( C^3\Pi_g^- \)**

The \( C^3\Pi_g^- \) excited state follows Hund’s case (a) coupling, shown in Figure 3.3. The orbital angular momentum, \( L \), is strongly coupled to the internuclear axis and the electronic spin angular momentum, \( S \), is strongly coupled to \( L \) by spin-orbit coupling. With both \( L \) and \( S \) coupled to the internuclear axis, they have clearly defined axial components, denoted as \( \Lambda \) and \( \Sigma \) respectively. Due to spin-orbit coupling, the electronic angular momentum, \( \Omega \), is the sum of the projections of the electronic orbital angular momentum and electronic spin angular momentum on the internuclear axis. The electronic angular momentum couples with the angular momentum of nuclear rotation, \( R \), to form the total angular momentum \( J \). Spin-orbit coupling produces multiplet states that are the result of different values of \( \Omega \). For \( C^3\Pi_g^- \) with \( \Lambda = 1 \) and \( \Sigma = 1 \), the electronic angular momentum can take the
Figure 3.3: Vector coupling diagram for Hund’s case (a) for the $C^3\Pi_g^-$ excited state of oxygen.

values $\Omega = |A + \Sigma| = 0, 1, 2$, resulting in the multiplets $^3\Pi_0, ^3\Pi_1$, and $^3\Pi_2$ which are referred to as $F_1, F_2$ and $F_3$ respectively. Here, $\Omega$ is the axial component of $J$ and hence $J$ cannot be smaller than $\Omega$. For a given multiplet, $J$ can take the values, $J = \Omega, \Omega + 1, \Omega + 2, \ldots$, and levels with $J < \Omega$ do not exist. The rotational energy level structure of the $C^3\Pi_g^-$ state is shown in Figure 3.4. The relation between $J$ and $N$ is different for each of the three multiplets. $N$ is the total angular momentum excluding electron spin, such that $N = J - S$. Thus, with $S = 1$, $J = |N + S|$ produces the components $J = N + 1, N$, and $N - 1$ which correspond to $F_1$, $F_2$ and $F_3$ respectively. In Hund’s case (a), the rotational energy levels are similar to that of a symmetric top [14]. However, for multiplet states such as $C^3\Pi_g^-$ the spectroscopic constants have different values for each component and the energy levels for each component must be calculated separately. The energy levels for each component are given by

$$F_{(i)}(J) = v_0^{(i)} + B_v^{(i)} J(J+1) - D_v^{(i)} J^2(J+1)^2$$

(3.7)

where the $v_0$ is the band origin, $B_v$ is the rotational constant and $D_v$ is the centrifugal distortion constant. In our calculations, we use the spectroscopic constants from [41]. Details of the excited energy level calculations are included in Appendix A.
For multiplet states, $\Lambda$-type doubling splits each $J$ into two components, one symmetric and one antisymmetric [14]. The splitting increases at higher rotational energy (i.e. higher $J$). However, for low $J$’s, the magnitude of the $\Lambda$-type splitting is a small fraction of a cm$^{-1}$. Our experimental resolution is on the order of a few cm$^{-1}$, thus the $\Lambda$-type splitting can be neglected for our calculations [14].

### 3.2.2 REMPI Spectra

The room temperature spectrum generated by the (2+1) REMPI transition, $C^3\Pi_g(v' = 2) \leftrightarrow X^3\Sigma_g^-(v'' = 0)$ in oxygen is shown in Figure 3.5. The contribution from each $F$-component is illustrated on the spectrum. At room temperature (300K) the $F$-components overlap each other, complicating the spectrum. The spectrum also exhibits energy dependent linewidths, likely due to the energy specific Rydberg-valence interaction in the $^3\Pi$ state [32]. The $F_1$ and $F_2$ components have very broad linewidths and little rotationally resolvable structure while the $F_3$ component has
much narrower linewidths and rotationally resolvable structure. In our work, we focus on the rotationally resolved structure of $F_3$ component. The experimental spectrum of jet-cooled oxygen in a supersonic molecular beam is shown in Figure 3.6. Here, only the lowest rotational levels are populated, corresponding to the rotational temperature of 8 K. The $F$-components are well separated and, as in Figure 3.5, the $F_3$ component shows well resolved structure. Figure 3.5 and Figure 3.6 illustrate that the well resolved structure in $F_3$ remains as higher rotational levels are populated, which occurs when temperature increases or when the molecules are rotationally excited by off-resonance femtosecond pulses. This allows the identification and measurement of individual rotational levels and populations.

**Selection Rules**

In order to simulate the REMPI spectrum and identify particular rotational states, we need to understand the selection rules and allowed transitions in addition to the energy level structure of the ground and excited states. The selection rule for the
Figure 3.6: Experimental REMPI spectrum of jet-cooled oxygen. The contributions from $F_2$ and $F_3$ are labelled. The $F_1$ component is to the left of the $F_2$ component and is not included on this plot. At the low temperature of the supersonic beam ($T = 8 \text{ K}$), only the lowest rotational levels are populated and the $F$-components do not overlap.

Quantum number $J$ in the two-photon transition, $^3\Pi_g \leftarrow ^3 \Sigma_g^-$, is

$$\Delta J = J' - J'' = 0, \pm 1, \pm 2 \quad (3.8)$$

where $J'$ indicates the excited state $J$ and $J''$ indicates the ground state $J$. For homonuclear diatomic molecules, the symmetry selection rules are

$$s \leftrightarrow s, a \leftrightarrow a, s \not\leftrightarrow a \quad (3.9)$$

where $s$ indicates a symmetric state and $a$ indicates an antisymmetric state with respect to an exchange of nuclei. In the $X^3\Sigma_g^-$ ground state, each rotational level is symmetric, so transitions can only occur to symmetric rotational levels in the excited state. In the $C^3\Pi_g^-$ excited state, each rotational level is split into a symmetric and antisymmetric level due to $\Lambda$-type doubling. As a result, transitions to each $J'$ are allowed as transitions can occur to the symmetric component of each $J'$. 

22
Figure 3.7: Allowed two-photon transitions from the \( N'' = 5 \) rotational level of \( X^3\Sigma_g^- \) to \( 3\Sigma_3^- (F_3) \). Transitions occur to each \( F \)-component of the excited state. Here, only \( F_3 \) is shown for clarity. On the left, the five allowed transitions are shown for each \( J^0 \) state in the ground state triplet. On the right the same transitions are grouped by \( \Delta N \) and show the seven allowed transitions, \( \Delta N = -2, -1, 0, 1, 2, 3, 4 \).

In our experiments, the spin structure of the ground state is not resolved and only individual \( N'' \) levels, not individual \( J'' \) levels, can be observed. As a result, the selection rules for \( \Delta J \) become selection rules for \( \Delta N \) [32]. The selection rule for the quantum number \( N \) is

\[
\Delta N = N' - N'' = 0, \pm 1, \pm 2, 3, 4.
\]  

The transition from \( \Delta J \rightarrow \Delta N \) selection rules is illustrated in Figure 3.7. The 5 allowed transitions (Equation 3.8) from each level of the \( \rho \)-type triplet in the ground state produce 15 rotational branches. These 15 branches turn into 7 rotational branches (Equation 3.10) when grouped in terms of \( \Delta N \).
branches are labelled by a letter as follows: O($\Delta N = -2$), P($\Delta N = -1$), Q($\Delta N = 0$), R($\Delta N = 1$), S($\Delta N = 2$), T($\Delta N = 3$), U($\Delta N = 4$).

**Numerical Simulations**

To simulate the REMPI spectrum, we first calculate the energy levels for the ground state and the excited state. We can then apply the selection rules and calculate the transition frequencies, $\nu = F_{(0)}(J'') - F(J^0)$, of the allowed transitions (Equation 3.10). The spin splitting components ($F_1$, $F_2$, and $F_3$) are treated as separate excited states for the transition calculations and recombined to simulate the spectrum. In order to simulate the REMPI spectrum, we need to know the transition intensities as well as the transition frequencies. The transition intensity can be determined from the population of each state and the transition probability,

$$I_{J'\rightarrow J''} = \frac{\nu C_F}{Q_r} (J' + J'' + 1)e^{-F(J'')hc/kT}$$

(3.11)

where $Q_r$ is the rotational partition function,

$$Q_r = \sum_{J''=0}^{\infty} (2J'' + 1)e^{-F(J'')hc/kT},$$

(3.12)

$C_F$ is the intensity factor of the transition, $F(J'')$ is the energy of the ground state rotational level in wavenumbers, and $\nu$ is the transition frequency [14]. The transition probability is not the same for each band and depends on both $J$ and $\Delta J$. The factor $(J' + J'' + 1)$ is used, instead of the degeneracy factor $(2J'' + 1)$, so that the intensity depends on the mean value of $(2J + 1)$ for the upper and lower states [14]. The intensity factor, $C_F$, is different for transitions to the different spin splitting components, $F_1$, $F_2$, and $F_3$. We obtain the intensity factors by fitting the simulation to experimental spectra at various temperatures. Once we have calculated the transition frequencies and intensities, we overlay the spectrum with a lorentzian function to simulate the linewidth. The linewidth is then a parameter we can input into our simulations.
Two-photon Energy (cm$^{-1}$)

REMPI Signal

69324
69444
69565
69686
69808
69930

Experiment, thermal
Simulation, 300 K

Friday, May 25, 12

Figure 3.8: Experimental (top) and simulated (bottom) REMPI spectra of O$_2$ at 300 K.

Spectral Analysis

The REMPI spectra provide information about the rotational state populations in the ground state. We simulate room-temperature and low-temperature REMPI spectra and compare to the experimental spectra to match the transition frequencies and identify which rotational state each peak corresponds to. Using the results of the simulation, we can assign branches ($\Delta N$) as well as the initial rotational state ($N''$) to the peaks [32]. The experimental and simulated spectra for $T=300K$ and $T=8K$ ($F_3$) are shown in Figure 3.8 and Figure 3.9. Only five $\Delta N$ branches ($\Delta N = 0, 1, 2, 3, 4$) are seen rather than the seven branches from Equation 3.10. This is because, when $T=8K$, only $N'' = 1$ and $N'' = 3$ are populated. The lowest $N'$ level in the $F_3$ component of the excited state is $N' = 3$ so the lowest $\Delta N$ transition that can occur is $\Delta N = 0$ from $N'' = 3$.

3.3 Nitrogen

The second molecule we used in experiments was molecular nitrogen, N$_2$. The rotational distribution was probed with (2+2) REMPI using the two-photon reso-
Two-photon Energy (cm$^{-1}$)

$Q (\Delta N=0)$

$R (\Delta N=1)$

$S (\Delta N=2)$

$T (\Delta N=3)$

$U (\Delta N=4)$

Figure 3.9: Experimental (top) and simulated (bottom) REMPI spectra of $O_2$ at 8 K. Line assignments are shown. At 8 K, only $N'' = 1, 3$ are populated.

rotant transition, $a^1\Pi_g (v' = 1) \leftrightarrow X^1\Sigma_g^+ (v'' = 0)$. Nitrogen was used because the REMPI spectrum is much less congested than oxygen, allowing rotational state resolved detection for many initial states.

3.3.1 Rotational Structure

Ground State: $X^1\Sigma_g^+$

The singlet $\Sigma$ ground state of nitrogen has zero spin ($S = 0$) and zero orbital angular momentum ($\Lambda = 0$). Thus, the angular momentum of nuclear rotation is the same as the total angular momentum, $J$ and the molecule behaves like a rigid rotor [14]. For a simple rotor, there is no distinction between Hund’s case (a) and (b). The energy level structure for the $X^1\Sigma_g^+$ is shown in Figure 3.10. Unlike oxygen, there
Figure 3.10: Rotational energy level structure for the $X^1\Sigma_g^+$ ground state (including $J = 0$ dashed line) and the $a^1\Pi_g$ excited state (excluding the $J = 0$ dashed line) of nitrogen.

is no spin-splitting in singlet ground states and both even and odd $J$ levels exist. For $\Sigma^+$ states, the even rotational levels are symmetric and the odd rotational levels are antisymmetric [14]. As a result there are two possible $J$ parities, resulting in spin isomers, which will be discussed further in Section 3.3.2. Additionally, there is no need to use the quantum number $N$ because for singlet states, $J = N$.

Excited State: $a^1\Pi_g$

The excited state, $a^1\Pi_g$, is a singlet state ($S = 0$) with a non-zero orbital angular momentum ($\Lambda = 1$). Like the ground state, there is no distinction between Hund’s case (a) and (b) and the state behaves like a symmetric top, shown in Figure 3.11. The energy level structure of $a^1\Pi_g$ is the same as the ground state structure shown in Figure 3.10 except it has no $J = 0$ level. The total angular momentum cannot be smaller than the axial component of the electronic orbital angular momentum, $\Lambda$, and for a given $\Lambda$,
Figure 3.11: Vector coupling diagram for the symmetric top.

\[ J = \Lambda, \Lambda + 1, \Lambda + 2, \ldots \] (3.13)

In a \( \Pi \) state, \( \Lambda = 1 \), so \( J = 1 \) is the lowest rotational level in the excited state. In the excited state, \( \Lambda \)-type doubling splits each \( J \) into two components, one symmetric and one antisymmetric. The magnitude of the \( \Lambda \)-type splitting is very small and is neglected in our calculations.

The energy levels of the ground and excited states are calculated in the same way, using the appropriate rotational constants, \( T_e, \omega_e, \omega_ex_e, \omega_ey_e, B_e, D_e, \alpha_e, \gamma_e \), and \( \beta_e \) from [15]. The energy of a particular rotational level is calculated as the sum of the vibrational and rotational energy, given by

\[ T(v, J) = G(v) + F(v, J) \] (3.14)

where the vibrational energy is

\[ G(v) = \omega_e(v + \frac{1}{2}) - \omega_ex_e(v + \frac{1}{2})^2 + \omega_ey_e(v + \frac{1}{2})^3 \] (3.15)

and the rotational energy is

\[ F(v, J) = T_e + B_vJ(J + 1) - D_vJ^2(J + 1)^2 \] (3.16)
with

\[ B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 \]  
(3.17)

\[ D_v = D_e + \beta_e(v + \frac{1}{2}) \]  
(3.18)

The constants \( B_v \) and \( D_v \) are calculated to include the effects of vibration on rotation.

### 3.3.2 REMPI Spectra

#### Selection Rules

The selection rule for the quantum number \( J \) in the two-photon transition, \( ^1\Pi_g \leftarrow ^1\Sigma^+ \) is

\[ \Delta J = J' - J'' = 0, \pm 1, \pm 2 \]  
(3.19)

The five allowed transitions lead to five branches: O(\( \Delta J = -2 \)), P(\( \Delta J = -1 \)), Q(\( \Delta J = 0 \)), R(\( \Delta J = 1 \)) and S(\( \Delta J = 2 \)). Although the \( J \) levels in the excited state are split due to \( \Lambda \)-type doubling, the rotational branches do not get split into two components because of the symmetry selection rules. Nitrogen is a homonuclear diatomic molecule and has the same symmetry selection rules as oxygen,

\[ s \leftrightarrow s, a \leftrightarrow a, s \leftrightarrow a \]  
(3.20)

Because the ground state rotational levels are either symmetric or antisymmetric, transitions only occur to one component of the \( \Lambda \)-type doubling.

#### Numerical Simulations

To simulate the REMPI spectrum, we first calculate the energy levels for the ground state and the excited state, then we apply the selection rules and calculate the frequencies, \( \nu = T(1, J') - T(0, J'') \), of the allowed transitions (Equation 3.19). The intensity of each transition is calculated using the method of Aoiz et al. [1]. The
intensity of given transitions is given by

\[ I_{J' \rightarrow J''} = g_{J''} \frac{S_{J'J''}}{2J'' + 1} P_{J''} \]  

(3.21)

where \( g_{J''} \) is the spin-degeneracy factor for ortho- and para-nitrogen, \( S_{J'J''} \) is the rotational transition strength (i.e. two-photon H"onl-London factor) for the \( J' \leftrightarrow J'' \) transition. \( P_{J''} \) is the relative population of each rotational level, \( J'' \), in the ground state. In this work we simulate thermal rotational distributions using a Boltzmann distribution. The thermal ground state population is given by,

\[ P_{J''} = \frac{(2J'' + 1)}{Q} e^{-T(0,J'')\hbar c/kT_{rot}} \]  

(3.22)

where \( T(0,J'') \) is the ground state energy (in wavenumbers) from Equation 3.14, \( Q \) is the partition function and \( T_{rot} \) is the rotational temperature.

The spin-degeneracy factor depends on the parity of \( J'' \) and takes on different values for odd \( J'' \) and even \( J'' \). Linear symmetric molecules with non-zero nuclear spin can exist in nuclear states with differing symmetry, called ortho or para spin isomers. For \(^{14}\text{N}_2\), the nuclei are bosons with nuclear spin \( I = 1 \). With \( I = 1 \), the possible components of nuclear spin angular momentum are \( M_I = +1, 0, -1 \) and the resulting nuclear wavefunctions are:

\[ \psi^{(1)} = \psi^{+1} \psi^{+1} \quad \psi^{(4,5)} = \psi^{+1} \psi^{0} \pm \psi^{0} \psi^{+1} \]  

(3.23a)

\[ \psi^{(2)} = \psi^{0} \psi^{0} \quad \psi^{(6,7)} = \psi^{+1} \psi^{-1} \pm \psi^{-1} \psi^{+1} \]  

(3.23b)

\[ \psi^{(3)} = \psi^{-1} \psi^{-1} \quad \psi^{(8,9)} = \psi^{-1} \psi^{0} \pm \psi^{0} \psi^{-1} \]  

(3.23c)

where there are 6 symmetric (\( \psi^{1,2,3,4,6,8} \)) and 3 antisymmetric (\( \psi^{5,7,9} \)) nuclear wavefunctions. The total wavefunction of the molecule must be symmetric with respect to exchange of the nuclei. Therefore, the symmetric nuclear wavefunctions are combined with the symmetric rotational wavefunctions and the antisymmetric nuclear wavefunctions are combined with the antisymmetric rotational wavefunctions to produce a symmetric total wavefunction. As mentioned previously, in the ground state of nitrogen, even \( J'' \) rotational levels are symmetric and odd \( J'' \) rotational levels are antisymmetric. The molecules with symmetric nuclear wave-
The rotational transition strengths, $S_{J''J'''}$, for the five rotational branches are given in Table 3.1 [1, 25]. The $M(O)$-$M(S)$ constants are transition dipole factors that depend on the rotational branch and control the relative strength of the branches [25]. The $M$-constants are independent of $J''$ and are constant within a rotational branch. In our simulation, the $M$-constants are determined by fitting to experimental spectra.

Once we have calculated the transition frequencies and intensities, we convolve the spectrum with a lorentzian function to simulate the linewidth. We determine the linewidth by fitting our simulation to experimental data.

### Spectral Analysis

The REMPI spectra provide information about the rotational state populations in the ground state. We simulate room-temperature and low-temperature REMPI spectra and compare to the experimental spectra to match the transition frequencies and identify which initial rotational state each peak corresponds to. Using the results

---

**Table 3.1**: Two-photon Hönl-London factors for the $a^1\Pi_g \leftrightarrow X^1\Sigma_g^+$ transition in N$_2$ [1, 25]. M(O)-M(S) are transition dipole factors that depend on the rotational branch and control the relative strength of the branches.

<table>
<thead>
<tr>
<th>Branch</th>
<th>$S_{J''J'''}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O ($\Delta J = -2$)</td>
<td>$M(O) \frac{J''(J''-2)}{3(2J''-1)}$</td>
</tr>
<tr>
<td>P ($\Delta J = -1$)</td>
<td>$M(P) \frac{(J''+1)}{6}$</td>
</tr>
<tr>
<td>Q ($\Delta J = 0$)</td>
<td>$M(Q) \frac{(2J''+1)}{2(2J''-1)(2J''+3)}$</td>
</tr>
<tr>
<td>R ($\Delta J = 1$)</td>
<td>$M(R) \frac{J''}{6}$</td>
</tr>
<tr>
<td>S ($\Delta J = 2$)</td>
<td>$M(S) \frac{(J''+3)(J''+1)}{3(2J''+3)}$</td>
</tr>
</tbody>
</table>

functions (even $J''$) are called ortho-nitrogen and the molecules with antisymmetric nuclear wavefunctions (odd $J''$) are called para-nitrogen. The ortho/para ratio is 2:1 and so in Equation 3.21, $g_{\text{even}J''} = 2$ and $g_{\text{odd}J''} = 1$.

The rotational transition strengths, $S_{J''J'''}$, for the five rotational branches are given in Table 3.1 [1, 25]. The $M(O)$-$M(S)$ constants are transition dipole factors that depend on the rotational branch and control the relative strength of the branches [25]. The $M$-constants are independent of $J''$ and are constant within a rotational branch. In our simulation, the $M$-constants are determined by fitting to experimental spectra.

Once we have calculated the transition frequencies and intensities, we convolve the spectrum with a lorentzian function to simulate the linewidth. We determine the linewidth by fitting our simulation to experimental data.

### Spectral Analysis

The REMPI spectra provide information about the rotational state populations in the ground state. We simulate room-temperature and low-temperature REMPI spectra and compare to the experimental spectra to match the transition frequencies and identify which initial rotational state each peak corresponds to. Using the results
of the simulation, we can assign branches ($\Delta J$) as well as the initial rotational state ($J''$) to the peaks. We confirm our line assignments by comparing with [1]. Experimental and simulated spectra for $T=300 \text{ K}$ and $T=6.3 \text{ K}$ are shown in Figure 3.12 and Figure 3.13. The 300 K simulation shows very good agreement with the experimental spectrum. The linewidth is small (simulated linewidth = 0.4 cm$^{-1}$) and even at 300 K the peaks are, for the most part, distinct and well separated. Some spectral congestion occurs, especially in the S-branch, and some peaks are overlapped. The line assignments are shown for $T = 6.3 \text{ K}$ in Figure 3.13 and only the P, Q, R, and S branches are seen. The first O-branch transition is from $J'' = 3$ but at $T=6.3 \text{ K}$, only $J'' = 0, 1, 2$ are significantly populated. Also, the R-branch transition from $J'' = 0$ does not appear because the transition strength for the R-branch (Table 3.1) is zero when $J'' = 0$. The S-branch shows well separated peaks, allowing the measurement of individual $J''$ state populations. This separation continues $J'' = 0 - 7$ but after $J'' = 7$, successive transitions of the S-branch occur at lower and lower energies producing a band head at around 70660 cm$^{-1}$ (as seen on the

**Figure 3.12:** Experimental (top) and simulated (bottom) REMPI spectra of $N_2$ at 300 K.
Figure 3.13: Experimental (top) and simulated (bottom) REMPI spectra of $N_2$ at 6.3 K. Line assignments are shown. At 6.3 K, only $J'' = 0, 1, 2$ are populated. The O-branch does not appear because the first O-branch transition is from $J'' = 3$. far right of Figure 3.12).
Chapter 4

Experimental Setup

4.1 Molecular Source

To generate unidirectional molecular rotation, one needs molecules with a high polarizability anisotropy ($\Delta \alpha$) (see Equation 2.2). We used oxygen and nitrogen for our experiments. For oxygen ($\Delta \alpha = 7.26 \text{ a.u}$) and nitrogen ($\Delta \alpha = 4.87 \text{ a.u}$), the polarizibility anisotropy is sufficient to generate efficient laser-induced rotational excitation (kick strength of $P \approx 7$ for oxygen and $P \approx 5$ for nitrogen) [30]. Also, as previously mentioned, the duration of the laser pulse must be shorter than the period of the fastest molecular rotation. The period of molecular rotation for a particular $J$ can be approximated as $T_{\text{rev}}/J$, where for oxygen, $T_{\text{rev}} = 11.6 \text{ ps}$, and for nitrogen, $T_{\text{rev}} = 8.38 \text{ ps}$. In the oxygen experiments, we excite up to $\approx J = 20$, resulting in a period of molecular rotation of 580 fs and in the nitrogen experiments we excite up to $\approx J = 10$, resulting in a period of molecular rotation of 840 fs. With a pulse duration on the order of 100-200 fs, the duration of the laser pulse remains shorter than the period of molecular rotation for $J$’s much higher than we excite in our experiments.

In order to observe laser-induced rotational excitation, one needs molecules prepared in the low rotational states i.e. low rotational temperature. In our experiments, this is achieved by supersonic gas expansion. A pulsed valve is used for the supersonic expansion, rather than a continuous jet, to reduce the background pressure and vacuum pump load. The cold molecule source, shown in Figure 4.1,
was composed of a vacuum chamber and pumps, a pulsed valve and nozzle, and a skimmer. The vacuum chamber was pumped by a 1000 l/sec turbomolecular pump backed by an Edwards 40 oil rotary pump (74 m³/hr pumping speed). For oxygen, we used a General Valve with a 200 µm nozzle diameter which produced 250 µs pulses. With the valve operating at 10 Hz repetition rate and 6-8 bar of back pressure, a pressure of 10⁻⁴ Torr was maintained in the source chamber. For nitrogen, we used an Even-Lavie valve, model EL-5-C-S.S.-2020, with a 150 µm nozzle diameter which produced 20-30 µs pulses. With the valve operating at 10 Hz repetition rate and 6-10 bar of back pressure, a pressure of 10⁻⁵ Torr was maintained in the source chamber. The jet passes through a 1 mm diameter skimmer and enters the source chamber. The nozzle was mounted on a movable stage and the distance between the nozzle and the skimmer was controlled from outside the chamber. The rotational temperature of the jet depends on the back pressure and the ratio between the nozzle diameter and the nozzle-to-skimmer distance. For oxygen experiments, the nozzle-to-skimmer distance was approximately 4 cm and for nitrogen experiments, the nozzle-to-skimmer distance varied from 2-7 cm.

Figure 4.1: Cold molecule source setup.
In our setup, we achieved rotational temperatures as low as 7-8 K for oxygen and 6-7 K for nitrogen. The rotational temperature was determined by fitting the REMPI spectra of the jet-cooled molecules to the simulation. Figure 3.9 and Figure 3.13 show the low temperature REMPI and simulation fit for oxygen and nitrogen, respectively.

### 4.2 Detection Chamber

After the molecules leave the source chamber they enter the detection chamber and are detected with a combination of REMPI and TOF mass spectrometry. Molecules are ionized by (2+1) or (2+2) REMPI and then detected using a TOF apparatus as shown in Figure 4.2. The molecular ions are extracted from the interaction region and accelerated by electric fields between the plates. The bottom plate repels the positive ions, extracting them from the interaction region. The second set of plates accelerates the ions into the free flight region. The middle plate has a 1.5 mm orifice to limit the size of the sampling zone along the laser beam direction. After travelling through the drift tube, the ions are detected by a Micro Channel Plate (MCP) detector.
The MCP detector is 18 mm in diameter and is concentric with the 1.5 mm hole in the middle of the second TOF plate. The molecules from the supersonic expansion have significant longitudinal velocity before ionization. Thus, if the time of flight was long enough, the ion trajectory could miss the active area of the MCP. In our experiments, the time of flight was less than 5 µs for both oxygen and nitrogen, allowing detection of molecules with longitudinal speeds of up to 1800 m/s.

TOF mass spectrometry is used to mass discriminate between ions and ensure that we detect the correct molecules. All ions are given the same energy in the extraction, so light ions will travel faster than heavy ions. In the free-flight tube the electric field is zero and, if the flight time is long enough, the ions travelling with different velocities become separated in time. We observe the MCP signal as a function of time which shows the mass spectrum of the ionized molecules. Using the mass spectrum, we can confirm that we are detecting our target molecule and not a background molecule.

The chamber was pumped by a turbomolecular pump (210 l/sec pumping speed) producing pressures on the order of $10^{-9}$ Torr without the pulsed molecular beam and $10^{-7}$ while the beam was operating. The detected ion signal from the MCP was gated and integrated with a boxcar integrator. Typically, the detected ion signal was averaged over 10-100 probe pulses.

### 4.3 Probe Techniques

The REMPI technique was discussed in Chapter 3. Here we describe the experimental details of the REMPI detection.

The REMPI probe is generated by a tunable dye laser (Sirah PrecisionScan) pumped by a Nd:YAG laser (Quanta-Ray GCR-4, 3.4 W at 532 nm). The probe laser system operates at 10 Hz and produces narrowband, nanosecond pulses. The dye laser output is frequency doubled to obtain the wavelength needed for the REMPI transitions in oxygen and nitrogen. The laser wavelength range required for the REMPI transition in oxygen is 285-289 nm and in nitrogen is 283-285 nm. The dye used to achieve both wavelength ranges was Rhodamine 6G (tuning range: 559-576 nm, efficiency: 28%, peak efficiency: 566 nm). The Sirah dye laser has
three dye cells: a preamplifier and two amplifiers. The dye concentrations used for the preamplifier, first amplifier and second amplifier were 0.09, 0.045 and 0.0225 grams/liter for oxygen and 0.105, 0.066 and 0.043 grams/liter for nitrogen. The concentrations were adjusted for nitrogen REMPI to move the peak efficiency to the middle of the nitrogen wavelength range.

The frequency doubled dye laser output is separated from the fundamental radiation with a dichroic mirror and sent to the chamber using prisms. The beam is sent through a telescope to increase the beam diameter to avoid damaging the polarization optics and a polarizing cube to produce linear polarization. A Pockels cell is used to alternate circular polarization of the consecutive probe pulses between left and right to measure the directionality of molecular rotation with high accuracy and low susceptibility to the power fluctuations of the nanosecond dye laser. Details can be found in Chapter 5 and in [46]. The beam is sent to the chamber using a dichroic mirror and focused with a 150 mm focal length lens to an estimated beam diameter of 20-30 µm. Probe energies at the entrance to the detection chamber of 1-3 mJ/pulse for oxygen and 2-4 mJ/pulse for nitrogen were necessary to sufficiently ionize molecules for REMPI detection. The probe energy was monitored throughout the experiments.

4.4 Pump Techniques

The method for generating unidirectional molecular rotation with ultrashort pulses is discussed in Chapter 2. In this section we discuss the technical details of the two techniques we use, the double-kick and the chiral train. The double-kick is a sequence of two pulses, delayed by a time τ with respect to one another and with pulse-to-pulse polarization rotation by an angle δ [10, 19]. An illustration of the double-kick is shown in Figure 4.3(a). The chiral train is a train of ultrashort pulses, each delayed by a time τ with respect to the previous pulse, and with pulse-to-pulse polarization rotation by an angle δ [46]. An illustration of the chiral train is shown in Figure 4.3(b).

The double-kick and chiral train are obtained by shaping the output of a linearly polarized pulse from a regenerative amplifier (Spectra-Physics, Spitfire, 120 fs, 2 mJ at 800 nm and 1 KHz repetition rate). The shaping techniques for the double-
Figure 4.3: (a) Double-kick, two ultrashort pulses are delayed by time $\tau$ and the polarization is rotated pulse-to-pulse by an angle $\delta$. (b) Chiral train, a train of ultrashort pulses are delayed by time $\tau$ and the polarization is rotated pulse-to-pulse by an angle $\delta$.

kick and chiral train are shown in Figure 4.4 and Figure 4.5, respectively.

Double-Kick

The double-kick is obtained using a beamsplitter with a tunable time delay arm as shown in Figure 4.4. The energy of the two pulses is equalized with an input half-wave plate. One pulse is sent to a stage-mounted retroreflector, and a second half-wave plate to control both the time delay $\tau$, and polarization angle, $\delta$, relative to the other pulse. In order to preserve the polarization rotation between the beams, the beams are not recombined but rather sent in parallel and focused by a 150 mm-focal length lens. After the focusing lens, a thin window picks off a small fraction of the beams. To obtain temporal alignment, the pick off beams are first overlapped on a Charge-Coupled Device (CCD) camera and then sent through a second harmonic crystal. The delay arm on the double kick setup (Figure 4.4) is adjusted until the sum-frequency signal is observed, indicating the beams are overlapped in time. Spatial alignment in the detection chamber is obtained by first setting the probe wavelength to a known peak and finding the ionization signal from
rotating polarization. The time delay of the reference pulse was set to overlap with
have no effect on this state of polarization. The cross-correlation of the pulse train
with constant vertical polarization is created by the shaper. The
angle of the half-wave plate.

Figure 3.4: Pulse shaping used for the double-kick technique.

Figure 3.5: Pulse shaping used for the chiral train technique.

each beam. Then the probe wavelength is set to a non-excited peak and the beams
are adjusted until an ionization signal is observed, indicating that both beams are
simultaneously exciting the molecules.

Chiral Train

A comprehensive explanation of the chiral train can be found in [45]. The chiral pulse train was obtained by phase-only shaping from a spectral pulse shaper implemented in a standard 4f geometry with a double-layer Spatial Light Mod-
ulator (SLM) in its Fourier plane as shown in Figure 4.5 [39]. The two shaper masks control the spectral phase, \( \varphi_{1,2}(\omega) \), of the two polarization components of an input pulse along the two orthogonal axes of the shaper, \( \hat{e}_1 \) and \( \hat{e}_2 \). If \( \varphi_{1,2}(\omega) = A \sin[(\omega - \omega_0)\tau + \delta_{1,2}] \), where \( \omega_0 \) is the central pulse frequency, \( A \) is the modulation amplitude, \( \tau \) is the train period and \( \delta_{1,2} \) are two arbitrary angles, the resulting field is:

\[
E(t) = \sum_{i=1,2} \hat{e}_i(\hat{e}_1 \cdot \hat{e}_{\text{in}}) \sum_{n=-\infty}^{\infty} J_n(A) \epsilon(t + n\tau) \cos[\omega_0 t + n\delta], \quad (4.1)
\]

where \( \epsilon(t) \) is the electric field envelope of the original pulse polarized along \( \hat{e}_{\text{in}} \). Equation 4.1 describes a train of elliptically polarized pulses, with the polarization ellipticity of the \( n \)-th pulse defined by the phase difference \( n(\delta_1 - \delta_2) \). A quarter-wave plate, oriented along \( \hat{e}_{\text{in}} \), converts this elliptical polarization back to linear polarization, rotated by an angle \( n(\delta_1 - \delta_2)/2 \) with respect to the input polarization. By choosing \( \delta_1 = -\delta_2 = \delta \), we can create a pulse train where the polarization of each pulse is rotated with respect to the previous one by angle \( \delta \). The period of the polarization rotation is \( T_p = 2\pi\tau/\delta \).

We experimentally characterized the train with a polarization sensitive cross-correlation technique using the setup shown in Figure 4.6 [45]. The laser beam is split and one beam is used to create the pulse train while the other is used as a reference pulse. The two beams are spatially overlapped on a nonlinear crystal. A delay line is used to delay the reference pulse, allowing the reference pulse to be overlapped with any pulse in the pulse train. The \( \lambda/2 \) plate is mounted on a computer controlled rotational stage.

To characterize the train, we first generate a pulse train with constant vertical polarization, set the \( \lambda/2 \) plate to have no effect on the train polarization and measure the cross-correlation of the pulse train with the reference pulse. The result of this measurement with train period \( \tau = 8 \) ps is shown in the top panel of Figure 4.7.

Then, pulse shaping is applied to generate a chiral train with rotating polarization and the same train period. The time delay of the reference pulse is set to overlap a particular pulse in the pulse train and the cross-correlation signal is measured while the \( \lambda/2 \) plate is rotated. The result for a chiral train with \( \delta = \pi/4 \) is shown in the bottom panel of Figure 4.7. Maximizing the cross-correlation sig-
Pulse shaping was then applied to obtain a train with the same train period and rotating polarization. The time delay of the reference pulse was set to overlap with a pulse train with a period of about 8 ps is shown in Fig. 3.5, upper panel. To characterize a pulse train two measurements were done. First, a pulse train of the same polarization was obtained. An example of cross-correlation of a pulse train (top) and polarization graph for a pulse train with the same train period and polarization is shown in Fig. 3.5, bottom. Figure 4.6: Polarization sensitive cross-correlation setup.

Figure 4.7: Polarization sensitive cross-correlation results for chiral train with \( \delta = \pi/4 \). Top panel shows the measured (red) and calculated (green) pulse trains with non-rotating polarization and train period \( \tau = 8 \) ps. Lower panel shows the results of the polarization sensitive cross-correlation measurement for the chiral pulse train. White diamonds and dashed lines mark the peak positions of the non-linear signal for the 7 pulses in the train. The half-wave plate is rotated by \( \approx 22.5^\circ \) from peak to peak, indicating that the polarization is rotated by \( 45^\circ \) between consecutive pulses (\( \delta = \pi/4 \)).

Figure 3.5: Cross-correlation of a pulse train (top) and polarization graph for a pulse train with the same train period and polarization is shown in Fig. 3.5, bottom.
Figure 4.8: Dependence of directionality signal on input power for chiral train (black triangles) and double-kick (red circles).

For each consecutive pulse requires rotating the \( \frac{\lambda}{2} \) plate by \( \approx 22.5^\circ \), which corresponds to a pulse to pulse polarization rotation of \( 45^\circ \) (\( \pi/4 \) rad).

**Power Considerations**

To achieve the high laser field intensity required to drive multiple Raman transitions between the rotational levels, pump and probe beams were focused by a 150 mm-focal length lens. After measuring the focal spot size, the pump laser intensity for the chiral train was estimated on the order of \( 10^{13} \) W/cm\(^2\) for a 150 fs duration, 150 \( \mu \)J pulse. This corresponds to the dimensionless total kick strength (Equation 2.8) of \( P \approx 7 \) for oxygen and \( P \approx 5 \) for nitrogen.

For the double-kick, the full pump laser power could be sent into the pulse shaping setup. In our experiments, the pump laser was attenuated to 850 mW, which resulted in 250 mW in each beam before focusing. For the chiral train, the pump laser power cannot exceed 600-700 mW or it will damage the SLM.
our experiments, the pump laser was attenuated to 590 mW, which resulted in 190 mW in the beam before focusing. The different beam sizes in the double-kick and chiral train techniques lead to different focal spots and intensities, making it difficult to generate the same rotational excitation with both techniques. As such, we cannot compare the degree of directionality generated by each technique at the same intensity. The degree of directionality, or directionality signal, is defined as
\[ \varepsilon = \frac{S_L - S_R}{S_L + S_R} \]
where \( S_L \) is the signal from the left circularly polarized probe and \( S_R \) is the signal from the right circularly polarized probe. Figure 4.8 shows the dependence of directionality signal on input power. Higher directionality can be achieved with the double-kick because more power can be sent into the shaping setup.

### 4.5 General Experimental Setup

The general experimental setup is shown in Figure 4.9. Cold molecules are generated in the source chamber by supersonic expansion from a pulsed valve. The molecules enter the detection chamber through a 1 mm diameter skimmer. Room-temperature molecules can be sent to the detection chamber using a bypass valve. The probe beam passes through the pulse shaper (double-kick or chiral train) then is sent to the chamber. The pump and probe beams are combined on a dichroic mirror (CVI LWP-45-Rp-266-Tu-800-PW-2025-UV) and focused on the molecular beam with a 150 mm focal length lens. The focal spot is located inside the chamber, between the extraction plates of the TOF. A steering mirror is used to move the focal spot along the molecular beam.

The position of the pump beam is shifted by a few hundred \( \mu \text{m} \) upstream with respect to the probe beam to reduce the ionization background from pump pulses and the time delay between the pump and probe pulses is set to let the excited molecules reach the probe focal spot. A thin fused silica plane window is inserted after the lens which picks off a small fraction of both beams and is used to overlap the beams in the image of the interaction zone outside of the vacuum chamber. After the chamber, the beams are separated by another dichroic mirror and the beam energies are monitored using photodiodes.
4.6 Experimental Procedure

To begin the REMPI measurements we must first optimize the probe beam. To do so, we fill the chamber with room temperature molecules at atmospheric pressure and set dye laser wavelength in the middle of the spectrum range (see Figure 3.8, Figure 3.12). The ion signal is optimized when the focal spot is directly underneath the small orifice in the middle of the TOF plates. We move the probe beam in space using a steering mirror and monitor the REMPI signal to find the ion signal and ensure the beam is under the orifice. Once the ion signal is found, the ion signal is maximized by moving the lens along the optical axis to move the focal spot longitudinally. The REMPI spectrum is measured to compare with the simulated spectrum and confirm spectral line locations.

Next, we need to find the REMPI signal from the molecular beam. The probe wavelength is set to match a peak of the cold spectrum (see Figure 3.9 and Fig-
ure 3.13.) To synchronize the valve and the probe laser pulses we scan the time delay of the valve and find the maximal ionization signal, indicating the center of the molecular pulse. The valve delay was set at around 2.35 ms for oxygen and around 2.63 ms for nitrogen. The difference in delay times was due to the difference in molecular velocities. Once the valve delay is optimized, the cold REMPI spectrum can be obtained.

Now the pump beam must be aligned and optimized. When the pump focal spot is near the probe focal spot, the ion signal from the probe beam can be seen. The ion signal from the pump pulse is maximized by moving the focusing lens along the optical axis with the probe beam blocked to ensure that the pump focal plane is directly underneath the small orifice in the middle of the TOF plates. Probe focusing is reoptimized by adjusting the telescope in the probe beam line. The beams are not focused in exactly the same plane due to dispersion from the lens. The pickoff mirror and screen are used to overlap the beams. The screen is moved to the focal plane of the probe beam where a hole is burned in the screen by the probe beam. Then the pump beam is sent through the hole in the screen by adjusting a steering mirror.

When the beams are overlapped in the detection chamber, we see ion signal from both the pump and probe beams. In order to measure the REMPI spectrum we need to separate the ion signals and clearly observe the ion signal from the probe beam. The width of the signals is about 20-30 ns, so a time delay between the pump and probe pulses of 100 ns is sufficient to separate the ion signals in time. However, due to molecular motion and with beams that are overlapped in space, the molecules that are excited by the pump beam travel out of the probe focal spot and are not detected. In order to detect the molecules that are affected by the pump beam, the time delay between the beams is compensated by moving the pump beam upstream from the probe.

The optimal upstream location is determined by monitoring the ion signal at a wavelength corresponding to an initially non-populated state as the pump beam is moved upstream of the probe. As explained in Chapter 2, the pump beam transfers angular momentum to the molecules, populating higher rotational states. When the beams are overlapped, the ion signal is zero because only the lowest rotational states are populated in the cold molecular beam. As the pump beam is moved
Figure 4.10: Normalized REMPI spectra of cold oxygen: experimental results (lower solid curve) and calculations (lower dashed line). Upper solid curve shows the spectrum of rotationally excited molecules (shifted up for clarity). Dashed vertical lines indicate the frequencies of transitions originated from a certain rotational state, labeled with the corresponding $N''$ numbers. Vertical arrows point at the two peaks which correspond mostly to $N''=3$, and $N''=5$ initial rotational states. Upstream, molecules that are excited by the pump beam are ionized by the probe beam. The ion signal of the excited molecules is optimized to determine the correct position of the pump beam. Then, the REMPI spectrum of the rotationally excited molecules can be obtained.

The REMPI spectrum of rotationally excited oxygen is shown in Figure 4.10, along with the experimental and simulated cold REMPI spectra. At $T = 8$ K, the majority of molecules are in the lowest rotational state $N'' = 1$ with some population in $N'' = 3$. Application of a pump pulse changes the spectrum dramatically by increasing the intensity of lines originated from $N'' > 3$. The REMPI spectrum of rotationally excited oxygen shows populated peaks for the rotational number as high as $N'' = 19$. Unfortunately, different rotational transitions in oxygen overlap with one another and it is generally difficult to have a REMPI peak corresponding to a single initial state (see line assignments in Figure 4.10). We use two spectral
Figure 4.11: Normalized REMPI spectra of $^{14}$N$_2$. Relevant peaks of the S-branch are labeled by the corresponding $N''$ numbers. Prior to the application of a femtosecond pulse train, the distribution of rotational population is thermal and corresponds to 6.3K (lower solid blue line - experiment, dashed green line - calculations [14]). At this temperature, only $J'' = 0, 1$ and 2 are populated significantly. An example of the REMPI spectrum of rotationally excited molecules is shown by upper solid red line. For the total laser kick strength used in our experiments, rotational states up to $J'' = 7$ are populated.

lines at 287.25 nm and 287.14 nm, where the majority of ions originate from the $N'' = 3$ and $N'' = 5$ rotational states, respectively. Even though the individual lines are not resolved, the relative contribution of the neighboring states to the total ion signal in both cases is estimated as $< 18\%$.

The REMPI spectrum of rotationally excited nitrogen is shown in Figure 4.11 along with the experimental and simulated cold REMPI spectra and relevant line assignments. At $T = 6.3$ K, the majority of molecules are in the lowest rotational states, $J'' = 0, 1, 2$. The REMPI spectrum of rotationally excited nitrogen shows populated peaks up to $J'' = 7$. The frequencies of the S-branch transitions ($\Delta J = 2$) are well separated and the linewidth is narrow, allowing us to detect the population.
of the first eight rotational levels $N'' = 0, 1, ..., 7$ of the ground electronic state. For most of our measurements we use the $J'' = 3$ and $J'' = 4$ peaks of the S-branch because they are the most populated levels consisting of only excited population.

Now, we set the probe wavelength to a particular rotational state peak and measure the ion signal as a function of the parameters of the double-kick or chiral train (time delay between pulses, $\tau$ and pulse-to-pulse polarization rotation, $\delta$). We record the total ionization signal for left and right circularly polarized probe, $S_L$ and $S_R$, respectively. The sum of the two signals, $S = S_L + S_R$, represents the average total excitation efficiency. The degree of rotational directionality is defined as $\varepsilon = (S_L - S_R)/(S_L + S_R)$. 

49
Chapter 5

Results

In this chapter I present and discuss our experimental results. First, we introduce the chiral train technique and present our work on the ability to control molecular rotation and generate unidirectional rotation with a chiral train. In the second section, we perform experiments with both the double-kick and chiral train techniques for thorough comparison and characterization of both methods.

5.1 Control of Molecular Rotation with a Chiral Train of Ultrashort Pulses

Creating molecular ensembles with a preferred direction of rotation has been reported in both adiabatic (“optical centrifuge”) [6, 17, 37, 38, 42] and non-adiabatic [10, 19] regimes of excitation using a pair of laser pulses with different polarization. In this work we demonstrate an alternative way of exciting unidirectional rotational motion with a “chiral pulse train”, in which the polarization of the excitation field rotates from pulse to pulse by a controllable angle, in either clockwise or counter-clockwise direction. The time delay between the pulses is much shorter than the revival period. We show that by varying the train parameters using the technique of polarization shaping [3, 40], one can achieve selectivity in the rotational excitation and control its directionality. By matching the rotational period of the field polarization to the period of molecular rotation, molecules in a particular angular momentum state can be excited more efficiently than others. The chirality
Figure 5.1: Total excitation efficiency of oxygen molecules excited to $N'' = 3$ (a,c) and $N'' = 5$ (b,d) rotational state (note the difference in time scale). (a,b) - experimental data, (c,d) - numerical calculations. Each experimental data point represents an average over 150 probe pulses. Grayscale coding: (a,b) min: $S = 0$, max: $S = 1$ (arb.units); (c) min $P = 0.1$, max $P = 0.6$; (d) min: $P = 0$, max: $P = 0.35$.

and the period of the pulse train define the direction of rotation.

Our main results are shown in Figure 5.1 and Figure 5.2. With the probe wavelength set to 287.25 nm ($N'' = 3$) and 287.14 nm ($N'' = 5$), we vary $\delta$ and $\tau$ while keeping the pulse train envelope and energy (140 $\mu$J) constant. We record the total ionization signal for left and right circularly polarized probe, $S_L$ and $S_R$, respectively. The sum of the two signals, $S = S_L + S_R$, is plotted in Figure 5.1 and represents the average total efficiency of exciting the molecules to $N'' = 3$ and 5 as a function of $\delta$ and $\tau$.

The experimental results are compared with a theoretical analysis of the population distribution of various rotational states of oxygen excited by the chiral train. In our model, the pulses were considered as $\delta$-kicks, and the molecular wavefunction was expanded in the Hund’s case (b) basis. The non-perturbative modification of the expansion coefficients due to the interaction with every pulse was determined with the help of the numerical procedure described in [10]. Thermal averaging over initial molecular states was done to account for thermal effects. As the observables related to the measured signals, we calculated $P_L$ ($P_R$) - the total population of the $N$-states with positive (negative) projection $M_J$ of the total angular momentum $J$ onto the propagation direction of the chiral pulse train. The population of the $M_J = 0$ state was equally divided between $P_L$ and $P_R$. The sum of these calcu-
Figure 5.2: Directionality of molecular rotation for $N'' = 3$ (a,c) and $N'' = 5$ (b,d) state (note the difference in time scale). Grayscale coding: (a) min: $\varepsilon = -0.2$, max: $\varepsilon = +0.2$; (b) min: $\varepsilon = -0.4$, max: $\varepsilon = +0.4$; (c) min: $\varepsilon = -0.7$, max: $\varepsilon = +0.7$; (d) min: $\varepsilon = -0.8$, max: $\varepsilon = +0.8$.

lated populations ($P$) for $N'' = 3$ and $N'' = 5$ is shown in Figure 5.1 (c) and (d), respectively.

Both experimental (a) and theoretical (c) plots of Figure 5.1 show that for $\delta = 0, \pi$ (non-rotating polarization) the total signal exhibits well pronounced maxima at $\tau \approx 2400$ fs and $\tau \approx 4700$ fs. As expected, these times correspond to one and two periods of “rotation” for $N'' = 3$, defined as $T_{N''=3} = h/(E_{N''=3} - E_{N''=1}) = 2340$ fs. Of course, the picture of classical rotation is not applicable for such low rotational numbers, and the “period of rotation” simply means the evolution period of a rotational wavepacket consisting of only two states, $N'' = 1$ and $N'' = 3$. Similar maxima are observed in panels (b) and (d) for about twice lower values of $\tau$ corresponding to the faster evolution of a higher angular momentum state, $N'' = 5$.

All panels of Figure 5.1 show a characteristic “X” pattern with clear diagonal lines. Their slope defines a constant period of polarization rotation in the chiral train, $T_p = 2\pi \tau / \delta$. Diagonals with a positive slope, e.g. from point $(\tau = 0, \delta = 0)$ to point $(\tau = 2400, \delta = \pi)$ in plots (a,c), correspond to the polarization rotating clockwise, while a negative-slope diagonal corresponds to counter-clockwise polarization rotation. The population of the corresponding state is clearly higher along these diagonal lines, reflecting a higher degree of rotational excitation by a pulse train whose polarization is rotating in sync with the molecules. Note that the lines of enhanced excitation correspond to the train polarization rotating twice
slower than the molecules, e.g. $T_p = 2T_{N=3}$. The effect is reproduced in the numerical calculations shown in panels (c,d), and can be attributed to the inversion symmetry of the oxygen molecule.

Aside from the diagonals, the plots of Figure 5.1 exhibit rich two-dimensional structure with notably more features visible in the case of lower ($N''=3$) rotational excitation. Our numerical analysis attributes this difference to the following two reasons. First, the spin-rotation splitting of the $N''=3$ state is more than 7 times that of $N''=5$, which makes a simple two-level wavepacket model less applicable. Second, with an estimated rotational kick strength of $P \approx 7$, the lower state undergoes stronger perturbation than the upper one. Theoretical calculations with neglected spin-rotation coupling and weaker field strength result in a higher degree of similarity between the $N''=3$ and $N''=5$ cases.

Figure 5.2 shows the degree of rotational directionality, defined as $\varepsilon = (S_L - S_R)/(S_L + S_R)$ or $\varepsilon = (P_L - P_R)/(P_L + P_R)$ for the experimental observations and numerical calculations, respectively. Similar “X” pattern can be recognized on all panels, confirming the directionality of molecular rotation along the “resonant” diagonals. Indeed, the dark positive-slope traces correspond to $\varepsilon < 0$ (clockwise rotation), whereas the bright ones with a negative slope - to $\varepsilon > 0$ (counter-clockwise rotation).

The end and center points of the “X” pattern in Figure 5.1 (i.e. at $\delta = 0, \pi/2$ and $\pi$) exhibit higher signal in comparison to the intermediate values of $\delta$. This is the result of a bi-directional rotational excitation at those points, where the pulse train is resonant with both clockwise and counter-clockwise rotating molecules, and the total number of excited molecules is therefore higher. This conclusion is evident in Figure 5.2, where no circular anisotropy ($\varepsilon = 0$) is observed and calculated around $\delta = 0, \pi/2, \pi$.

An interesting increase in the directionality of the excited rotation is observed for low train period ($\tau = 100$ fs) and polarization rotation angle $\delta \approx \pi/2$. In this case, pulses of the chiral train are overlapping in time, forming a single pulse with gradually rotating polarization. This is almost the centrifuge field of [6, 17, 37, 42]. In contrast to the latter, here the polarization rotation is fast at the beginning of the pulse; it then slows down to zero in the middle, and accelerates in the opposite direction towards the end of the pulse. Even though our pulse is of much lower
strength and duration than that needed for spinning molecules to high angular frequencies, its effect on low rotational state is quite evident for both \( N'' = 3 \) and \( N'' = 5 \) (Figure 5.2(a,b)). The centrifuge effect is not observed in the numerical calculations, which assume an infinitely short duration of pulses in the chiral pulse train.

### 5.2 Directional Spinning of Molecules with Sequences of Femtosecond Pulses

We present an analysis of two experimental approaches to controlling the directionality of molecular rotation with ultrashort laser pulses. The two methods are based on the molecular interaction with either a pair of pulses (a “double kick” scheme) or a longer pulse sequence (a “chiral pulse train” scheme). In both cases, rotational control is achieved by varying the polarization of and the time delay between the consecutive laser pulses. Using the technique of polarization sensitive resonance-enhanced multi-photon ionization, we show that both methods produce significant rotational directionality. We demonstrate that increasing the number of excitation pulses supplements the ability to control the sense of molecular rotation with quantum state selectivity, i.e. predominant excitation of a single rotational state. We also demonstrate the ability of both techniques to generate counter-rotation of molecular nuclear spin isomers (here, ortho- and para-nitrogen) and molecular isotopologues (here, \(^{14}N_{2}\) and \(^{15}N_{2}\)).

We compare the two methods of rotational excitation of nitrogen in Figures 5.3 and 5.4. With the probe wavelength set to 283.06 nm (\( J'' = 3 \)) and 283.05 nm (\( J'' = 4 \)), we vary \( \delta \) and \( \tau \) while keeping the total energy, and hence the total rotational kick strength, constant. Figure 5.3 presents the measured excitation efficiency as a function of \( \delta \) and \( \tau \), whereas directionality is shown in Figure 5.4.

Fig. 5.3 shows the total excitation efficiency for the double-kick (a,b) and the chiral train (c,d) scheme. For each technique we measure the rotational state population of \( J'' = 3 \) (a,c) and \( J'' = 4 \) (b,d). Plots corresponding to the same value of \( J'' \) show maxima in the similar locations (e.g. a maximum at \( \delta = \pi/2, \tau \approx 800 \) fs on both Fig.5.3 (a) and (c)). For a sequence of pulses with constant polarization \( (\delta = 0, \pi) \), the total excitation efficiency for \( J = 3 \) and \( J'' = 4 \) show maxima at \( \tau \approx \)
Figure 5.3: Total excitation efficiency for $J'' = 3$ (a), (c) and $J'' = 4$ (b), (d) rotational states of nitrogen. (a), (b): double-kick excitation scheme, (c), (d): excitation with the chiral pulse train. In panel (b), the drop-off in signal at higher $\delta$ is caused by a drift of probe wavelength over the course of the scan (2-3 hours).

1700, 3500 fs and $\tau \approx 1250, 2500, 3750$ fs, respectively. These times correspond to integer multiples of the “period of rotation” for the corresponding rotational states, which refers to the evolution period of a rotational wavepacket consisting of two rotational states separated by $\Delta J = \pm 2$, for example $J'' = 3$ and $J'' = 4$. Defined as $T_J = h/(E_J - E_{J-2})$, it results in $T_{J=3} = 1677$ fs and $T_{J=4} = 1198$ fs.

As shown in our recent Letter [46], higher excitation efficiency signal occurs when the laser polarization rotates “in-sync” with the molecules. This effect is demonstrated clearly in the chiral train results (Fig.5.3 (c,d)) where the lines of enhanced excitation form a distinct “X” pattern. The slope of the lines defines a constant period of polarization rotation in the chiral train, $T_p = 2\pi \tau / \delta$. A positive slope corresponds to the polarization rotating clockwise, while a negative slope corresponds to the counter-clockwise rotating polarization. The classical state of enhanced molecular rotation, synchronous with the applied laser field, corresponds to a quantum wavepacket whose amplitude is coherently accumulating with each consecutive laser pulse. With fewer pulses, the excitation efficiency is less sensitive to the train period and polarization angle, resulting in the blurring of the “X” pattern in the double-kick results (Fig.5.3 (a,b)). For both techniques, the excitation signal is stronger at $\delta = 0, \pi/2, \pi$ (middle and end points of the “X” pattern) where the conditions of synchronous excitation are satisfied for both directions of rotation.
Figure 5.4: Directionality of molecular rotation for \( J'' = 3 \) (a),(c) and \( J'' = 4 \) (b),(d) rotational states. (a),(b): double-kick excitation scheme, (c),(d): excitation with the chiral pulse train. The maximum/minimum directionality achieved is \( \varepsilon = \pm 0.7 \) with the double-kick and \( \varepsilon = \pm 0.4 \) with the chiral train technique.

Fig.5.4 shows the degree of rotational directionality, \( \varepsilon = (S_L - S_R)/(S_L + S_R) \), measured with the double-kick (a,b) and chiral train (c,d) method. As with excitation efficiency, we measure the rotational state population of \( J'' = 3 \) (a,c) and \( J'' = 4 \) (b,d) for each technique. No directionality is measured for \( \delta = 0, \pi \) (non-rotating polarization) or at \( \delta = \pi/2 \) for which clockwise and counter-clockwise rotating molecules are equally excited, resulting in no preferential sense of rotation in the ensemble. Both methods exhibit the ability to control the direction of molecular rotation. In Fig.5.4(a) and (c) at \( \delta = \pi/4, \tau \approx 500 \text{ fs} \), both techniques produce clockwise rotation (\( \varepsilon < 0 \)), whereas counter-clockwise rotation (\( \varepsilon > 0 \)) is observed at \( \delta = 3\pi/4, \tau \approx 500 \text{ fs} \). The results for the double-kick scheme show that the strongest directionality is produced when \( \delta = \pi/4, 3\pi/4 \), in agreement with the calculations of [10]. At these angles, the torque applied to the molecular ensemble by the laser field reaches maximum, resulting in the highest degree of directional excitation. The chiral train also produces the strongest directionality signal when \( \delta \approx \pi/4, 3\pi/4 \).

The “X” patterns of Fig.5.3 (c,d) correspond directly to those in Fig.5.4 (c,d), confirming the directionality of molecular rotation along the lines of maximum excitation efficiency. As expected, middle and end points of the “X” pattern (\( \delta = 0, \pi/2, \pi \)) show \( \varepsilon \approx 0 \) reflecting bi-directional excitation with no preferential sense.
Figure 5.5: Directionality of molecular rotation for $J'' = 2 - 4$ with the double-kick (upper panel) and chiral pulse train (lower panel) excitation techniques. In both cases, the relative polarization angle between consecutive pulses is $\delta = \pi/4$. Vertical dashed lines denote $\frac{1}{4}T_{\text{rev}}, \frac{1}{2}T_{\text{rev}}, \frac{3}{4}T_{\text{rev}}$ and full revival time $T_{\text{rev}}$. Higher $J$'s are not shown due to the low signal-to-noise ratio.

To further compare the two techniques, we investigate the degree of rotational directionality as a function of pulse separation $\tau$ at a fixed polarization angle between pulses, $\delta = \pi/4$. Fig.5.5 shows $\varepsilon(\tau)$ for $J'' = 2 - 4$ measured with each technique. Both techniques produce very similar structure, particularly at quarter, half, three-quarters and full revival times (vertical dashed lines, $T_{\text{rev}} = 8.38$ ps). The behavior around $\frac{1}{2}T_{\text{rev}}$ mirrors the behavior at $T_{\text{rev}}$, with the directionality for all $J$'s going from negative to positive at $\frac{1}{2}T_{\text{rev}}$ and positive to negative at $T_{\text{rev}}$. At $\frac{1}{4}T_{\text{rev}}$ and $\frac{3}{4}T_{\text{rev}}$, the states with even and odd values of angular momentum exhibit opposite sense of rotation. Larger number of pulses in the chiral pulse train (in comparison with the double-kick scheme) leads to higher sensitivity to $\tau$ and correspondingly narrower features in the observed time dependence.
Molecular spin isomers, such as para- and ortho- isomers of $^{14}\text{N}_2$, exhibit identical revival times yet different structure of rotational levels. Paranitrogen does not have odd $J$ states in its rotational spectrum, whereas even $J$'s are missing in the spectrum of orthonitrogen. After the excitation by a short laser pulse, the alignment factors for spin isomers evolve differently. Around quarter-revival time, they are exactly out of phase, meaning that the ortho molecules are maximally aligned when the para molecules are maximally anti-aligned. Previously, this effect has been used to selectively excite one spin isomer with a sequence of two pulses [9] or a train of equally polarized pulses [47], leaving the other isomer in its ground rotational state. Excitation fields with time-dependent polarization, considered here, produce a very different result. Both the double-kick and chiral pulse train techniques can create a molecular ensemble of oppositely rotating spin isomers. This is shown in Fig.5.5 where at $\tau = \frac{1}{4}T_{rev} = 2100$ fs, positive directionality is detected for even rotational states ($J'' = 2, 4$) and negative directionality for odd rotational states ($J'' = 3$).

Notably, the technique of chiral pulse train enables selective directional excitation of not only a set of rotational levels (as in the case with spin isomers described above), but also of individual $J$-states. This is demonstrated in figure 5.6 where we show the normalized excitation signal (a) and the degree of directionality (b) for $J'' = 2 – 5$ as a function of the pulse train period $\tau$, at $\delta = \pi/4$. Various dashed lines mark periods that result in a preferential excitation of a particular rotational state and the corresponding directionality at that value of $\tau$. For example, the three train periods that result in the excitation of $J'' = 3$ while leaving other $J$’s almost unexcited, are labeled $\tau_{1,2,3}^{(3)} \approx 1300, 3000$, and 7100 fs. As can be seen in the lower panel of Fig.5.6, at $\tau_1^{(3)}$ and $\tau_2^{(3)}$ positive directionality is measured, indicating counter-clockwise rotation, whereas at $\tau_3^{(3)}$ the directionality signal is negative, corresponding to clockwise rotation. Other dashed lines similarly point to values of $\tau$ which provide selective excitation of $J'' = 2, 4$ and 5 in either clockwise or counter-clockwise direction (minimum or maximum in the corresponding directionality signal, respectively). Note that at $\tau = \frac{1}{4}T_{rev}$ and $\tau = \frac{3}{4}T_{rev}$ (vertical solid lines), all states are excited with maximum efficiency as required for creating an ensemble of counter-rotating isomers discussed above.

The double-kick technique enables an equally efficient control of rotational
Figure 5.6: Normalized excitation efficiency (upper panel) and degree of directionality (lower panel) for $J = 2 - 5$ states excited with the chiral pulse train of period $\tau$ and pulse-to-pulse polarization angle of $\delta = \pi / 4$. Vertical dashed lines indicate pulse periods for selective excitation of a particular rotational state and the corresponding directionality at that time (see text for details). Solid black vertical lines mark $\frac{1}{4} T_{\text{rev}}$ and $\frac{3}{4} T_{\text{rev}}$.

directionality, but does not offer selectivity in $J$ due to the small number of laser pulses and correspondingly lower time resolution. Inspecting Fig.5.3 (a) and (b), one can see that although some limited selectivity of excitation exists at $\delta = 0$, it is quite poor at $\delta = \pm \pi / 4$ - the angle necessary to induce maximum degree of directionality.

Selective alignment of two molecular isotopologues, $^{14}\text{N}_2$ and $^{15}\text{N}_2$, has been first proposed and demonstrated with a sequence of two equally polarized laser pulses [8]. In our recent work [47], we have used the effect of quantum resonance in the periodically kicked rotor system to selectively excite a particular isotopologue of nitrogen with a train of femtosecond pulses of constant polarization. In both approaches, one exploits the fact that different isotopologues exhibit different revival times. Here, we discuss the possibility of creating an ensemble of counter-
Figure 5.7: Degree of rotational directionality for nitrogen isotopologues, $^{14}N_2$ (upper panel) and $^{15}N_2$ (lower panel), induced with the double-kick technique at $\delta = \pi/4$. Solid (dashed) lines indicate full (half) revival time for each molecule, $T_{rev} = 8.38$ ps for $^{14}N_2$, and $T_{rev} = 8.98$ ps for $^{15}N_2$. Black squares (circles) mark the values of $\tau$ resulting in clockwise (counter-clockwise) rotation for $J = 3$ and $J = 4$.

rotating molecular isotopologues. Fig.5.7 shows the experimentally observed degree of rotational directionality in $^{14}N_2$ and $^{15}N_2$, excited with the double-kick method. The directionality signal oscillates as a function of $\tau$ with the oscillation period being different for different molecules.

Similarly to the results of Fig.5.5, the directionality signal for both isotopologues changes from negative (clockwise rotation) to positive (counter-clockwise rotation) at $\frac{1}{2}T_{rev}$ and vice versa at $T_{rev}$. Because of the difference in rotational constants, a full revival time of $^{15}N_2$ will coincide with a half revival time of $^{14}N_2$ at 70.9 ps [8]. A second laser pulse polarized at an angle of $\delta = \pi/4$ with respect to the first one and applied shortly before or after this characteristic time will produce negative directionality in one isotope and positive directionality in the other. This
Figure 5.8: Directionality measurements for $J'' = 3$ and $A = 2 - 4$ (left panel).

The plots for each $A$ are offset for clarity. Right panel shows the calculated electric field envelopes for values of the modulation amplitude, $A$, from 2 to 4. The train period is $\tau = 4.5$ ps. Polarization rotation that occurs from pulse to pulse in a chiral pulse train is not shown in this figure.

A relatively long time delay can be achieved by the double-kick technique but is beyond the capability of the chiral train method, which is limited by the resolution of a pulse shaper to $\tau \lesssim 10$ ps.

We also explore the effect of different numbers of pulses in the chiral pulse train by varying the modulation amplitude $A$ (see Eq. 4.1). Left panel of Fig. 5.8 shows the degree of observed directionality at $J'' = 3$ with train parameters $\delta = \pi/4$ and variable $A = 2.5 - 4$. Calculated train envelopes for these values of $A$ are shown in the right panel. As the number of pulses in the train increases, the directionality peaks become narrower and new “side band” peaks begin to appear. For example, around 1300 fs there are 3 distinct peaks when $A = 2.5$ and 5 peaks when $A = 4$. This observation agrees well with the theoretical model which shows that the number of local minima between the resonant peaks of $\varepsilon(\tau)$ is approximately equal to the number of pulses in the train [11].
Chapter 6

Conclusion

In summary, we have characterized two experimental techniques for controlling the direction of molecular rotation using sequences of laser pulses with rotating polarization. We have proposed and implemented a new method of exciting unidirectional molecular rotation with polarization-shaped femtosecond laser pulses. The technique of generating a sequence of pulses with field polarization rotating from pulse to pulse by a predefined constant angle - a chiral pulse train, has been demonstrated and utilized for the rotational control of molecular oxygen. Also, we built and characterized an existing technique, the double-kick, to thoroughly compare the double-kick and chiral train techniques. We have confirmed the ability to control the sense of molecular rotation with both techniques.

Using a polarization sensitive and state-selective detection technique has allowed us to investigate directionality in a unique way, by observing the directionality of individual rotational states. We have shown that increasing the number of excitation pulses allows one to control the direction of molecular rotation simultaneously with quantum state selectivity. Using the chiral pulse train method, we have tuned the time delay between pulses and the pulse-to-pulse polarization rotation angle in such a way as to excite a particular rotational state and control the direction of molecular rotation for that state. We have also demonstrated the ability to rotate molecular spin isomers and isotopologues in opposite directions.

This thesis has demonstrated and characterized new and interesting methods of the coherent control of molecules. The results of this thesis work will be partic-
ularly useful for surface scattering experiments and selectivity in molecular mix-
tures. In surface scattering experiments, control of the incident molecular ensem-
ble is very important to learning more about the molecule-surface interaction. The
ability to scatter ensembles of clockwise or counter clockwise rotating molecules
will be a useful tool. Additionally, with the chiral train, one would be able to
scatter molecules with a controllable direction of rotation and rotational energy.
This work also offers new tools of rotational control in molecular mixtures. With
both techniques, we have extended previously demonstrated selective excitation of
molecular spin isomers and isotopologues by demonstrating the ability to rotate
them in opposite directions.
Bibliography


Appendix A

Details of Spectral Simulations

A.1 Oxygen

A.1.1 Ground State: $X^3\Sigma_g^-$

Spectroscopic constants
Spectroscopic constants from [24]. All values in cm$^{-1}$.

$B = 1.4337$

$D = -4.7 \times 10^{-6}$

$\lambda_0 = 1.9847$

$\mu = -0.0084$

$\lambda_D = 2 \times 10^{-6}$
Energy level calculations

Recall from Section 3.2.1, the matrix elements of the Hamiltonian are given in Equation A.1 as

\[
H =
\begin{pmatrix}
B_0 J(J-1) + B_1 J^2 (J-1)^2 & 0 & 0 \\
0 & B_0 (J+1)(J+2) + B_1 (J+1)^2 (J+2)^2 & 0 \\
0 & 0 & B_0 J(J+1) + B_1 J^2 (J+1)^2 \\
\end{pmatrix}
\]

The secular equation can be solved to for the energies \( F_1, F_2 \) and \( F_3 \) of the \( \rho \)-type triplet, where \( F_1, F_2 \) and \( F_3 \) refer to levels with \( J = N+1, N, \) and \( N-1 \) respectively. One solution is \( H = B_0 J(J+1) + B_1 J^2 (J+1)^2 \) which gives the energy of the \( F_2 \) component (\( J = N \)). To solve for \( F_1 \) and \( F_3 \), let

\[
\alpha = B_0 J(J-1) + D J^2 (J-1)^2 + \mu J \\
\beta = B_0 (J+1)(J+2) + D(J+1)^2 (J+1)^2 - \mu (J+1) \\
\gamma = -2J\{\lambda_0 + J(J-1)\lambda_1\} \\
\delta = -2(J+1)\{\lambda_0 + (J+1)(J+2)\lambda_1\} \\
\lambda = 2\{\lambda_0 + (J^2 + J+1)\lambda_1\}\{J(J+1)\}^{\frac{1}{2}} \\
\]

so then, the secular equation becomes
\[ \chi(x) = \begin{vmatrix} \alpha - \gamma - x & \lambda \\ \lambda & \beta + \delta - x \end{vmatrix} = 0. \quad (A.2) \]

Solving the secular equation gives,

\[ (\alpha + \gamma - x)(\beta + \delta - x) - \lambda^2 = 0 \]

\[ x^2 - (\alpha + \beta + \gamma + \delta)x + \alpha\beta + \alpha\delta + \gamma\beta + \gamma\delta - \lambda^2 \]

which can be solved using the quadratic equation,

\[ x = \frac{\alpha + \beta + \gamma + \delta}{2} \pm \frac{1}{2} \sqrt{(\alpha + \beta + \gamma + \delta)^2 - 4(\alpha\beta + \alpha\delta + \gamma\beta + \gamma\delta - \lambda^2)} \quad (A.3) \]

The energies, \( F_1, F_2 \) and \( F_3 \), are

\[
F_1 = \frac{\alpha + \beta + \gamma + \delta}{2} + \frac{1}{2} \sqrt{(\alpha + \beta + \gamma + \delta)^2 - 4(\alpha\beta + \alpha\delta + \gamma\beta + \gamma\delta - \lambda^2)} \\
F_2 = B_0J(J+1) + B_1J^2(J+1)^2 \\
F_3 = \frac{\alpha + \beta + \gamma + \delta}{2} - \frac{1}{2} \sqrt{(\alpha + \beta + \gamma + \delta)^2 - 4(\alpha\beta + \alpha\delta + \gamma\beta + \gamma\delta - \lambda^2)}
\]

Note, for \( N = 1, J = 0 \), the sign in front of the square root is inverted [14].

**A.1.2 Excited State: \( C^3\Pi_g^- \)**

**Spectroscopic constants**

Spectroscopic constants from [41]. All values in \( \text{cm}^{-1} \). \( E_0 \) is the band origin.

\[
F_1 \\
E_0 = 69353 \\
B = 1.63 \\
D = 1.5 \times 10^{-6} \\
F_2
\]
\[ E_0 = 69437 \]
\[ B = 1.66 \]
\[ D = 1.0 \times 10^{-6} \]

\[ F_3 \]
\[ E_0 = 69548 \]
\[ B = 1.685 \]
\[ D = 1.3 \times 10^{-6} \]

**Energy level calculations**

Energy = \( BJ(J + 1) - DJ^2(J + 1)^2 + E_0 \)

## A.2 Nitrogen

Here we list the spectroscopic constants for nitrogen from [15], all values are in \( \text{cm}^{-1} \). The energy level calculations for the ground and excited states of nitrogen were explained in Section 3.3.1.

### A.2.1 Ground State: \( X^1\Sigma_g^+ \)

\[ T_e = 0 \]
\[ \omega_e = 2358.57 \]
\[ \omega_e x_e = 14.324 \]
\[ \omega_e y_e = -2.26 \times 10^{-3} \]
\[ B_e = 1.99824 \]
\[ \alpha_e = 0.017318 \]
\[ \gamma_e = 0 \]
\[ D_e = 5.7 \times 10^{-6} \]
\[ \beta_e = 0 \]

### A.2.2 Excited State: \( a^1\Pi_g \)

\[ T_e = 69283.06 \]
\[ \omega_e = 1694.20 \]
\[ \omega_e x_e = 13.949 \]
\( \omega_{e} y_{e} = 7.93 \times 10^{-3} \)

\( B_{e} = 1.6169 \)

\( \alpha_{e} = 0.01793 \)

\( \gamma_{e} = -2.9 \times 10^{-5} \)

\( D_{e} = 5.89 \times 10^{-6} \)

\( \beta_{e} = 0 \)