

Investigation of laser-driven ionization and dissociation using
spin-rotational dynamics

by

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IMSc, University of Hyderabad, 2015

AN ABSTRACT OF A DISSERTATION

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Abstract

One of the most important goals of doing research in ultrafast molecular dynamics is to make molecular movies and the reason to make molecular movies is to understand the molecular dynamics which occurs during a chemical reaction. Given the fast timescales of molecular motion, typically ranging from a few nanoseconds to attoseconds and the motion can be only be resolved using ultrafast lasers. In this thesis we will study dynamics in diatomic molecules using the pump-probe technique. We will use an intense pump laser to coherently excite rotational wave-packets in either the ground state of the neutral molecule or low-lying states of the molecular cation and probe the dynamics induced by the pump pulse using photoionization and photodissociation process.

Following the previous work done by Makhija *et al.*¹ and Lam *et al.*² on strong-field ionization after impulsive molecular alignment using a time-domain approach called Orientation Resolution through Rotational Coherence Spectroscopy (ORRCS) we will explore the strong-field ionization process from triplet ground state molecular oxygen³. In this thesis, we will expand the work done previously into spin-coupled rotational wave-packets. When spin is coupled to the rotation, the wave packet is no longer purely rotational, and the delay-dependent ionization yield becomes non-periodic. We report the first measurement of such non-periodic dynamics in oxygen. With long delay-dependent data we obtain a high-resolution frequency spectrum after doing Fast Fourier Transform (FFT). With the high resolution frequency spectrum we are able to identify rotational Raman lines from the triplet ground state of molecular oxygen. We have used both time and frequency-domain analysis to gain insights into the role played by spin during strong-field ionization.

In the second part of the work we have used time, frequency, and Kinetic energy release spectroscopy with data acquired using the Velocity Map Imaging (VMI) spectrometer to

uncover the intricate chemical pathways involved in photo-dissociation following a strong-field ionization of oxygen (O_2), nitrogen (N_2), and deuterium (D_2) molecules. With the calculated rotational frequencies and KER from the low-lying potential curves of O_2^+ , N_2^+ , and D_2^+ cations, we are able to uniquely identify the intermediate electronic states involved. In the O_2^+ , we have shown the role of the resonant coupling in the 800 nm pump pulses as proposed by Xue *et al.*⁴ with $b^4\Sigma_g^-$ state rotational coherences dominating the FFT spectrum. We also found a vibrational Cooper minimum⁵ in the O_2^+ between the intermediate a-state and the dissociative f-state. In both O_2^+ and N_2^+ , we have found the strong effect of the few photon resonance-enhanced dissociation with a 264 nm probe. We anticipate that this technique will have broad applicability to ultrafast-laser driven processes in molecules, offering distinct insights into molecular physics and chemistry.

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Approved by:

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Table of Contents

List of Figures	xi
List of Tables	xx
Acknowledgements	xxii
1 Introduction	1
1.1 Motivation	1
1.2 Structure of the dissertation	4
2 Experimental and theoretical techniques	7
2.1 Experimental tools	8
2.1.1 Light source	8
2.1.2 Experimental setup	11
2.1.3 Cold molecule source	12
2.1.4 Velocity map imaging spectrometer (VMI)	15
2.1.5 Time of flight spectrometer	18
2.1.6 Detectors	19
2.1.7 Ultrahigh vacuum chambers	21
2.1.8 Data acquisition	21
2.2 Theoretical tools	25
2.2.1 Molecules as rigid rotors	25
2.2.2 Laboratory and molecular coordinates	26
2.2.3 Impulsive molecular alignment	27

2.2.4	Angular momentum coupling in diatomic molecules	33
2.2.5	Orientation resolution through rotational coherence spectroscopy (OR- RCS)	41
2.2.6	Wave-packet dynamics after strong-field ionization	43
3	Strong-field ionization of the triplet ground state of O ₂	46
3.1	Introduction	46
3.2	Experimental setup	49
3.3	Model and analysis	50
3.4	Results and discussion	52
3.5	Conclusion	56
4	High-resolution FFT spectroscopy of spin-rotation wavepackets in N ₂ ⁺ following strong-field ionization	58
4.1	Introduction	58
4.2	Experimental setup	60
4.3	Analysis	62
4.4	Results and discussion	65
4.4.1	B ² Σ _u ⁺	66
4.4.2	A ² Π _u	69
4.4.3	X ² Σ _g ⁺	72
4.4.4	Dissociative pathways	73
4.4.5	Spin-orbit coupling effect in A ² Π _u (v = 4)	76
4.5	Conclusion	79
5	Strong-field induced rotational coherences in the cationic states of O ₂	81
5.1	Introduction	82
5.2	Methodology	83
5.3	Results and discussion: 800 nm Probe	84

5.3.1	Kinetic energy release	84
5.3.2	The 0-250 meV band	84
5.3.3	The 0.75-1.5 eV band	90
5.4	Results and discussions: 264 nm probe	92
5.4.1	Multiple states can be observed in the KER-FFT spectrum with the third harmonic probe	92
5.4.2	$b^4\Sigma_g^-(v = 3, 4)$ state	92
5.4.3	$X^2\Pi_g$ state	93
5.4.4	$a^4\Pi_u$ to $f^4\Pi_g$ transition	95
5.5	Conclusion	97
6	Work in Progress : Probing Light-Induced Potential in D_2^+	99
6.1	Introduction	99
6.2	Methodology	101
6.3	Summary	104
7	Summary and outlook	106
	Bibliography	109
A	Calculation of rotational energy levels	130
B	List of calculated and experimentally observed rotational lines	132
C	List of dissociation limits for N_2^+ and O_2^+	139

List of Figures

1.1	Typical characteristic time scales involved in ultrafast studies.	2
2.1	The top panel shows the collinear scheme for third harmonic generation (THG). The setup's implementation is portable. Starting with an input mirror, second harmonic generation BBO-crystal followed by calcite plate, half wave plate for 800 nm and third harmonic generation BBO-crystal. This is followed by third harmonic separator which reflects the third harmonic by >99% and transmits the residual 800 nm and 400 nm by >90% to separate the TH beam. We have four of them. The white double sided arrow shows the polarization of the light, where the input is vertically polarized with respect to the table plane (out of the plane).	10
2.2	Experimental Setup, DS: Delay stage, BW: Brewster window, BS: Beam splitter, TL: Telescope, SF11: SF11 glass, P: Polarizer, OP: Optical chopper, VC1: Source chamber, VC2: Middle chamber, VC3: Target chamber	12
2.3	The Newton sphere generated by the ions from the break-up of molecules by the laser is projected to form the VMI images.	17
2.4	(a) The electronics and the connections schematics of the whole data acquisition setup and (b) the LEDs that are use to distinguish between different trigger conditions as seen on the camera. In the text we describe how these signals are read from each frame from the camera. This image is taken from Huynh Van Sa Lam's thesis ⁶	22

2.5	The first panel in (a) shows the initial trigger which is fed to the camera/probe pulse(1 kHz for HITS and 3 kHz (not shown) for FLAME). The second panel shows the set of LED outouts from the Even-Lavie valve driver. The opening time of the jet is set $\approx 10 \mu s$, and it runs at 500 Hz repetition rate. The set of pulses on the third panel of (a) shows the LED output signal from the chopped pump pulse triggered at 500 Hz and it chops the pump pulse allowing every 2 pulses in and 2 pulse out as shown in the diagram, every other 4 consecutive pulses. The second panel (b) shows the all the possible trigger outputs from pump (chopped by the chopper), gas, and probe and the combinations made by them.	23
2.6	(a) The axes in the solid blue line labeled with small letters represents the molecular frame (x, y and z) and the axes in the solid-red line labeled with capital letters represents the laboratory frame (X, Y and Z). (b) The laboratory frame coordinate is generally described by the laser polarization as shown here. For a diatomic molecule in a linearly polarized electric field (double-sided red arrow) the angle θ is defined by the angle between molecular axis and the electric field polarization.	27
2.7	$\langle \cos^2 \theta \rangle (t)$ trace obtained by solving the TDSE for N_2 molecule. The intensity, pulse duration and temperature used in the calculation is shown in the inset. The time axis is made unitless by dividing it with the rotational period of N_2 which is 8.38 ps. This image is taken from Huynh Van Sa Lam's thesis ⁶ . . .	33
2.8	Angular momentum vectors schematic for Hund's case (a) and (b) in panels (a) and (b) respectively. In (a) the dotted circles shows the precession of L and S around Ω , which is along the z direction and the solid circle shows the nutation of Ω around J . In (b), the dotted circle shows the precession of N 's projection on the inter-nuclear axis and the solid circles shows the nutation of N around J	35

2.9	Jucys diagram for J' , J , N' , N , S and l	38
2.10	ORRCS schematics showing the multiple iterations of the fitting procedure with different input parameters starting from the TDSE till the χ^2 converges to the minimum.	42
2.11	Application of ORRCS in strong field ionization of CO_2 ⁶ . The yield of CO_2^+ is fitted using the ORRCS procedure, the image is taken from Huynh Van Sa Lam's thesis ⁶	43
2.12	Schematic diagram of the pumping mechanism in the 800 nm laser field. In region I photo-ionization is assumed to be weak, near the the peak of the pulse (region II) tunneling ionization has the maximum differential cross-section, populating the low-lying electronic states and in the tail of the pulse (region III) resonant coupling happens. This schematic is adapted from Yao <i>et al.</i> ⁷	45
3.1	Normalized delay-dependent O_2^+ yield for different pump intensities (black lines) and their corresponding best fits (orange/gray lines). The probe is the same in all cases with intensity of 260 TW/cm ² . For clarity, the data and fits for 2.24 and 3.64 J/cm ² pump fluences are shifted vertically by 0.35 and 0.75 units, respectively. The pump fluences are estimated from the fits are shown below the corresponding plot lines in the graphs. Statistical error estimates ($\pm 3\sigma$) for the data are shown as light-gray shaded bands. Data near the end of the scan is shown on an expanded horizontal scale to show detail. The strong nonperiodic behavior is a consequence of the spin-rotation and the spin-spin couplings, as discussed in the text.	48
3.2	Fourier spectra of the delay-dependent data (solid) and the best fits (dotted) shown in Fig. 3.1. We have vertically shifted the spectra corresponding to 2.24 J/cm ² by 4.5 units and the one corresponding to 1.14 J/cm ² by 11.5 units. See text for details of spectroscopic notation and discussion on transition lines.	50

3.3	The expectation value of $\cos^2 \theta$ for spin-rotation wavepackets that best fit the data shown in Fig. 3.1. The plots for 2.24 J/cm ² and 3.64 J/cm ² fluences were shifted up by 0.5 and 1.1, respectively, for visual clarity.	53
3.4	Angle-dependent ionization rates retrieved from data shown in Fig. 3.1 and calculated using MO-ADK. In each case, the angle-dependent ionization rate is normalized to its maximum value.	55
4.1	Angle and delay integrated KER distribution. The identified electronic states are shown in the graph and the inset shows the zoom-in version of the 0-1.2 eV ranges of the distribution as most of the identified states are densely observed in this energy range. The rectangular box shows the high energy band and the contribution of this band comes from pump alone see in the text.	62
4.2	The 2D KER-FFT plot for $L = 0$ coefficients with KER range from 0 to 4 eV and the QB frequency from 0 to 200 cm ⁻¹ . States identified with the Raman lines are marked along with dissociation channels and the required number (264 nm) photon for achieving the KER, read discussion for details.	64
4.3	The relevant potential curves showing the low-lying states of N ₂ ⁺ . Purple arrows denotes the 264 nm probe and it highlights the possible dissociation pathways. The red arrows denotes the 790 nm pump. Here the near-resonant pathways between different vibrational states of these low-lying sates are identified. L1, L3, L6 and L7 are the dissociation levels as per ^{8:9} (see appendix C). These potential energy curves are recovered from ¹⁰	65
4.4	Plots of $FFT[C_0(t)]$ with the states and integrated KER range shown in the inset. The peaks are highlighted with black sqaure dots to easily identify the overlap with the calculated Raman lines.	67

- 4.5 (a) KER integrated delay dependence of the $A^2\Pi_u$ ($v=4$) channel integrated over 1.8-2.2 eV. As shown in the (b), the consecutive QB separation for F_1 and F_2 corresponds to the half revival in the delay dependence. (b) FFT of the $A^2\Pi_u$ ($v=4$) channel integrated over 1.8-2.2 eV. The peaks are shown in red dots as per the peak finding algorithm and drop down line on it is the calculated $\Delta J = 2$ frequencies using the energy equation for $A^2\Pi_{3/2}$ (F_1) and $A^2\Pi_{1/2}$ (F_2), shown by the blue and purple drop down lines respectively. (c) Frequency and KER (1.8-2.2 eV) filtered delay dependent yield of $A^2\Pi_{3/2}$ (F_1) and $A^2\Pi_{1/2}$ (F_2). The inset shows red curve belongs to $A^2\Pi_{3/2}$ (F_1) and the black curve belongs to $A^2\Pi_{1/2}$ (F_2). An offset of 20 units is added to the delay dependent yield of $A^2\Pi_{1/2}$ (F_2). 70
- 4.6 Frequency and KER filtered $\langle P_0 \rangle(t)$ and $\langle P_2 \rangle(t)$ delay-dependent intensity of (a) $X^2\Sigma_g^+$ ($v = 1$) (b) $B^2\Sigma_u^+$ ($v = 5$) (c) $B^2\Sigma_u^+$ ($v = 5$) and (d) $A^2\Pi_u$. The black curves are $\langle P_0 \rangle(t)$ and the red curves are $\langle P_2 \rangle(t)$. All the delay axis are from 40 to 60 ps. $X^2\Sigma_g^+$ ($v = 1$) (b) $B^2\Sigma_u^+$ ($v = 5$) (c) $B^2\Sigma_u^+$ ($v = 5$) are dissociating to L1 asymptote whereas (d) $A^2\Pi_u$ is dissociating to L3 asymptote. The inset text and the legends shows the state for which frequency filter and KER band filter was applied. 75
- 4.7 Reduced χ^2 of the linear model fit Vs spin-orbit interaction constant. The dotted blue line shows the spin-orbit interaction constant values for $A^2\Pi_u$. As indicated in the inset the red and black curves correspond to reduced χ^2 values for $\Omega = 1/2$ (F_2) and $\Omega = 3/2$ (F_1) respectively. 78
- 5.1 KER spectrum integrated over all delays from 1 to 198.95 ps. The regions 0–250 meV and 0.75–1.5 eV, where FFT spectra show bound wave packets, are highlighted by colored vertical bands in the inset 85

5.2	Quantum beat spectra of the 0-250 meV band. (a) Power spectrum of $\langle P_0 \rangle$ where the KER is integrated over the range of 0 to 130 meV. (b) Same as (a) but the KER is not integrated. (c) Same as (b) but for $\langle P_2 \rangle$. ν is the vibration quantum number, N is the rotational quantum number of the lower state, and ΔN indicates the transition of rotational states. The QB spectrum trends upwards in KER at higher N because the pump pulse excites molecules well past the threshold for predissociation (see Sec. 5.3.2 for more details and refer to Fig. 5.3 for a sketch of relevant potential energy curves).	86
5.3	Sketch of relevant potential energy curves (adapted from Ref. ¹¹ and ⁴) for the dissociation of the $b^4\Sigma_g^-$ state. The pump excites a broad rotational wave packet in $O_2^+ b^4\Sigma_g^-$. This bound wave packet can then predissociate or dissociate by the probe via multiple pathways as discussed in Sec. 5.3.2.	87
5.4	FFT spectra of the delay-dependent KER for $\langle P_2 \rangle$ of the high energy band (0.75-1.5 eV). In panel (a), the KER is integrated over the range of 1.0 to 1.4 eV. In panel (b), the KER is not integrated. The dominant channel is $\nu = 3$, channels $\nu = 4$ and $\nu = 2$ are weaker. In this case, the $b^4\Sigma_g^-$ state absorbs two photons and dissociate into the second dissociation limit.	89
5.5	(a) FFT spectra of the delay-dependent KER for $\langle P_0 \rangle$ in the IR-UV pump-probe experiment. Panel (b) shows the FFT spectrum of the $b^4\Sigma_g^-$ state dissociated into the first dissociation limit (L_1) after absorbing one UV photon (the KER is integrated over the range of 4.8 to 5.4 eV). Panel (c) shows the FFT spectrum of the $X^2\Pi_g$ state dissociated into the first dissociation limit (L_1) after absorbing two UV photons. The KER is integrated over the range of 1.3 to 1.8 eV. The expected positions of Raman lines corresponding to $\Delta N = 2$ are shown above the spectra in (b) and (c). For $b^4\Sigma_g^-$, only odd N is allowed while for $X^2\Pi_g$, both odd and even N are allowed. See Sec. 5.4 for more details.	91

5.6	Sketch of relevant potential energy curves for the dissociation of the $X^2\Pi_g$ state. The potential curves are adapted from Ref. 11 . The pump excites a rotational wave packet on $O_2^+ X^2\Pi_g$ state. This wave packet absorbs two UV probe photons and dissociates into different dissociation limits. The A-X transition is resonant with our probe wavelength at 264 nm. See Sec. 5.4.3 for more details.	94
5.7	Due to the spin-orbit coupling, the time-dependent yield of $X^2\Pi_g(v = 3)$ dissociated into L_2 channel (integrating KER range from 1.3 eV to 1.8 eV) (black, bottom) is complicated and nonperiodic without any regular revival structures. Filtering in the frequency domain shows different time evolution of F_1 and F_2 series. The $\Omega = 3/2$ (blue, top) exhibits clear quarter revivals while it is not clear the $\Omega = 1/2$ (red, middle). The F_1 and F_2 curves are shifted up for clarity.	95

5.8	(a) A portion of the frequency-KER data selected to highlight the single-photon dissociation of the $a^4\Pi_u$ state of O_2^+ by 264-nm pulses. Stick spectra show the expected location of $v=0-5$, $\Delta J = 2$, $\Delta\Omega = 0$ Raman lines in the $\Omega = 1/2$ and $\Omega = 3/2$ fine-structure levels. The signal visible between approximately 28 cm^{-1} and 31 cm^{-1} shows the typical dependence of KER on the vibrational level—internuclear distance increases with vibrational quantum number v due to the anharmonicity of the potential, which results in quantum beat frequencies decreasing with v . The absence of $v = 2$ is immediately evident. The same pattern of four vertical lines repeats for different values of J' and Ω , four of which are highlighted by the stick spectra. (b) KER spectra integrated over quantum beat frequency for $v=0-4$ for the lines identified by $J' = 11/2$ (magenta, on the left) stick spectrum. In each case a width of 0.2 cm^{-1} was used, with the center located at the calculated frequency of the quantum beat. (c) QB spectrum integrated from 2.1 to 2.4 eV, with the range selected to highlight $v = 0$ and $v = 1$	96
6.1	(a) 2D surface potential of H_2^+ adopted from work done by A.Natan <i>et al.</i> ¹² (b) Relevant light-induced potential energy of D_2^+ adopted from thesis of D. Pavičić's thesis ¹³ . In panel (a), the potential is generated using the light-induced adiabatic coupling term which contains both the angle θ which is the angle between the polarization axis and the inter-nuclear distance and the coupling strength which is determine by the electric field strength and the dipole value at the inter-nuclear distance. In panel (b), the generated plots are for different electric field strengths as shown in the legend and the dipole value at the inter-nuclear distance only but the angle is fixed with $\theta = 0$. . .	102
6.2	(a) Delay-integrated VMI image of D^+ photo-fragments (b) Angle and delay-integrated KER distribution of D^+ photo-fragments	103

6.3	2D KER-FFT plot of $L = 0$ coefficients from the VMI images of D^+ photo- fragments showing QB frequencies in different vibrational levels of Duetrium molecular ion. In this yield KER-FFT plot, we can already identify the dif- ferent vibrational levels of $1s\sigma_g$	104
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List of Tables

B.1	Calculated and measured rotational quantum beats for the B $^2\Sigma_u^+$ state (KER is integrated over the range of 200 to 270 meV for $\nu = 4$, 600 to 700 meV for $\nu = 5$ and 850 to 1000 meV for $\nu = 6$). This data is discussed in Sec. 4.4.1. .	133
B.2	Calculated and measured rotational quantum beats for the X $^2\Sigma_g^+$ state (KER is integrated over the range of 850 to 1000 meV for $\nu = 1$). This data is discussed in Sec. 4.4.3.	134
B.3	Calculated and measured rotational quantum beats for the $A^2\Pi_u(\nu = 4)$ state. The KER is integrated over the range of 1.8 to 2.2 eV. This data is discussed in Sec. 4.4.2.	135
B.4	Calculated and measured rotational quantum beats for the $b^4\Sigma_g^-$ state (KER is integrated over the range of 0 to 130 meV). This data is discussed in Sec. 5.3.2.	136
B.5	Calculated and measured rotational quantum beats for the $b^4\Sigma_g^-$ state dissociated into the first dissociation limit (L_1). The KER is integrated over the range of 4.8 to 5.4 eV. This data is discussed in Sec. 5.3.3.	137
B.6	Calculated and measured rotational quantum beats for the $b^4\Sigma_g^-$ state dissociated into the first dissociation limit (L_1). The KER is integrated over the range of 4.8 to 5.4 eV. This data is discussed in Sec. 5.4.2.	137
B.7	Calculated and measured rotational quantum beats for the $X^2\Pi_g(\nu = 1)$ state dissociating into L_2 . The KER is integrated over the range of 1.3 to 1.8 eV. This data is discussed in Sec. 5.4.3.	138

C.1	Dissociation energies for the lowest ten dissociation limits of N_2^+ . All energies are measured with respect to $X^1\Sigma_g^+ v = 0$ state (N_2 ground state). This table is adapted from Aoto <i>et al.</i> ⁹	139
C.2	Dissociation energies for the lowest three dissociation limits of O_2^+ . All energies are measured with respect to lowest dissociation limit L1 of O_2^+ . This table is adapted from Liu <i>et al.</i> ¹⁴	140

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Chapter 1

Introduction

This chapter aims to provide a brief overview of relevant topics in ultrafast atomic, molecular, and optical physics while reviewing key studies that have been conducted to elucidate the fundamental processes occurring in light-matter interaction in the strong-field process. Following this introduction, I will shed light on the work done in this dissertation, the explored aspects, and the motivation behind the projects. Finally, I will briefly go over how each chapter is structured in this dissertation.

1.1 Motivation

In the field of ultrafast atomic, molecular, and optical physics one of the important goal is to understand the properties of molecules and to control them. The first step is to understand ultrafast processes that occur during light-matter interactions. This requires a tool that can discern these ultrafast motions. Ultrashort pulsed lasers provide the essential components of a wide variety of techniques^{15–17}. With the introduction of femtosecond pulsed lasers, the exploration of ultrafast rotational, vibrational and electronic motion of molecules, which are on the order of few picoseconds, femtoseconds, and attoseconds, respectively can be resolved. This field of chemistry is called femtochemistry, it was first introduced Ahmed Zewail¹⁸, for which he was awarded the 1999 Nobel Prize in Chemistry. Using the pump-probe technique

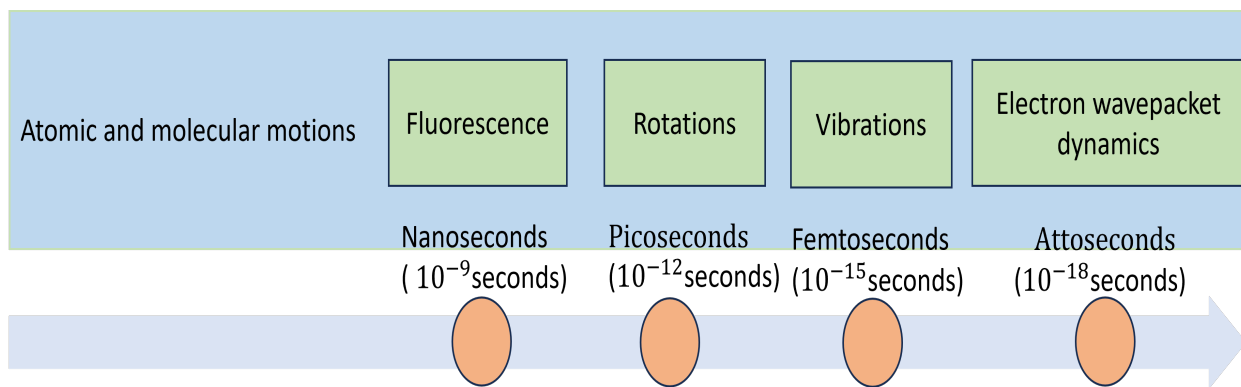


Figure 1.1: *Typical characteristic time scales involved in ultrafast studies.*

introduced by Zewail with ultrashort laser pulses enables the monitoring of molecular motion, including vibrations and the formation and cleavage of molecular bonds. Another growing field alongside the technology offered by ultrafast laser was strong field physics starting with the discovery of Above Threshold Ionization (ATI)^{19;20}, multiphoton-ionization²¹, and higher harmonic generation (HHG)^{22–26}. HHG gave birth to the technology of tabletop extreme ultraviolet (XUV) and soft X-ray sources which are generated with high-order harmonics of the fundamental laser radiation produced in noble gas atoms. Such radiation has proven successful in generating pulses with durations in the attosecond range (1 attosecond = 10^{-18} s)^{23;27;28} and giving rise to attosecond science. To give a perspective, the period of the electron’s motion around the hydrogen atom calculated with Bohr’s formula is ~ 150 as; see Fig. 1.1 for typical timescales for ultrafast microscopic processes. Concurrently, both theoretical and experimental endeavors have been undertaken to characterize the duration of attosecond XUV pulses^{29;30}. In 2023, Pierre Agostini, Ferenc Krausz, and Anne L’Huillier were awarded the Nobel Prize in physics for their pioneering work in this field.

Some of the important chemical and biological processes that are already investigated with light using pump-probe spectroscopy are photosynthesis^{31;32}, DNA damage^{33;34}, stability of DNA under UV radiation^{35;36} and the photo-isomerization process involved in vision^{37;38}. Another direct application of strong field phenomena (HHG) is the used of attosecond pulses in Extreme ultraviolet (EUV) lithography³⁹ which is used in making modern semiconductor chips.

Throughout the dissertation we will be using molecular alignment so here is a brief history of about it. Molecular alignment was done using static electric fields to study the effects of orientation on chemical reactions⁴⁰ and ionization process⁴¹ which gradually evolved to pulsed laser fields with pulse durations much longer than the rotational time periods^{42;43}. These types of molecular alignment comes under adiabatic alignment. Friedrich and Herschbach⁴³ predicted its application to trapped cold molecules. Finally, molecular alignment using short pulses is called the impulsive alignment and this technique manifests as a significant enhancement in the alignment of rotational wave packets occurring under field-free conditions^{44–46}. Many experimental studies done on gas phase have benefited using aligned molecules. The experiments performed on aligned gas-phase molecules have shown to provide richer information as shown by Yang *et al.*⁴⁷ in Ultrafast Electron Diffraction (UED) experiments, Wolter *et al.*⁴⁸ and Krecinic *et al.*⁴⁹ in Laser-Induced Electron Diffraction (LIED) experiments, and Küpper *et al.*⁵⁰ in ultrafast x-ray diffraction experiments. This enhancement enables the direct extraction of molecular structures in both two and three dimensions for all these techniques.

In this dissertation, we investigate strong-field induced processes in diatomic molecules by photodissociating and photoionizing them using an ultrafast laser. Our technique is closely related to rotational coherence spectroscopy (RCS)⁵¹, where time-domain measurements of rotational wavepackets used to study geometries of large gas-phase molecules whereas the method we will be using is Orientation Resolution through Rotational Coherence Spectroscopy (ORRCS) developed by Makhija *et al.*¹ is done with cold molecules. The time scale of our measurements hence will stick to picoseconds as shown in the Fig. 1.1.

In the time evolution of rotational wavepacket in oxygen (a diatomic molecule), we observed an interesting non-periodic behavior. For the first part of the thesis, we focused on investigating what led to this non-periodic behavior, which is related non-periodic behavior observed in both impulsively aligned molecular iodine⁵² and NO^{53;54}. In case of NO the non-periodicity was attributed to the spin-orbit coupling in the low-lying $^2\Pi$ states and in case of molecular iodine it was the hyperfine coupling between the electric quadrupole moments of the atomic nuclei and the gradient of the electric field. However in case of neutral oxygen we

found out that the reason for this non-periodicity was electronic spin coupling to rotational motion in the $^3\Sigma_g$ ground state of oxygen³. Following this experiment, we also investigated the cationic states of N_2^+ , O_2^+ , and D_2^+ which also showed the spin coupling behavior in the low-lying states of the cation.

In our photodissociation measurements of N_2^+ , O_2^+ , and D_2^+ we specifically use available information on rotational spectroscopy of electronic levels for each specie to uncouple all the possible states involved which allow us almost always unambiguously identify a vibronic level. Especially it is a very useful tool to have in studying strong-field processes as it involves multiple photons to complete a process, and our measurement gives insight into the intermediate step with just the knowledge of rotational lines of the expected electronic states and no theoretical calculations is required. We have shown that it is also applicable in region of potential energy curves which are moderately dense with electronic states, where a non-adiabatic coupling among different electronic states is likely. For such regions of interest in potential energy curves, the technique will have limitations due to its highly dense nature and broadened spectral features. We have extracted information by employing complementary time-dependent methods with sufficient temporal resolution for rotational wavepacket evolution.

1.2 Structure of the dissertation

The measurements done in this dissertation revolve around elucidating crucial light-matter interaction, including strong-field ionization, strong-field induced processes in the excited states of diatomic molecules, and photodissociation via few-photon process. A pump-probe scheme is employed across all experiments: an initial pump pulse impulsively aligns the molecules non-resonantly, generating a coherent broadband rotational wave packet in either neutral or cations. In the case of cations, the first half of the pulse prepares the electronically excited cationic states following a strong-field ionization, followed by impulsive alignment in the later portion of the pulse. Subsequently, a probe pulse administered at a later time induces the specific process of interest, such as ionization or dissociation. The observables

used are ion yield in the case of the strong-field ionization experiment and the momentum distribution of ion fragments in the case of photodissociation experiments. These observables are measured as a function of the pump-probe delay, capturing the evolution of the rotational wave packet under field-free conditions after the aligning pulse has dissipated. Due to the rotational coherent excitation that occurred during the pump, we would be able to recover the excited rotational coherences in the frequency domain by doing a Fourier transform of the time-domain measurements, and using this frequency and the Kinetic energy release information acquired from the momentum distribution of the fragments we will deduce the chemical pathways induced by the strong-field in case photodissociation experiments.

Chapter 2 endeavors to comprehensively cover the experimental techniques employed in this work, with a particular emphasis on the experimental setup, namely the velocity map imaging spectrometer. Additionally, this chapter also offers detailed insights into the light sources and quantitatively discusses the theoretical and analytical techniques utilized throughout the experiments outlined in this thesis.

In chapter 3 we discuss the detection of a markedly non-periodic evolution in the spin-rotation wave packet initiated by a non-ionizing femtosecond pulse in molecular oxygen ground state. We observe the yield of the parent ion by employing strong-field ionization as a probe. This lack of periodicity is evident exclusively in rotationally cold molecules that have been subjected to an weak alignment pulse. Our analysis reveals that this phenomenon stems from the interplay of spin-rotation and spin-spin couplings within the triplet ground state of the neutral molecule. We have also discussed the results acquired from the spin-rotation coupled Orientation Resolution through Rotational Coherence Spectroscopy³ which was developed for this project and verified the angle-dependent ionization rate in our experiment qualitatively matches with what is predicted by Molecular Ammosov-Delone-Krainov⁵⁵.

Chapter 4, 5 and 6 contains the results obtained by the measuring photodissociation process of N_2^+ , O_2^+ , and D_2^+ respectively. For all these chapters with photodissociation measurements, the sample to be probed is prepared by strong-field ionizing the neutral coming from the high-pressure gas jet (Even-Lavie valve⁵⁶), which cools the molecules to a rotational temperature of about $\sim 1\text{-}3$ K. The ~ 790 nm pump prepares a bound-wavepacket

in the low-lying states of N_2^+ , O_2^+ , and D_2^+ and it is probed using photodissociation by 264 nm wavelength probe creating the fragments of the molecular ions. Chapter 4 deals with the X $^2\Sigma_g^+$, A $^2\Pi_u$ and B $^2\Sigma_u^+$ states of N_2^+ that are involved in controversial air-lasing experiments^{7;14;57-64}. We observe these low-lying ionic states get aligned and also observe their time-dependent behavior in yield and spatial anisotropy becomes out-of-phase for different vibronic manifolds. Chapter 5 deals with X $^2\Pi_g$, b $^4\Sigma_g^-$, a $^4\Pi_u$, and f $^4\Pi_g$ states of O_2^+ , the previous measurement done by De *et al.*⁶⁵ using an 8 fs, 800 nm pulses. Here we aim to understand the disparities observed in the measurement done by De *et al.*⁶⁵ and also reconcile with the theoretical frameworks done by Xue *et al.*⁴ which predicts the involvement of b $^4\Sigma_g^-$ state as the intermediate state O_2^+ before photodissociation. We also found a vibrational Cooper minimum going from a $^4\Pi_u$ to f $^4\Pi_g$ state of O_2^+ . Chapter 6 is a work in progress and it deals with $1s\sigma_g$ and $2p\sigma_u$ states of D_2^+ , which get light-dressed in the presence of strong-field laser radiation. In this work, we have already identified some of the dissociative pathways of D^+ that are coming from the light-induced potential. In the future of this project, we would like to obtain a theoretically calculated momentum distribution of the D^+ coming from a single rotational coherence of the $1s\sigma_g$ and compare it to our results.

Finally, chapter 7 contains a summary and outlook related to studies presented in this thesis.

Chapter 2

Experimental and theoretical techniques

In this chapter, we will present and explore various experimental and theoretical methods which will be employed throughout the remainder of this dissertation. The first part of this chapter will describe the experimental setup which mainly consist of the light sources, optical systems, ultrahigh vacuum system and velocity map imaging spectrometer. Secondly, description of the data acquisition system is provided with relevant schematics and diagrams. Lastly, in the theoretical tools section we will discuss the molecular impulsive alignment, relevant Hund's cases with description of coupling of rotational and electronic spin angular momentum, the Hamiltonian used for the molecular alignment simulation, Orientation resolution through rotational coherence spectroscopy (ORRCS) and the understanding of the wavepacket dynamics in the cationic state.

2.1 Experimental tools

2.1.1 Light source

Femtosecond lasers

A femtosecond laser is a crucial component of our experimental setup. In this dissertation we have used two commercial femtosecond systems HITS (High-Intensity Tunable Source) and FLAME (Femtosecond Laser for Multi-color Experiments). Both LASER systems are commercially available, and the specs can be looked up on their respective company websites; HITS (operates with customized version of RedDragon amplifier) was bought from KM labs, and FLAME (operates with customized version of Legend Elite Duo amplifier) was bought from Coherent Incorporated. Both the Lasers have central wavelength 800 nm , pulse duration (~ 25 fs and ~ 30 fs for HITS and FLAME respectively), the repetition rate of the laser(1 kHz and 3 kHz for HITS and FLAME respectively), and the output energy is less than ~ 5 mJ/pulse depending on the how hard the amplifier is driven. Both systems consist of a self-mode-locked oscillator with Ti:sapphire crystal and the femtosecond pulse output from the oscillator is amplified using the chirped pulse amplification (CPA) technique¹⁶ which allows pulse energy amplification for short pulses without damage to the optical components. It involves stretching the pulses temporally before amplification, amplifying them, and then compressing them back to femtosecond pulses. The HITS's multi-pass-amplifier system uses a cold Helium which is cryo-cooled by a Gifford-McMahon cycle cryocooler and the FLAME's regenerative amplifier uses a water-cooling technique to take the heat out of the Ti:sapphire amplification crystal. Typically the output from the oscillator is a few nanojoules per pulse and it is amplified to a few millijoules of pulse energy but with a reduced repetition rate. For FLAME unit before stretching, the oscillator beam goes through a special spatial filter (SSF), a notch filter which reduces the beam intensity around 800 nm. It is done to make the a flat spectral profile after amplification through the Ti:Sapphire crystal. The 80 MHz (pulses from Coherent's Vitara oscillator) are stretched and it enters a Signal Delay Generator Elite(SDG-Elite) and a Pockels cell to convert the

repetition rate to 3 kHz. The amplification in Elite Legend Duo system is done using a Revolution diode-pump, Q-switched 527 nm Nd:YLF laser. The output of pump laser is overlapped with the stretched seed pulses and it is directed into the regenerative cavity with a Ti:Sapphire crystal. The amplifier output is split into two arms (each will have their corresponding all reflective compressors) one will go into a commercial High Energy Traveling-Wave Optical Parametric Amplifier and the other arm will be sent to a external compressor to be used as a 800 nm arm.

Third-harmonic source

We have built our own third harmonic source for ~ 790 nm which produces ~ 264 nm light. It has a bandwidth of ~ 1.5 nm FWHM and a pulse duration of ~ 120 fs. We will take advantage of the fewer photons (weaker intensity) with higher energy light in this wavelength in our N_2^+ , O_2^+ study at chapter 4 and 5 respectively. The scheme we have used to create the third harmonic (3ω) is by firstly doing a second harmonic generation (SHG)⁶⁶ col-linearly using a $\chi^{(2)}$ non-linear crystal and then using a sum frequency generation (SFG)⁶⁶ of the fundamental (ω) and the second harmonic (2ω) using another non-linear crystal as shown in the schematic in Fig. 2.1. It consists of two type-1 beta barium borate crystals (BBO of 100-micron thickness) as the $\chi^{(2)}$ non-linear crystals, a calcite plate which compensates the delay generated between the ω and the 2ω after the SHG process, and since half wave plate for 800 nm acts as half wave-plate for the ω and full wave-plate for the 2ω . The polarization of both the input fundamental and output TH is perpendicular to the optical table. We have verified the polarization of the ω and the 2ω using polarizers of the corresponding wavelength. The 3ω is filtered out using a series of separators (5 separators) which reflects the 3ω and transmits residual ω and 2ω . The assembly is mounted on an optical board which makes it portable as shown in the Fig. 2.1. An estimate of the pulse duration is made by measuring the difference frequency generation signal of ω and the 3ω using another type-1 BBO crystal and measuring the cross-correlation trace⁶⁷ of the 2ω which is separated from ω and the 3ω using a prism made of calcium fluoride. With the pulse duration of ω (τ_ω)

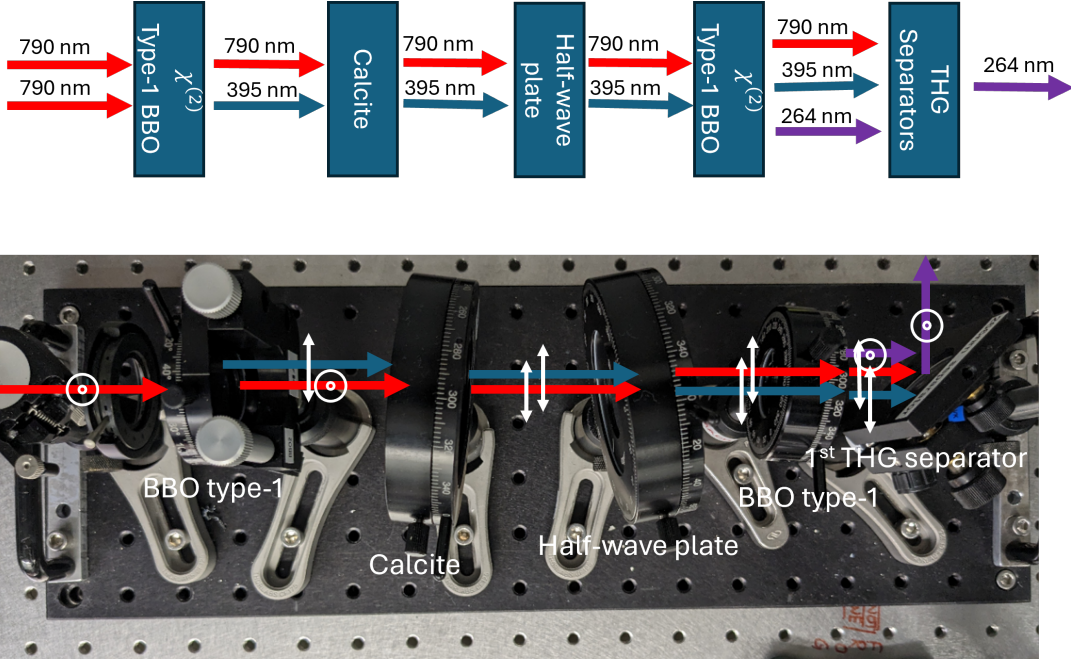


Figure 2.1: The top panel shows the collinear scheme for third harmonic generation (THG). The setup's implementation is portable. Starting with an input mirror, second harmonic generation BBO-crystal followed by calcite plate, half wave plate for 800 nm and third harmonic generation BBO-crystal. This is followed by third harmonic separator which reflects the third harmonic by $>99\%$ and transmits the residual 800 nm and 400 nm by $>90\%$ to separate the TH beam. We have four of them. The white double sided arrow shows the polarization of the light, where the input is vertically polarized with respect to the table plane (out of the plane).

measured from FROG, we used the relation $\tau_{3\omega} = \sqrt{\tau_{2\omega}^2 - \tau_{\omega}^2}$ to get the pulse duration of 3ω ($\tau_{3\omega}$).

2.1.2 Experimental setup

We transport the laser pulses from HITS/FLAME to our setup (the schematics is shown in the Fig. 2.2). For our experiments, we get ≈ 1.2 mJ and ≈ 2.5 mJ per pulse energy from HITS and FLAME, respectively, at the entrance of the setup. The laser output is split into two beams using a broadband beamsplitter which reflects 75% and transmits 25%. The reflected pulse will be used as a probe while the transmitted pulse is down-collimated by a telescope to use it as a pump pulse. By down collimating the pump beam, the focus spot of the pump is ≈ 2 times larger than the probe focal spot. This design choice allows signal measurement exclusively from well-aligned molecules, effectively minimizing the impact of averaging over the pump intensity distribution at the focus. We used achromatic zero-order half-wave plates and cube polarizers to control the power in both the beam paths. This power control only works for lower energy HITS pulses but when we started using the FLAME beam, we used a pair of thin film polarizers in place of the cube polarizers. The delay between the pump and the probe pulse is adjusted using a computer-controlled translation stage. For the O_2 ionization experiment³, the compressor grating was optimized for the shortest probe pulse and the pump pulse was used to align the molecules. The pump beam is stretched by placing a 10 mm thick SF-11 glass in its path. For dissociation experiments of N_2^+ , O_2^+ and D_2^+ , the pump pulse was optimized for the shortest pulse using the compressor. Therefore, there was no SF11 glass in its path. The role of the pump pulse in these experiments was to ionize the neutral samples and simultaneously align the cations by the tail of the pulse see Fig. 2.12. The third harmonic probe beam for the dissociation experiments is longer than the pump pulse which have a pulse duration about 120 fs, and the IR probe beam have similar pulse duration of about 35 fs. Before entering the vacuum chamber, pulse durations were measured using frequency-resolved optical gating (FROG)⁶⁸ of the 800 nm pulses. A window was introduced prior to the FROG setup to account for dispersion in the chamber window.

To determine focal spot sizes, we image the focal spot on a camera. To avoid burning and saturation of the camera pixels, we reduced the power of the laser and used neutral density filters. We also adjust the filters so that the pixels are near towards the saturation point. By utilizing the pulse duration and focal spot size measurements, the pulse intensity was estimated under the assumption of Gaussian spatial and temporal profiles. These beams are then combined using either a mirror with hole at the center or a beam splitter. For a third harmonic probe, we use a separator which reflects the 800 nm and transmits the 266 nm beam as the recombination mirror. Subsequently, the combined beams are focused inside a vacuum chamber using a dielectric concave mirror with a focal length of 20 cm. This back-focusing mirror has a high reflection rating for $267\text{nm} > 99.5\%$ and $400+800\text{nm} > 99.7\%$ with group delay dispersion (GDD) optimized. Within the vacuum chamber, the pulses interact with rotationally cold molecules generated through the supersonic expansion of seeded gas using a 500 Hz Even-Lavie valve (see section 2.1.3).

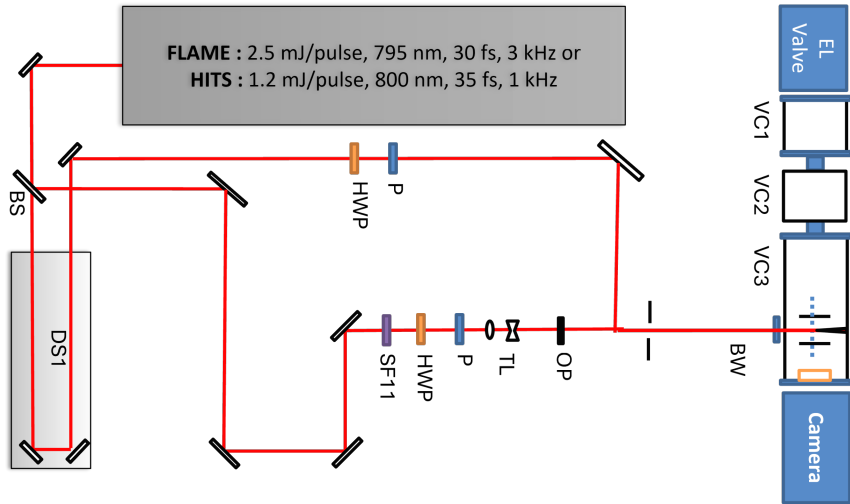


Figure 2.2: *Experimental Setup, DS: Delay stage, BW: Brewster window, BS: Beam splitter, TL: Telescope, SF11: SF11 glass, P: Polarizer, OP: Optical chopper, VC1: Source chamber, VC2: Middle chamber, VC3: Target chamber*

2.1.3 Cold molecule source

Molecules at room temperature (~ 300 K) have an energy of ~ 25 meV, and to give a perspective the rotational energy level difference between two same symmetry (even or odd)

consecutive rotational states of molecular nitrogen is ~ 0.495 meV (~ 2 B). To ensure the initial states of the molecules are localized near the ground state, we use cold molecules in our experiment. This limits the thermal spread in the laser-induced coherent spectra, hence reducing the number of spectral lines and simplifying the analysis. It has also been shown that the best laser induced molecular alignments were achieved using cold molecular samples⁶⁹.

In this section, we will briefly discuss how we get a cold molecular beam from a supersonic expansion using an Evan-Lavie valve⁷⁰ and some crucial things to keep in mind during a design of a cold target source with pulsed jets. The following discussion is partly from the text Atomic and Molecular Beam Methods: Vol. 1⁷¹. One of the important parameters that dictates the supersonic expansion is the pressure ratio of the source-gas bottle (P_o) and the background in the vacuum chamber (P_b). Due to the pressure difference between the background and source (a ≈ 2000 psi gas bottle) the gas expands into the vacuum chamber when they are connected. For pressure ratio P_o/P_b greater than G where $G = ((\gamma + 1)/2)^{\gamma/(\gamma-1)}$ (here γ is the ratio of the heat capacity measured at constant pressure and constant volume (C_p/C_v))-for all the gases G is less than 2.1) then the mean velocity of the molecules can reach up to the local speed of sound (Mach number (M)= 1) at the exit which is the hole connecting the source and the chamber. The pressure in the supersonic expansion region becomes independent of background pressure, and it is equal to P_o/G , and the gas keeps expanding with increasing velocity due to this until it hits the boundary condition of the background pressure. This implies that the gas in supersonic expansion cannot sense any downstream boundary condition as there is no information transfer between the molecules ($M > 1$). Hence this zone is referred to as the zone of silence. Thermodynamically, it is an isentropic expansion as there is no information swap until the molecules experiences shock which adapts the expansion to the boundary condition. At the shock, the expansion becomes a subsonic process again ($M < 1$). The shock along the centerline of the stream of molecules is called Mach disc and the shock along the transverse direction of the centerline is called

Barrel shock. We can estimate the position of Mach disc using the following equation,

$$x_M = 0.67D\sqrt{\frac{P_o}{P_b}} \quad (2.1)$$

For our setup, $D \approx 100\mu m$, $P_o \approx 5 \times 10^4$ Torr, and $P_b \approx 1 \times 10^{-5}$ Torr, thus $x_M \approx 4.7m$. The entire vacuum chamber setup is about 1.5 m long in our experiment chamber; therefore, the experiments are performed within the zone of silence. We also use skimmers to collimate and transmit the molecular beam through differential pumping stages. The skimmers reduce the transverse velocity spread and therefore the transverse translational further reduce the translational temperature of the molecules. For an isentropic ideal gas expansion with $\gamma = \text{constant}$, the relationship between initial and final state of the thermodynamics variables can be written in terms of the Mach number M for a continuous flow. The zone of silence is further divided into the continuous flow and the molecular flow. The mean velocity across the flow direction quickly rises approach the terminal velocity. Terminal velocity can be computed using,

$$V_\infty = \sqrt{\frac{2R\gamma T_0}{W(\gamma - 1)}} \quad (2.2)$$

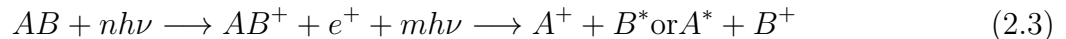
Here W is the molecular weight of the gas and T_0 is the initial temperature. At a point where velocity is approximately equal to 0.98 times terminal velocity marks the breakdown of the continuum flow, and the flow becomes almost collision-less hence the molecular flow. There is internal energy relaxation involved in the initial expansion process and it has been studied by Gallagher and Fenn(1974)⁷².

In our setup, we used an Evan-Lavie valve⁷⁰ to produce a cold molecular jet, and some important features of the valve can be found here⁵⁶. It has been demonstrated that in the pulsed mode with a cryogenic stagnation temperature, the valve can cool helium to sub-Kelvin temperature⁷⁰. Our valve has been configured to run with hot temperature equipped with a heater. Usually we end up with 1-10 K cold (rotational temperature) jet for diatomic molecules like O_2 and N_2 after the expansion. The valve is equipped with a trumpet shaped

nozzle of a 100 μm hole to deliver high density sample to the source chamber. Due to the short duration of the gas pulses, our source chamber can support high stagnation pressure of sample gas (~ 1000 psi) with a turbo molecular pump of 2400 l/s pumping rate and can maintain a background pressure of $\sim 5 \times 10^{-5}$. The high stagnation pressure improves the cooling (lower final temperature) which can be seen from the ideal gas thermodynamic state equation during the expansion phase. We pulsed the valve with 500 Hz external trigger for an opening time of $\sim 10 \mu s$ for all the experiments shown in this dissertation. The 0.5 % duty cycle reduces the throughput of the pumping system (estimated by product of pumping speed and background pressure) by a factor of 100 or more compared to running in 50 % duty cycle jet, thus allowing the turbo molecular pump to run in a stable mode. As shown by U.Even⁷⁰ the valve gets unreliable with frequency higher than 500 Hz. We can observe this effect in background counts of our experiments. We scan the start timing of the trigger pulse and sit at the position where the yield profile is maximum.

2.1.4 Velocity map imaging spectrometer (VMI)

Considering a photo-ionization or photo-dissociation process in a diatomic molecule AB , we can write the following equation representing the intermediate and final product relevant for the work done in this dissertation.



After the photo-dissociation or photo-ionization process, the two fragments generated move in opposing directions with conservation of momentum and conservation of energy in play. A sphere is formed for a single fragment energy in real space. This distribution is known as the Newton sphere. The radius of the Newton sphere which is proportional to the speed of the fragments and the angular distribution on the Newton sphere depends on the angular momentum of the fragments. The angular momentum distribution provides insights to the photo-ionization and photo-dissociation process⁷³. The VMI spectrometer

allows us to image this Newton sphere by projecting it onto a 2D surface on the detector. This projection is done in such a way that the fragments with same velocity components in the detector plane to hit on the same position on the 2D surface of the detector. This was first introduced by Eppink and Parker⁷⁴.

Traditionally, to achieve this projection of the Newton sphere in a VMI spectrometer, three-plate ion-imaging electrodes were used. These electrodes are commonly called the repeller, extractor and ground plate⁷⁴. These plates function as an electrostatic lens manipulating the equipotential surfaces of the whole spectrometer space. This lens directs the fragment ions with matching velocity components parallel to the detector plane towards a single point on the focal plane. The most important parameter to control the ion fragments focusing condition is the ratio of electric potential of the repeller (V_{rep}) and the extractor (V_{ext}). This ratio ($\frac{V_{ext}}{V_{rep}}$) varies depending on the geometry of VMI spectrometer. For our spectrometer it is ≈ 0.908 , and we usually set the repeller voltages to be at 1250 V and the extractor voltages to be at 1135 V while running at focusing condition.

The VMI spectrometer in our setup has a similar design to the thick lens VMI which was built by N.J Kling *et al.*⁷⁵ who show that the resolution achieved using the thick lens-VMI remains consistent across the energy spectrum and exhibits an enhancement of approximately 2 times compared to the standard three plate design. Our VMI consists of 8 extractor plates rather than a single extractor plate, 1 ground and 1 repeller plate separated by polyether-ether-ketone spacers. The extractor plates up to the ground plate are connected to each other through ultrahigh-vacuum-compatible 100M Ω resistors, forming a resistor ladder circuit. We feed voltage input only at the repeller and the first extractor plate using the SHV-5 feedthroughs with a high voltage source and the ground plate is wired to the body of the chamber. The stack of electrode plates and the flight tube are covered with μ -metal (nickel-iron soft ferromagnetic alloy) shield to avoid any magnetic field. We have a back focusing mirror geometry therefore the space between the repeller and the first extractor plate needs to be wide enough to fit and incoming and outgoing beam. The gas jet comes through the skimmer of 0.5 mm diameter at the center of the VMI along the axis of cylindrical symmetry, and this is where the light and the gas molecules interact [see Huynh Van Sa Lam's thesis⁶

for geometry]. We commonly refer to it as the interaction region.

Analysis of the VMI images

The acquired VMI image is a projection of the Newton sphere as shown in the Fig. 2.3 using the inverse Abel transformation we can retrieve the three-dimensional cylindrical symmetric distribution from the 2D projected images. Abel inversion works only when the fragment momentum distribution is cylindrically symmetric with the axis of symmetry parallel to the plane of the detector. There are several algorithms to get the Abel inverted images⁷⁶. We use

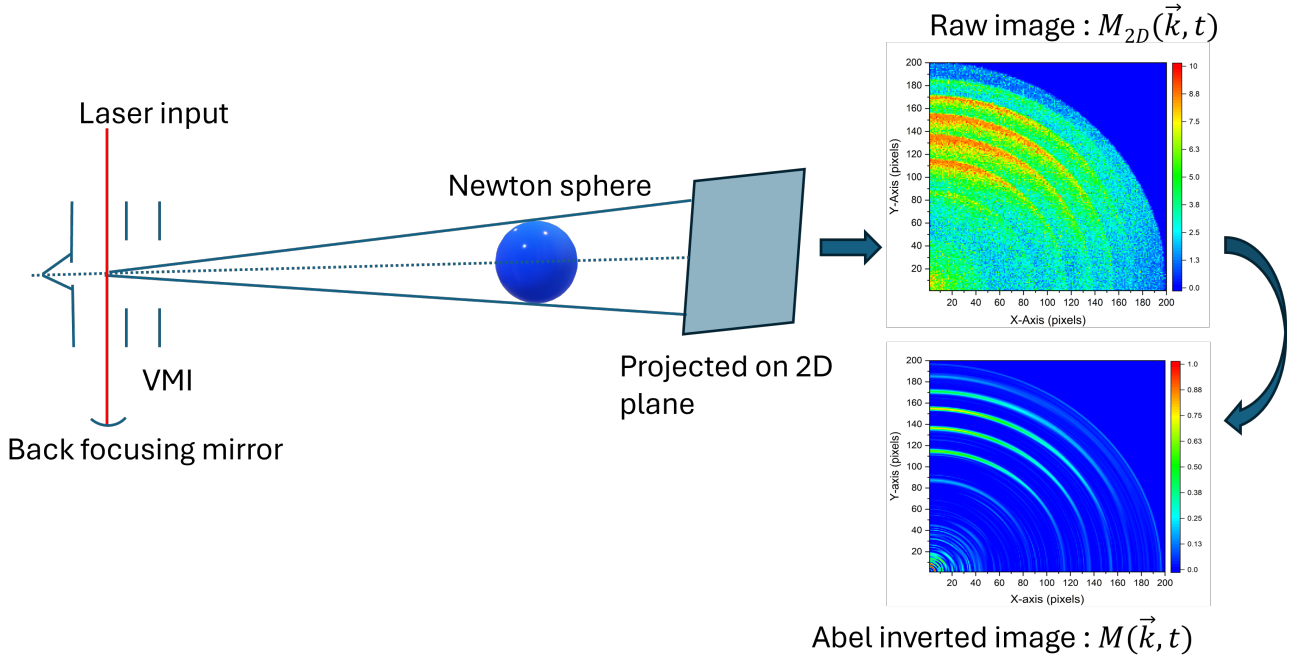


Figure 2.3: The Newton sphere generated by the ions from the break-up of molecules by the laser is projected to form the VMI images.

a method called pBasex⁷⁷ in our analysis. In this algorithm, we write the full 3D distribution in molecular frame with in a Legendre polynomial and Gaussian basis as,

$$M(k, t) = \sum_{k_0, L} C_{k_0, L}(t) e^{\frac{(k-k_0)^2}{\sigma}} P_L(\cos \theta) \quad (2.4)$$

Here $P_L(\cos \theta)$ is the the Legendre polynomial with L as the degree of the polynomial and k_0 defines the radius about which the Gaussian function is defined and the k is radius

and θ is angle between the laser polarization and the $\vec{k}$. Using the pBasex algorithm and the time dependence of the coefficients we extract the coefficient $C_{k_0,L}(t)$ for each delay t . $C_{k_0,L}$ represents the variation of the spectrum with the pump-probe delay. To get the radially integrated distribution we integrate $C_L = \sum_{k_0} C_{k_0,L}(t) e^{\frac{(k-k_0)^2}{\sigma}}$ over k_0 . And over this radially integrated coefficient we perform fast Fourier transform along the delay axis and calculate the power spectrum $C_L(k, \omega)$. This analysis procedure is used to acquire the 2D KER-FFT spectrum in chapter 4 and 5.

2.1.5 Time of flight spectrometer

We have used the VMI spectrometer chamber as a Time of flight (TOF) spectrometer and used to identify the species of the charged particle (ions) for gating on it or finding out any contamination in the chamber prior to any experiment. To do so we set a high voltage for repeller (usually 1250 V) and low voltage for extractor (usually 400 V) which is not in focusing condition. We also ground one of the plates of the MCP (the front plates) and do not apply any voltage to the phosphor for the TOF operating mode. We then measure the signal from the microchannel plate (MCP) (see Sec. 2.1.6) using a decoupling box with an oscilloscope (Lecroy Wavesurfer 42x). In the TOF spectrometer, the time of arrival (t) for the ions is governed by the mass-to-charge ratio (m/q) of the species and with the following equation of TOF we calibrate the TOF spectrum⁷⁴.

$$t = k \sqrt{\frac{m}{q}} + t_0 \quad (2.5)$$

Once we identify two peaks or species in the TOF spectrum we fit the above equation to find out the instrument calibration factors k and t_0 . Usually, the width of a peak are of ≈ 50 ns as observed in our oscilloscope.

2.1.6 Detectors

Initial designs and features of a microchannel plate detector can be found in the article by Wiza *et al.*⁷⁸. A microchannel plate comprises millions to tens of millions of ultra-thin conductive glass capillaries. These capillaries are fused together and then sliced into the form of a thin plate. Individually, each of these capillaries operates as an independent secondary electron multiplier, collectively forming a two-dimensional secondary electron multiplier array. The MCP in our experimental setup is from Photonis and it is made up of two stacks of channels commonly called chevron or two-stage MCP. The diameter of these channels in our MCP is $25\ \mu\text{m}$ (pore size), $32\ \mu\text{m}$ (center-to-center spacing) and bias angle of 8° . The ratio of pore size and the channel length ($\approx 1\text{mm}$) and the inherent secondary emission factor of the channel wall determines the gain. Each time the electron or ions hit the channel walls it multiplies, creating a cascading effect and our MCP has a gain of about $\approx 1 \times 10^7$ at an operating voltage of $\approx 2\ \text{kV}$. The quality diameter of our MCP is about $75\ \text{mm}$ in which 45% is open area of the pores. When we apply voltage across the plates, we expect it to have a resistance of $\approx 10\ \text{M}\Omega$. We must make sure the voltage applied versus current drawn of the MCP is linear when we condition the MCP. Conditioning of MCP is done by grounding the MCP front and applying voltages at MCP back very slowly (in steps of $100\ \text{V}$). During which the feedback signal from the decoupler and linearity of voltage applied verses current drawn by the MCP is monitored until we observe the dark counts (usually seen $\approx 1900\ \text{V}$ for our chevron MCP). If we observe any spike in the feedback signal, then we go back to the previous voltage step and wait. But if the V vs I is getting non-linear then we should stop applying voltage to the MCP and try debugging (it is likely that the detector is not working in this case). MCP conditioning is done after it has been in good vacuum (pressure less than $10^{-6}\ \text{torr}$) for at least 24 hours. It is a necessary procedure after it is being taken out of the UHV system. Air molecules can get trapped in the pores of the MCP and which can cause arcing in the channel damaging it permanently if we are not careful while conditioning the MCP. The MCP is operated near the saturation region for a good gain and over time we find the gain depletes and have increased the driving voltage of MCP slowly to maintain the

gain. In our practice we have increased the voltages by 50V after running for more than a year or so, but it depends on the frequency of the experiments yearly.

For the time-of-flight mode we ground the MCP front and apply ≈ 2000 V at the MCP back, see Sec. 2.1.5 for time of flight for VMI settings. For all the experiments in this dissertation, we will be gating on the MCP by using a high voltage switch. For this mode, we will apply -800 V on the MCP front and ≈ 1400 V on the MCP back and run the VMI on focusing conditions 2.1.4. The high voltage switch takes in a signal from the delay box which will dictate the status of the switch. At the high and low of this signal, the switch will be on and off respectively. We look at the time-of-flight signal to decide the position and width of the gate. Once the coarse settings are done, we decide the final position and width of the gate by optimizing the hits on the camera.

In our case we have a phosphor (P46) screen following the MCP, where the electrons from the MCP hit on it to create phosphorescence. For P46 the phosphorescence lifetime is ≈ 200 ns. We get the stack of MCP and phosphor from Photonis with the specifications mention above. For operation, we apply 5500 V on our phosphor using an SHV 10 feedthrough. The spectral emission of P46 is considered (wavelength range : 490 nm to 620 nm with maximum emission at 530 nm) as we used this in combination with imaging device (a CMOS camera) which has higher sensitivity towards the visible wavelength.

Images of the phosphor are captured on a shot-by-shot basis with a Basler A504k camera running at 1 kHz. To run at 1 kHz we set the image size at 500 x 500 pixels (12 μm pixel size) and the exposure time of 10 μs . We operate the camera in Programmable mode through a framegrabber connected with two cameraLink cables for data transfer. We have to set up the gain offset of the camera by looking at the hits observed and for each set of settings we save a background image by covering the camera lens. This image will be subtracted from every frame acquired. We count each hit on the camera using (a thresholding and centroiding) algorithm^{79;80} to locate each hit. Only the hit locations are saved to file.

2.1.7 Ultrahigh vacuum chambers

The source chamber where the Evan-Lavie valve is housed is pumped down using a turbo-molecular pump (Leybold Turbovac MAG Integra) which has a pumping speed of 2400 l/s (Helium rating). When we run the jet system as described as in Sec 2.1.3, it can maintain a background pressure of $\approx \text{low-}10^{-5}$ torr with a backing (roughing) pressure of $\approx \text{low-}10^{-1}$ to $\text{high-}10^{-2}$ torr maintained by a roughing oil pump. The separation between the source chamber (VC1) and both the middle differential pumping chamber (VC2) and the target chamber (VC3) is facilitated by two 3 mm diameter skimmers. Depending on the gas load and species, the middle pressure can be from $\approx \text{low-}10^{-7}$ to $\text{high/low-}10^{-8}$ torr and it is pumped with another turbo molecular pump (Pfeiffer Balzers TMU 260, 230 l/s Helium rating). The target chamber pressure when the jet is operating is $\text{low-}10^{-9}$ torr and it is pumped by a 600 l/s turbopump (Agilent Turbo-V 551), backed by another turbo pump (Pfeiffer TMH 261P) to improved the compression ratio of the pumping system by a factor of ≈ 100 for the Agilent pump. We used a Helium-Neon laser to align the center line of the gas jet through all the skimmers. This alignment is crucial to get a good overlap between the gas jet and the laser beam spatially and also the jet timing with the laser arrival time should be matched (see Sec. 2.1.8).

2.1.8 Data acquisition

Before we delve into the data acquisition, we should be clear about the trigger timings. The initial trigger is a 1 kHz signal taken from HITS Pockel's cell driver. This will be fed to an SRS delay generators model, DG-535. This first delay box provides trigger inputs for components that run at 1 kHz. This box will be used to trigger the camera (Basler Ace 504k) which will run at 1 kHz and the oscilloscope (Lecroy Wavesurfer 42Xs). The T_0 output of this delay box is fed into another DG-535. The second delay box provides trigger outputs at 500 Hz. The trigger pulses from this box will serve as triggers for the gas jet (controlled by the Even-Lavie valve driver) and the optical chopper. The connections between these two delay boxes and the equipment are made using BNC (Bayonet Neill–Concelman) connectors.

a)

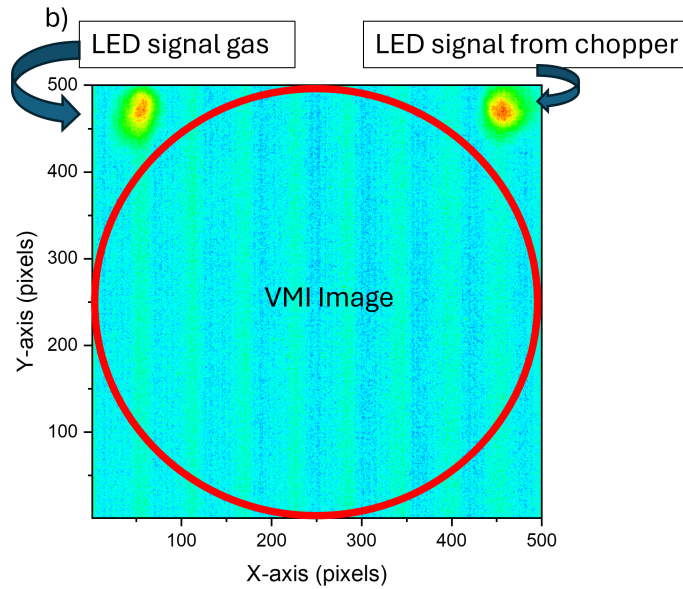
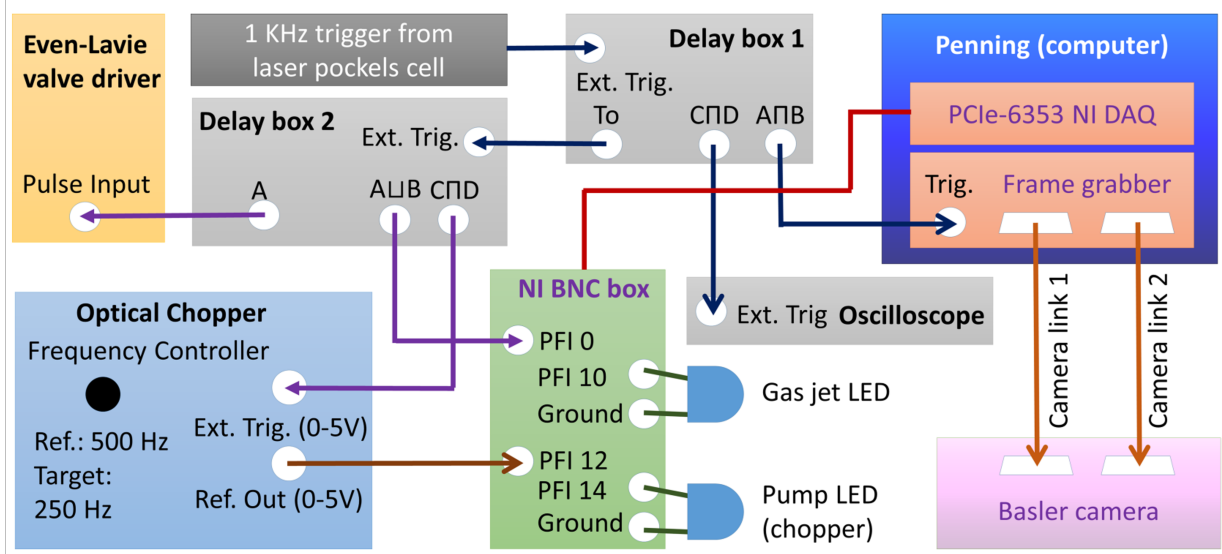


Figure 2.4: (a) The electronics and the connections schematics of the whole data acquisition setup and (b) the LEDs that are used to distinguish between different trigger conditions as seen on the camera. In the text we describe how these signals are read from each frame from the camera. This image is taken from Huynh Van Sa Lam's thesis⁶.

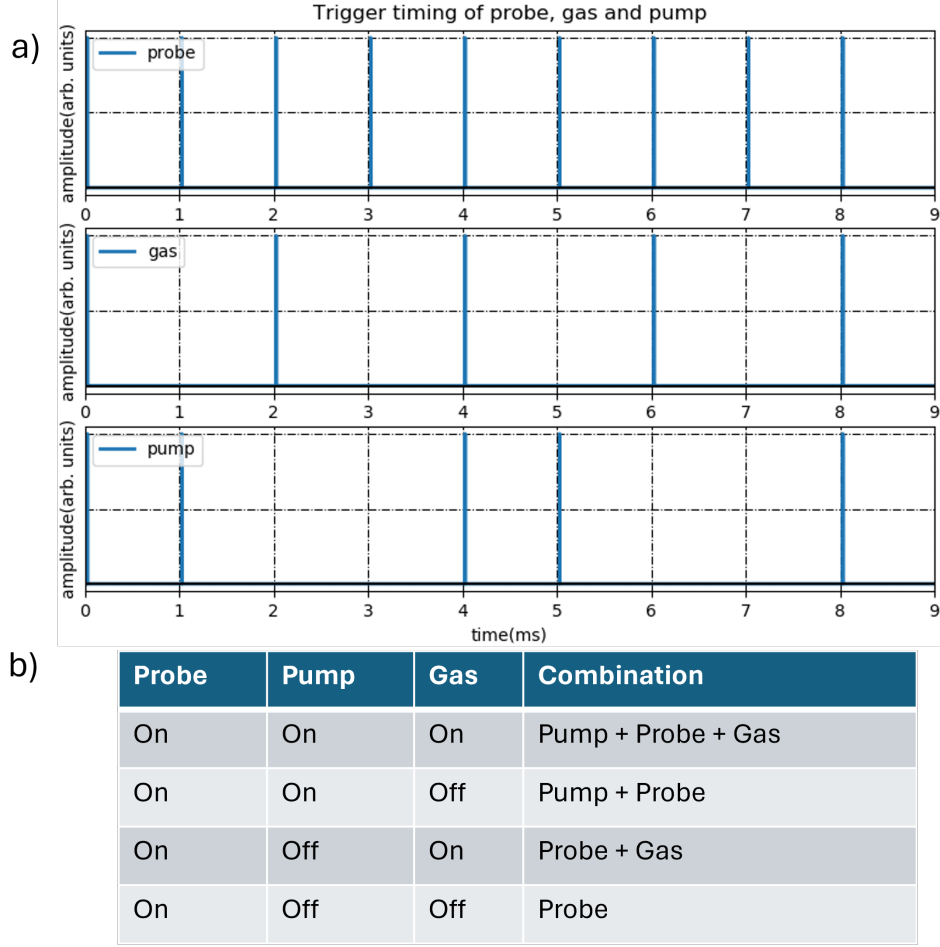


Figure 2.5: The first panel in (a) shows the initial trigger which is fed to the camera/probe pulse (1 kHz for HITS and 3 kHz (not shown) for FLAME). The second panel shows the set of LED outputs from the Even-Lavie valve driver. The opening time of the jet is set $\approx 10 \mu\text{s}$, and it runs at 500 Hz repetition rate. The set of pulses on the third panel of (a) shows the LED output signal from the chopped pump pulse triggered at 500 Hz and it chops the pump pulse allowing every 2 pulses in and 2 pulse out as shown in the diagram, every other 4 consecutive pulses. The second panel (b) shows the all the possible trigger outputs from pump (chopped by the chopper), gas, and probe and the combinations made by them.

The output trigger from the delay boxes is set to TTL (Transistor-Transistor-Logic) type with high impedance.

In our research group, the process of data acquisition is done through a LabVIEW virtual instrument (VI) named Nirvana. The VI was developed by Vinod and former members of the group. I have made refinements to the VI, and here I will provide an overview of how it collects data from individual shots. The timing details of the gas jet and the optical chopper

shown in (b) and (c) are sent to a National Instrument card (PCIe-6353 NI DAQ card) on the computer through a National Instruments BNC-2110 Terminal Block.

These external trigger pulses will be sent to the trigger counters in the BNC-2110 (PFI0/PI.0 and PFI12/PI.2). This trigger timing will be used by the PCIe-6353 NI DAQ card to switch two LEDs. These LEDs will be imaged by the camera simultaneously when collecting data. The LEDs are also connected to the digital and timing I/O of the BNC-2110, two terminal wires for each LEDs - negative terminals are connected to the ground (DGND) and the positives are connected to PFI10/P2.2 and PFI14/P2. The frame grabber will be running at 1 kHz with external trigger and the data is written when the delay stage (Newport's) is moved from one step to another (for example 50 fs step size). For each frame, the hit position will be recorded by thresholding and centroiding⁷⁹ and the raw data contains the (x,y) position of each hit. To avoid lags in the camera operation (1 kHz) - the thresholding, centroiding and the hit position finding is done in parallel computation using LabVIEW's queue architecture. Each frame is distinguished by the trigger status of the LEDs which will be written at the end of each frame raw data with a data separator -999 (jet LED status) and 999 (pump LED status). While reading the ".nirled" binary files, we have to sort out the trigger status for each frame. For each step of the delay stage, the time taken for acquisition is ≈ 2 seconds for 2000 shots (for which most the overhead is due to the motion of delay stage) with $\approx$ less than 10 hits per shot identified by the hit-finding algorithm.

2.2 Theoretical tools

2.2.1 Molecules as rigid rotors

Within the framework of the Born-Oppenheimer Approximation^{81;82}, the wave function of a molecule can be factored into distinct components: rotational, vibrational, and electronic (see Eqn. 2.6). We will not walk through mathematics of how the total wavefunction can be written as a product of these three different wavefunctions. But fundamentally, it means that the nuclei remain frozen within the fast time scale of the electron's motion. Under this framework the total Hamiltonian of the system which is a sum of all the Hamiltonian: rotational, vibrational, and electronic can be treated separately. We will be focusing on the rotational part of the system.

$$|\psi_{total}\rangle = |\psi_{elec}\rangle |\psi_{vib}\rangle |\psi_{rot}\rangle \quad (2.6)$$

Another approximation we will use is the rigid rotor approximation and we will describe the rotational wavefunction under this approximation. Under rigid rotor approximation, the bond lengths are fixed with no vibration. For the moment of inertia (I), only the masses of the nuclei are considered as the mass of an electron would be negligible. It is ≈ 1836 times smaller than the mass of hydrogen atom (lightest atom). We can write the rotational Hamiltonian of the as follows,

$$H_{rot} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \quad (2.7)$$

where I_a , I_b , and I_c are the three moments of inertia about the principle axes a, b and c with the center of mass as the origin and J_a , J_b , and J_c are the corresponding angular momentum about each axis. Conventionally, the principle axes are assigned according to $I_a \leq I_b \leq I_c$. Molecules are categorized based on their symmetry, including linear ($I_a = 0, I_b = I_c$), spherical ($I_a = I_b = I_c$), symmetric top ($I_a < I_b = I_c$) or ($I_a = I_b < I_c$), and asymmetric

top ($I_a \neq I_b \neq I_c$). Linear molecules exhibit a distinctive relationship between the moments of inertia: $I_a < I_b \approx I_c$, where I_a around the inter-nuclear axis is often approximated as close to zero. All the diatomic molecules like (N_2 , O_2 , and D_2) and other non-diatomic molecules like (CO_2 and CS_2) serve as examples of linear molecules. We will be focusing on diatomic molecules for the rest of the dissertation and the H_{rot} will be as follows,

$$H_{rot} = \frac{J^2}{2I} \quad (2.8)$$

The coordinate axes will be defined in the following section.

2.2.2 Laboratory and molecular coordinates

As a convention we define the laboratory axes as Z-axis along the laser polarization axis (for linearly polarized light) and Y-axis is defined along the laser propagation axis (see Fig. 2.6). The molecular frame is defined relative to the lab frame using the Euler angles (ϕ , θ , and χ) as shown in Fig. 2.6. The molecular frame axes are conventionally defined using principle axes of the polarizability with the magnitude of polarizability towards (x, y and z) directions dictating the order from most to least polarizable axis as z, x and y. For this dissertation we will only require a simple coordinate system shown in Fig. 2.6(b) and the angle θ . The transformation coordinates from (x,y,z) to (X,Y,Z) and vice-versa is done by the direction cosine matrix $\Phi(\phi, \theta, \chi)$ and the inverse $\Phi^{-1}(\phi, \theta, \chi)$ ⁸³.

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \cos(\phi) \cos(\theta) \cos(\chi) - \sin(\phi) \sin(\chi) & -\cos(\phi) \cos(\theta) \sin(\chi) - \sin(\phi) \cos(\chi) & \cos(\phi) \sin(\theta) \\ \sin(\phi) \cos(\theta) \cos(\chi) + \cos(\phi) \sin(\chi) & -\sin(\phi) \cos(\theta) \sin(\chi) + \cos(\phi) \cos(\chi) & \sin(\phi) \sin(\theta) \\ -\sin(\theta) \cos(\chi) & \sin(\theta) \sin(\chi) & \cos(\theta) \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (2.9)$$

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \cos(\phi) \cos(\theta) \cos(\chi) - \sin(\phi) \sin(\chi) & \sin(\phi) \cos(\theta) \cos(\chi) + \cos(\phi) \sin(\chi) & -\sin(\theta) \cos(\chi) \\ -\cos(\phi) \cos(\theta) \sin(\chi) - \sin(\phi) \cos(\chi) & -\sin(\phi) \cos(\theta) \sin(\chi) + \cos(\phi) \cos(\chi) & \sin(\theta) \sin(\chi) \\ \cos(\phi) \sin(\theta) & \sin(\phi) \sin(\theta) & \cos(\theta) \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \quad (2.10)$$

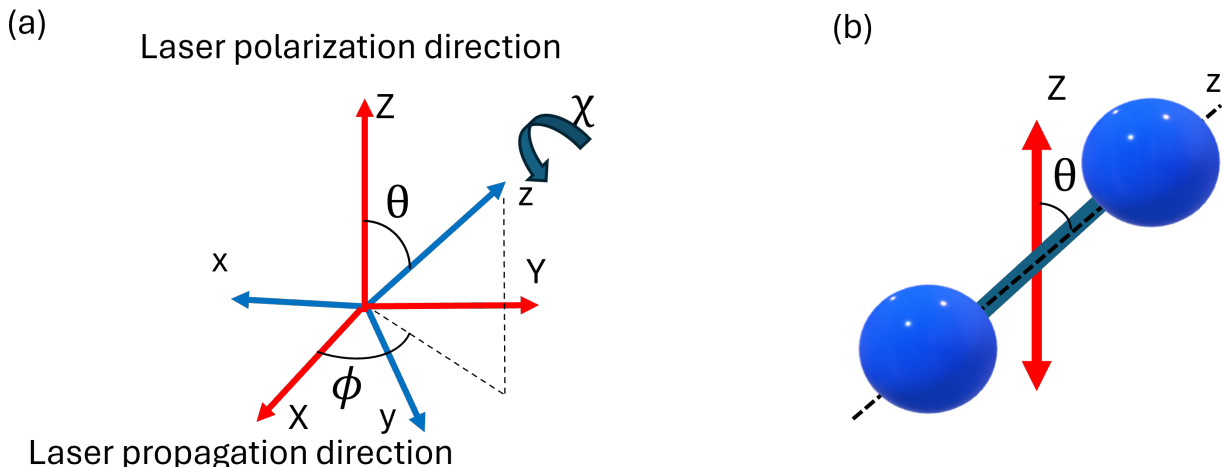


Figure 2.6: (a) The axes in the solid blue line labeled with small letters represents the molecular frame (x , y and z) and the axes in the solid-red line labeled with capital letters represents the laboratory frame (X , Y and Z). (b) The laboratory frame coordinate is generally described by the laser polarization as shown here. For a diatomic molecule in a linearly polarized electric field (double-sided red arrow) the angle θ is defined by the angle between molecular axis and the electric field polarization.

2.2.3 Impulsive molecular alignment

Interaction term

Assuming the rigid rotor model of the molecule as a dipole we can write the interaction of the electric field with the dipole as 2.11. The potential energy arising from the dipole interaction can be expressed using the following equation:

$$H_{int}(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t) \quad (2.11)$$

Molecules get aligned in the presence of an intense electric field due to the non-resonant interaction which is described by the product of polarizability of the molecule and the electric field. Mathematically, we can arrive at this point by using the Taylor expansion series on the term $\boldsymbol{\mu}$ in the previous Eqn. 2.11 and the second term in the expansion expresses the

polarizability.

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \frac{1}{2}\boldsymbol{\alpha} \cdot \mathbf{E}(t) + \dots \quad (2.12)$$

The first term signifies the permanent dipole interaction, which doesn't contribute to the potential. This is because, for a multi-cycle pulse $\mathbf{E}(t) = \mathbf{E}_0(t) \cos(\omega t)$, the rapid oscillations of the electric field will change directions every half cycle and it will average out the effects coming from the permanent dipole. The second term will be the only term which will significantly contribute to the potential as the average of the fast oscillation $\cos^2(\omega t)$ will be $1/2$. From this point we will only be concerned about the envelope of the pulse as the carrier envelope term doesn't contribute. The term $\boldsymbol{\alpha}$ is called the polarizability tensor, it is a tensor with nine elements. The second term can be written in terms of induced dipole where $\boldsymbol{\mu}_{ind} = \boldsymbol{\alpha} \cdot \mathbf{E}(t)$.

We can further simplify the interaction potential since we have a linearly polarized field along Z axis, by writing the $\boldsymbol{\mu}_{ind}$ into components. We will drop the subscript index to avoid confusion. The interaction potential $H_{int}(t)$ in lab frame becomes $\frac{1}{2}\mu_Z E_{0Z}^2(t)$. We have to keep in mind that $\boldsymbol{\alpha}$ the polarizability tensor is defined along the principle axes of the polarizability tensor. To resolve this, we rotate the lab frame expression of μ to molecular frame using the direction cosine (X,Y,Z) to (x,y,z) (see Eqn. 2.9).

$$\begin{bmatrix} \mu_X \\ \mu_Y \\ \mu_Z \end{bmatrix} = \begin{bmatrix} \cos(\phi) \cos(\theta) \cos(\chi) - \sin(\phi) \sin(\chi) & -\cos(\phi) \cos(\theta) \sin(\chi) - \sin(\phi) \cos(\chi) & \cos(\phi) \sin(\theta) \\ \sin(\phi) \cos(\theta) \cos(\chi) + \cos(\phi) \sin(\chi) & -\sin(\phi) \cos(\theta) \sin(\chi) + \cos(\phi) \cos(\chi) & \sin(\phi) \sin(\theta) \\ -\sin(\theta) \cos(\chi) & \sin(\theta) \sin(\chi) & \cos(\theta) \end{bmatrix} \begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} \quad (2.13)$$

We only need the μ_Z as the electric field in the other directions ($E_{0X}(t), E_{0Y}(t)$) is set to zero.

$$\mu_Z = -\cos(\phi) \sin(\theta) \mu_x + \sin(\phi) \sin(\theta) \mu_y + \cos(\theta) \mu_z \quad (2.14)$$

In equation $\mu_i = \sum \alpha_{ij} E_{0j}$ where the index i and j represents the direction in molecular frame, and the off-diagonal terms of α vanishes due to the choice of molecular frame. Thus leaving only three non-zero polarizabilities ($\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$) along the (x,y,z) directions respectively. Now plugging $\mu_x = \alpha_{xx} E_{0x}$, $\mu_y = \alpha_{yy} E_{0y}$ and $\mu_z = \alpha_{zz} E_{0z}$ to μ_Z we get,

$$\mu_Z = -\cos(\phi) \sin(\theta) \alpha_{xx} E_{0x} + \sin(\phi) \sin(\theta) \alpha_{yy} E_{0y} + \cos(\theta) \alpha_{zz} E_{0z}. \quad (2.15)$$

For a linear molecule we can write $\alpha_{xx} = \alpha_{yy}$ as there is no atom sticking out in the perpendicular directions to the molecular axis z. Now E_{0x} , E_{0y} and E_{0z} will have components in Z direction of the lab frame so we revert the space back to lab frame since we have a dot product waiting on μ_Z by $E_{0Z}(t)$. This operation is done with the inverse direction cosine matrix and we will get,

$$\begin{bmatrix} E_{0x} \\ E_{0y} \\ E_{0z} \end{bmatrix} = \begin{bmatrix} \cos(\phi) \cos(\theta) \cos(\chi) - \sin(\phi) \sin(\chi) & \sin(\phi) \cos(\theta) \cos(\chi) + \cos(\phi) \sin(\chi) & -\sin(\theta) \cos(\chi) \\ -\cos(\phi) \cos(\theta) \sin(\chi) - \sin(\phi) \cos(\chi) & -\sin(\phi) \cos(\theta) \sin(\chi) + \cos(\phi) \cos(\chi) & \sin(\theta) \sin(\chi) \\ \cos(\phi) \sin(\theta) & \sin(\phi) \sin(\theta) & \cos(\theta) \end{bmatrix} \begin{bmatrix} E_{0X} \\ E_{0Y} \\ E_{0Z} \end{bmatrix} \quad (2.16)$$

$$E_{0x} = -\sin(\theta) \cos(\chi) E_{0Z}, \quad E_{0y} = \sin(\theta) \sin(\chi) E_{0Z}, \quad E_{0z} = \cos(\theta) E_{0Z}; \quad (2.17)$$

$$\mu_Z = \cos^2(\chi) \sin^2(\theta) E_{0Z} \alpha_{xx} + \sin^2(\chi) \sin^2(\theta) E_{0Z} \alpha_{xx} + \cos^2(\theta) E_{0Z} \alpha_{zz}. \quad (2.18)$$

Now replacing $\alpha_{xx} = \alpha_{\perp}$ and $\alpha_{zz} = \alpha_{\parallel}$, we can write $\mu_Z E_{0Z}(t) = (\alpha_{\perp} - \alpha_{\parallel}) E_{0Z}^2(t) \cos^2(\theta) + \alpha_{\parallel} E_{0Z}^2(t)$ and $E_{0Z}^2(t) = 8\pi\alpha I_0(t)$ where $I_0(t)$ is the intensity of the laser and the α is the fine structure constant.

Due to the induced dipole interaction with the laser field, there is torque applied to the molecules by the field and driving them towards the laser polarization direction. For a neutral/ground state molecular alignment we treat the interaction of the molecules with the laser to be non-ionizing and this pulse is called the alignment pulse. When the pulse

duration τ of the alignment pulse is much less than rotational time period ($\frac{1}{2B}$), the action of alignment occurs after the pulse is over. This type of molecular alignment using the laser is called impulsive or field-free alignment. It was theoretically predicted and investigated by Seideman⁴⁵.

Rigid rotor in electric field

The Hamiltonian for a linear molecule in a linearly polarized light can be written as follows,

$$H = H_{rot} + H_{int}(t) \quad (2.19)$$

where H_{rot} is the field-free Hamiltonian described in the Sec. 2.2.1 and the $H_{int}(t)$ is the interaction potential term. We have to solve the following time-dependent Schrödinger's equation (TDSE) to look at the molecular dynamics which occurs during the presence of alignment pulse and in the field-free region.

$$i \frac{\partial}{\partial t} |\psi(t)\rangle = H_{rot} |\psi(t)\rangle + H_{int}(t) |\psi(t)\rangle \quad (2.20)$$

We solve this TDSE by expanding the $|\psi(t)\rangle$ into $|J, M\rangle$ where $|J, M\rangle$ is defined as $H_{rot} |J, M\rangle = E_J |J, M\rangle$. J is the total angular momentum quantum number, and M is the azimuthal quantum number. E_J is the rotational eigen energy of the $|JM\rangle$ state. For linear molecules we can write $E_J = B(J)(J + 1)$ in atomic units.

$$|\psi(t)\rangle = \sum_J C_{J,M}(t) |J, M\rangle \quad (2.21)$$

This series expansion is truncated by checking the value of square of the coefficient at J_{max} after the pulse is gone and comparing it with a low threshold value. In the real space, $|J, M\rangle$ state can be written as spherical harmonics and for a linearly polarized light, the quantum number M is conserved as per the selection rules. So the basis set expansion about the

$|J, M\rangle$ doesn't contain any summation over M . Substituting the expansion of $|\psi(t)\rangle$ in the TDSE (Eqn. 2.20), we will acquire a set of ordinary differential equations(ODEs) with the coefficients in the expansions of equation 2.22 as the unknown function and time as the variable.

$$\begin{aligned} \frac{dC_{J,M}(t)}{dt} &= -i \left[BJ(J+1) - \frac{E_{0Z}^2(t)}{4} \alpha_{\perp} \right] C_{J,M}(t) \\ &+ i \frac{E_{0Z}^2(t)}{4} \Delta\alpha \sum_{J'} C_{J',M} \langle J, M | \cos^2 \theta | J', M \rangle \end{aligned} \quad (2.22)$$

And the $\langle J, M | \cos^2 \theta | J', M \rangle$ can be written in terms of Wigner 3-J symbols. It will also decide the selection rule for which J state should be interacting with the J' ultimately contributing to the off-diagonal matrix element of the ODEs system.

$$\langle J', M | \cos^2(\theta) | J, M \rangle = \iint \delta(\Omega - \Omega') Y_{J'}^{M*}(\Omega) \cos^2(\theta) Y_J^M(\Omega') d\Omega' d\Omega \quad (2.23)$$

$$= \int \frac{1}{3} \left(Y_{J'}^{M*}(\Omega) \left(\frac{4\sqrt{\pi}}{\sqrt{5}} Y_2^0(\Omega) + 1 \right) Y_J^M(\Omega) \right) d\Omega \quad (2.24)$$

Using the special integral relation between product of three spherical harmonics and Clebsch-Gordan coefficient we will arrive at the following relation,

$$\langle J', M | \cos^2(\theta) | J, M \rangle = \frac{2}{3} \sqrt{2J+1} \sqrt{2J'+1} \langle JM, 20 | J'M \rangle \langle J0, 20 | J'0 \rangle + \frac{1}{3} \delta_{J,J'} \quad (2.25)$$

From this relation we can deduce the selection rules governing $\cos^2 \theta$ interaction in the first term of Eq. 2.25. This shows that the alignment pulse promotes the population of each initial rotational state to higher rotational states through Raman transitions with $\Delta J = 0, \pm 2$, and $\Delta M = 0$. The numerical solution to the system ODEs 2.22 is obtained using a Runge-Kutta method with adaptive step size. The code is implemented in C++ with the aid of OpenMP to perform parallel calculations across various values of M simultaneously.

Once we solve the ODEs numerically, we will obtain the rotational wavepacket in the in-field and field-free regions of the pulse. The initial states for the ODEs are treated as thermally populated states. Therefore, we solved the ODEs for each initial state J_i for all the possible M quantum numbers. And any observable acquired have to be thermally weighted as each process initiated by the initial state will be incoherent. We allowed the Boltzmann distribution to decide the maximum possible initial J_{maxT} states. This is done by adding the Boltzmann distribution term for each J_i to the partition function until $J_i = J_{maxT}$ where the summation of all the partition functions is 0.999. And the weight w_i is written as following the equation,

$$w_J = g_i \frac{\exp(-E_i/k_B T)}{\sum_j \exp(-E_j/k_B T)} \quad (2.26)$$

Here the $E_i = B(J_i)(J_i + 1)$ which is the field-free eigen energy of the i^{th} state, k_B is the Boltzmann constant, and g_i is the nuclear spin-statistics weight.

In the field-free region (where $t_{fieldfree}$ is defined as $t > 8\tau$) the evolution of rotational wavepackets can be written as

$$|\psi(t)\rangle = \sum_J C_{J,M}(t_{fieldfree}) \exp(-iE_J t) |J, M\rangle, \quad (2.27)$$

where $C_{J,M}(t_{fieldfree})$ is the coefficients of the rotational wavepackets $|J, M\rangle$ at the start of field free region at $t = t_{fieldfree}$. The time dependence of the wavefunction is only in the $\exp(-iE_J t)$ term. Until this point of time, the laser will induce multiple Raman excitation taking each initial states to higher rotational states. The coefficients in Eqn. 2.27 will have values other than zero because of this excitations. Since the energy levels of higher rotational states are integral multiples of the ground state energy level ($E_J = 2BJ(J + 1)$), due to this the rotational wave packet exhibits periodic patterns over time. At every nT_{rot} , $(n + 1/2)T_{rot}$ and $(n + 1/4)T_{rot}$ (n is an integer) the repeated structure can be observed. These recurring patterns are known as full, half and quarter revivals respectively^{45;84}.

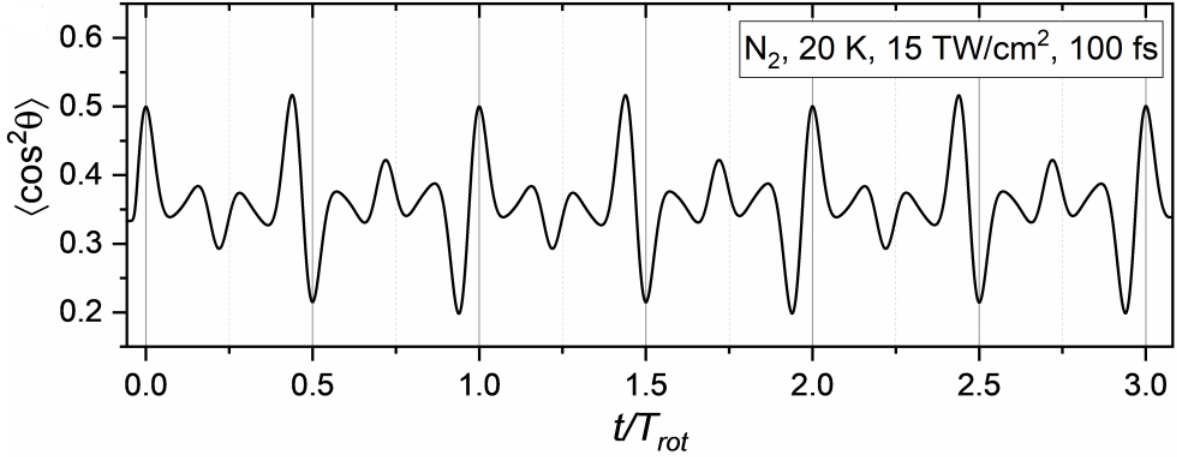


Figure 2.7: $\langle \cos^2 \theta \rangle (t)$ trace obtained by solving the TDSE for N_2 molecule. The intensity, pulse duration and temperature used in the calculation is shown in the inset. The time axis is made unitless by dividing it with the rotational period of N_2 which is 8.38 ps. This image is taken from Huynh Van Sa Lam's thesis⁶

The observable used to measure the degree of alignment in molecules is $\langle \cos^2 \theta \rangle (t)$. For the molecules which are not aligned and isotropic we get a $\langle \cos^2 \theta \rangle = 1/3$. As the alignment improves, the value of $\langle \cos^2 \theta \rangle (t)$ will go close to 1. For anti-aligned molecules, molecules which are perpendicularly aligned of the electric polarization, the value goes towards zero. To get the $\langle \cos^2 \theta \rangle (t)$ trace, at each time point we calculate $\langle \cos^2 \theta \rangle_i$ and weight i_{th} initial state with thermal weights w_i .

$$\langle \cos^2 \theta \rangle (t) = \sum_i w_i \langle \cos^2 \theta \rangle (t)_i \quad (2.28)$$

2.2.4 Angular momentum coupling in diatomic molecules

In molecular alignment, we look at the neutral molecular ground state which often happen to be in singlet symmetry and does not involve the coupling of rotational angular momentum to orbital, electronic or nuclear spin angular momentum. Due to that we can often neglect the coupling in the Hamiltonian model discuss in Sec. 2.2.3. However, ground state of molecules like O_2 ^{3;85}, NO ^{53;86}, I_2 ⁵² and many cationic states have a molecular symmetry other than

singlet (see chapters 4, 5, and 6). In this section we will introduce notation and general angular momentum coupling schemes in diatomic molecules and how we incorporate it in our calculation of molecular alignment in neutral ground state multiplet systems.

Hund's basis set

We will be following notation from the book Rotational Spectroscopy of Diatomic Molecules⁸¹. In this notation, the total angular momentum of a diatomic molecules can be written as

$$J = N + S, \quad (2.29)$$

ignoring the nuclear spin angular momentum. Here L is the electronic orbital angular momentum, S is the electronic spin angular momentum, $N = J - S$ is the total angular momentum excluding electron spin, and $R = N - L$ the rotational angular momentum of the nuclei. During an interaction, these components of angular momentum can get coupled and according to the coupling strengths of the different components of the angular momentum vectors their effect on the energy levels changes. Five limiting cases have been identified by Friedrich Hund and here we will only discuss two relevant cases, Hund's case (a) and (b). The limiting values of the three energies: ΔE_{elec} , A , and B makes up the different cases. ΔE_{elec} is the electrostatic interaction which is the magnitude of energy difference between two adjacent electronic levels with different Λ , A is the spin-orbit interaction and the B is the rotational constant.

For Hund's case (a), the magnitude of the energies involved compare to each other as way $\Delta E_{elec} \gg A \gg B$. With the axial symmetry in electrostatic interaction, this allows the orbital angular momentum L to precess about the inter-nuclear axis forming $L_z = \pm\Lambda$ (see in Fig. 2.8). With slow molecular rotation and large spin-orbit interaction, electronic spin angular momentum S also precesses about the inter-nuclear axis making the simultaneous eigenfunction S^2 and S_z with eigenvalues S and Σ (see in Fig. 2.8).

$$J_z = L_z + S_z; \quad \Omega = \pm\Lambda + \Sigma. \quad (2.30)$$

As the rotational angular momentum is perpendicular to the inter-nuclear axis there is no component of it along the z-axis and due to this the total angular momentum J is formed by introducing a vector Ω along the inter-nuclear axis and coupling it to the rotational angular momentum of the nuclei R . The conserved eigenfunctions are S^2, S_z, L_z, J^2 and J_z hence the normalized eigenvector of the molecular Hamiltonian can be written as $|S, \Sigma, \pm\Lambda, J, \Omega, M_J\rangle$. The angular momenta R and N are not conserved. The rotational energy E_{rot} is calculated by using the vector Ω by writing R in terms of J and the vector Ω as $R = J - \Omega$ and now we can write ,

$$E_{rot} = \frac{1}{2\mu R_0^2} \langle S, \Sigma, \pm\Lambda, J, \Omega, M_J | (J - \Omega)^2 | S, \Sigma, \pm\Lambda, J, \Omega, M_J \rangle = B[J(J+1) - \Omega^2] \quad (2.31)$$

We will see examples in of it in Chapter 4 and 5 in the low lying electronic states of N_2^+ and O_2^+ .

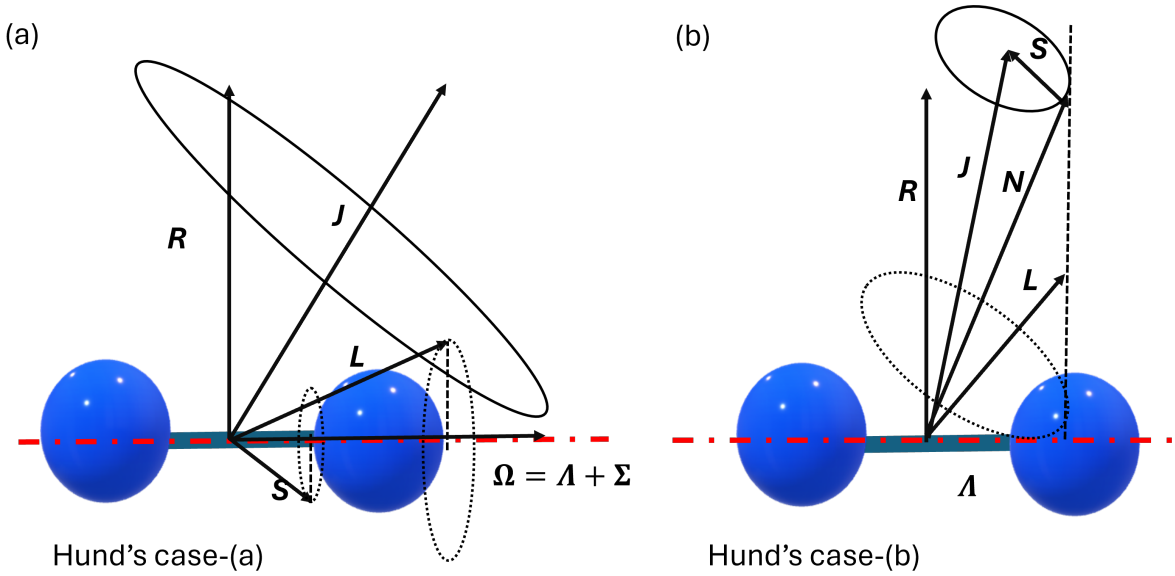


Figure 2.8: Angular momentum vectors schematic for Hund's case (a) and (b) in panels (a) and (b) respectively. In (a) the dotted circles shows the precession of L and S around Ω , which is along the z direction and the solid circle shows the nutation of Ω around J . In (b), the dotted circle shows the precession of N 's projection on the inter-nuclear axis and the solid circles shows the nutation of N around J .

For Hund's case (b), the energy comparison goes as $\Delta E_{elec} \gg B \gg A$. Since the spin-orbit interaction is much smaller than the rotational constant, the significance of coupling between spin and rotational motion takes over. This introduces a term $\gamma N \cdot S$ in the Hamiltonian which represents this coupling. As we can see from the Fig. 2.8(b) with L precessing about the inter-nuclear axis forming Λ and then the coupling between R with L form the vector N . Here N also precesses about the inter-nuclear axis. Finally the spin angular momentum S couples to the N vector forming the total angular momentum J . The conserved eigenfunctions in this basis are S^2, S_z, N_z, N^2, J^2 and J_z with the normalized eigenvector of the molecular Hamiltonian can be written as $|S, \Sigma, M_N, N, J, M_J\rangle$. The rotational energy E_{rot} is calculated as follows,

$$E_{rot} = \frac{1}{2\mu R_0^2} \langle S, \Sigma, M_N, N, J, M_J | (N - L)^2 | S, \Sigma, M_N, N, J, M_J \rangle \quad (2.32)$$

$$= B[N(N+1) + L^2 - 2N \cdot L] \quad (2.33)$$

As an example we have neutral ground state of O_2 , which is a $^3\Sigma$ state and the results will be discuss in Chapter 3. The last two terms have no effect in this basis set, even though for a transition between two different electronic states it adds to the off-diagonal element of the matrix.

Rotational and electronic spin-coupled interaction Hamiltonian

We have $H_{int}(t)$ in Eqn. 2.34 with static polarizability of the molecule and here the time dependence comes in from the fact the Intensity is time-dependent. We still need to resolve the $\cos^2(\theta)$ in the appropriate basis for TDSE calculation since the scheme that we use for solving the TDSE requires a wave function to be expanded in a good angular momentum basis. To proceed we write $\cos^2(\theta)$ in $|N, M_N\rangle$ and since $\cos^2(\theta)$ can be written in terms of spherical harmonics we can write it as in Eqn. 2.35 and from Zare⁸³ we will get,

$$H_{int}(t) = -\frac{1}{4}(\alpha_{\parallel} - \alpha_{\perp})I(t) \cos^2(\theta) \quad (2.34)$$

$$\langle N, M_N | \cos^2(\theta) | N', M'_N \rangle = \iint \delta(\Omega - \Omega') Y_N^{M_N*}(\Omega) \cos^2(\theta) Y_{N'}^{M'_N}(\Omega') d\Omega' d\Omega \quad (2.35)$$

$$= \int \frac{1}{3} (Y_N^{M_N*}(\Omega) (\frac{4\sqrt{\pi}}{\sqrt{5}} Y_2^0(\Omega) + 1) Y_{N'}^{M'_N}(\Omega)) d\Omega \quad (2.36)$$

$$= -1^{M_N} \frac{2}{3} \sqrt{2N+1} \sqrt{2N'+1} \begin{pmatrix} N' & 2 & N \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} N' & 2 & N \\ M'_N & 0 & -M_N \end{pmatrix} + \frac{1}{3} \delta_{N,N'} \delta_{M_N, M'_N} \quad (2.37)$$

Now we have the expression for interaction Hamiltonian in the $|N, M_N\rangle$ but the field free Hamiltonian is in the larger space where coupling occurs between the rotation and spin so, we have to convert the expression here in $\langle N, M_N | H_{int}(t) | N', M'_N \rangle$ to $\langle J, M_J | H_{int}(t) | J', M'_J \rangle$ where we have $J = |N - S|$ to $|N + S|$ and $M_J = -J$ to J , this can be done using the following relation,

$$|J, M_J\rangle = \sum_{M_N, M_S} \langle N, S; M_N, M_S | J, M_J \rangle |N, S; M_N, M_S\rangle \quad (2.38)$$

We will end up the same as in Eqn. 2.35 but this time it will be replaced with the summation in Eqn. 2.38, with the assumptions made that the alignment pulse does not mix up different spins and only allow transitions with the same spin state values so we can already drop the prime values M_S and $S = 1$ is true since we are in the ground state of the oxygen molecule, we can write the following Eqn. 2.38,

$$\begin{aligned} \langle J', M'_J | \cos^2(\theta) | J, M_J \rangle &= \sum_{M_N, M_S, M'_N} \langle J', M'_J | N', S; M'_N, M_S \rangle \langle N, S; M_N, M_S | J, M_J \rangle \\ &\quad \langle N', S; M'_N, M_S | \cos^2(\theta) | N, S; M_N, M_S \rangle \end{aligned} \quad (2.39)$$

From this point, we can write down the explicit equation of $\cos^2(\theta)$ in terms of total angular momentum quantum number. We will write out the Jucys diagram for the quantum numbers

involved and use Wigner 6j sum rule⁸³, for the rightmost corner-point in the Jucys diagram. In the diagram, l represents the rank of the operator that is 2 and the zeroth component for the specific case. Eqn. 2.41 is just a simplification in the phase factor since M_N, M_S and M'_N are just summed over. For the same reason we can flip the signs of M'_N in the right-hand side of the equation, this will help us in matching this with Eqn. 2.39.

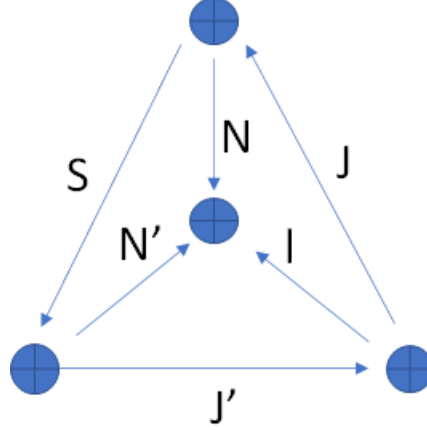


Figure 2.9: Jucys diagram for J', J, N', N, S and l

$$\begin{aligned} \begin{Bmatrix} N & N' & 2 \\ J' & J & S \end{Bmatrix} \begin{pmatrix} J' & J & 2 \\ -M'_J & M_J & 0 \end{pmatrix} &= \sum_{M_N, M_S, M'_N} -1^{(N+N'+1-M'_N-M_N-M_S)} \begin{pmatrix} N & N' & 2 \\ -M_N & -M'_N & 0 \end{pmatrix} \times \\ &\begin{pmatrix} N & J & 1 \\ M_N & -M_J & M_S \end{pmatrix} \begin{pmatrix} J' & N' & 1 \\ M'_J & M'_N & -M_S \end{pmatrix} \end{aligned} \quad (2.40)$$

$$\begin{aligned} \begin{Bmatrix} N & N' & 2 \\ J' & J & S \end{Bmatrix} \begin{pmatrix} J' & J & 2 \\ -M'_J & M_J & 0 \end{pmatrix} &= \sum_{M_N, M_S, M'_N} -1^{(N+N'+1-M'_N-M_J)} \begin{pmatrix} N & N' & 2 \\ -M_N & M'_N & 0 \end{pmatrix} \times \\ &\begin{pmatrix} N & J & 1 \\ M_N & -M_J & M_S \end{pmatrix} \begin{pmatrix} J' & N' & 1 \\ M'_J & -M'_N & -M_S \end{pmatrix} \end{aligned} \quad (2.41)$$

Revisiting Eqn. 2.39 we will start converting the Clebsch–Gordan coefficients in the first line of Eqn. 2.39 to Wigner 3-j symbols⁸³ and putting $S = 1$ we will get the following equation term by term,

$$\begin{aligned}
\langle N', S; M'_N, M'_S | J', M'_J \rangle &= -1^{(N'-1+M'_J)} \sqrt{2J'+1} \begin{pmatrix} N' & 1 & J' \\ M'_N & M'_S & -M'_J \end{pmatrix} \\
&= -1^{(N'-1+M'_J+N'+1+J')} \sqrt{2J'+1} \begin{pmatrix} N' & 1 & J' \\ -M'_N & -M'_S & M'_J \end{pmatrix} \quad (2.42) \\
&= -1^{(M'_J+J')} \sqrt{2J'+1} \begin{pmatrix} J' & N' & 1 \\ M'_J & -M'_N & -M'_S \end{pmatrix}
\end{aligned}$$

we arrive at the final form of Eqn. 2.42 by applying time reversal symmetry which introduces a phase factor $-1^{N'+1+J'}$ and an even permutation of the columns. Now for the next term, we just require an odd permutation of a column which gives rise to phase factor -1^{N+1+J} . With this, the last two terms in Eqn. 2.41 turn out to be the same as Eqn. 2.43 and 2.42 respectively with an extra factor in each term.

$$\begin{aligned}
\langle N, S; M_N, M_S | J, M_J \rangle &= -1^{(N-1+M_J)} \sqrt{2J+1} \begin{pmatrix} N & 1 & J \\ M_N & M_S & -M_J \end{pmatrix} \\
&= -1^{(M_J+J)} \sqrt{2J+1} \begin{pmatrix} N & J & 1 \\ M_N & -M_J & M_S \end{pmatrix} \quad (2.43)
\end{aligned}$$

Now, putting Eqn. 2.42 and Eqn. 2.43 in Eqn. 2.39 and we will also replace the second line with Eqn. 2.37 since the spin part is just replaced with 1 then we get the following,

$$\begin{aligned} \langle J', M_J' | \cos^2(\theta) | J, M_J \rangle = & \sum_{M_N, M_S, M_N'} -1^{(M_J+J+M_J'+J'+M_N)} \sqrt{2J+1} \sqrt{2J'+1} \sqrt{2N+1} \sqrt{2N'+1} \times \\ & \begin{pmatrix} N & J & 1 \\ M_N & -M_J & M_S \end{pmatrix} \begin{pmatrix} J' & N' & 1 \\ M_J' & -M_N' & -M_S \end{pmatrix} \times \\ & \begin{pmatrix} N' & 2 & N \\ M_N' & 0 & -M_N \end{pmatrix} \begin{pmatrix} N' & 2 & N \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (2.44)$$

And for the first term in Eqn. 2.41, we have to do two flips of columns and once it is done we can replace the first three Wigner 3j symbols in Eqn. 2.44 with the right-hand side of Eqn. 2.41 with the extra phase factor too.

$$\begin{aligned} \langle J', M_J' | \cos^2(\theta) | J, M_J \rangle = & \sum_{M_N, M_S, M_N'} -1^{(M_J+J+M_J'+J'-N-N'-1+M_N'+M_J+M_N)} \sqrt{2J+1} \sqrt{2J'+1} \times \\ & \sqrt{2N+1} \sqrt{2N'+1} \left\{ \begin{matrix} N & N' & 2 \\ J' & J & S \end{matrix} \right\} \begin{pmatrix} J' & J & 2 \\ -M_J' & M_J & 0 \end{pmatrix} \times \\ & \begin{pmatrix} N' & 2 & N \\ 0 & 0 & 0 \end{pmatrix} + \frac{1}{3} \delta_{J,J'} \delta_{M_J, M_J'} \end{aligned} \quad (2.45)$$

On Eqn. 2.45 phase factor can be further simplified -1^{2M_J} is just 1 and since N and N' can only be separated by two and zero as per the last term on Eqn. 2.45, we can write $-1^{-N-N'}$ as -1^{-2N-2} . $-1^{M_N'+M_N}$ will be 1 as it is been summed over and then finally the phase factor will be $-1^{J+J'-3+M_J'}$. This concludes writing out of the interaction Hamiltonian in Hund's basis (b).

2.2.5 Orientation resolution through rotational coherence spectroscopy (ORRCS)

Rotational Coherence Spectroscopy (RCS) involves observing the effects of quantized rotational motion in the time-domain using picosecond spectroscopy techniques⁵¹. In this method, a weak laser field is applied to excite a preferential vibronic levels from a cold gas phase molecules generated by a supersonic expansion. The species with transition dipoles that are aligned along its polarization vector will interact with the light. The species with initial alignment continues to rotate after the pulse, therefore the rotation of the initially-aligned species dephases and rephases momentarily creating the revival structures in time-domain observation. By characterizing this revival structure, geometric knowledge of the molecules is extracted. Whereas during a strong-field interaction, impulsive alignment takes over exciting multiple Raman transition creating a rotational wavepacket from an initial state⁸⁴. The rotational wavepacket are broadband and have good angular confinement.

This method has been extended by Varun Makhija¹ to determine the angular distribution in strong-field ionization probe using the time-domain information. The molecular polarizability and the structure are assumed to be static during the pump step. In this method, the delay-dependent yield of the ion $Y(t)$ in lab frame is written as the convolution of the molecular axis distribution $\rho(\theta, t)$ and the molecular frame angle-dependent yield $R(\theta)$ as follows,

$$Y(t) = 2\pi \iint \rho(\theta, t) R(\theta) \sin(\theta) d\theta, \quad (2.46)$$

where θ is the angle between the laser polarization axis and the inter-nuclear axis of the molecule see Fig. 2.6(a). The angle-dependent function $R(\theta)$, is expanded using the basis of Legendre polynomials as follows,

$$R(\theta) = \sum_{L=0}^{L_{max}} C_L P_L(\cos(\theta)), \quad (2.47)$$

Here L can only take even values due to the presence of a plane of symmetry perpendicular to the polarization vector. If we plugged in $R(\theta)$ to the yield model we will get the following equation for $Y(t)$ which is expressed in terms of the axis distribution moments $\langle P_L(\cos(\theta)) \rangle$.

$$Y(t) = \sum_L C_L \langle P_L(\cos(\theta)) \rangle(t) \quad (2.48)$$

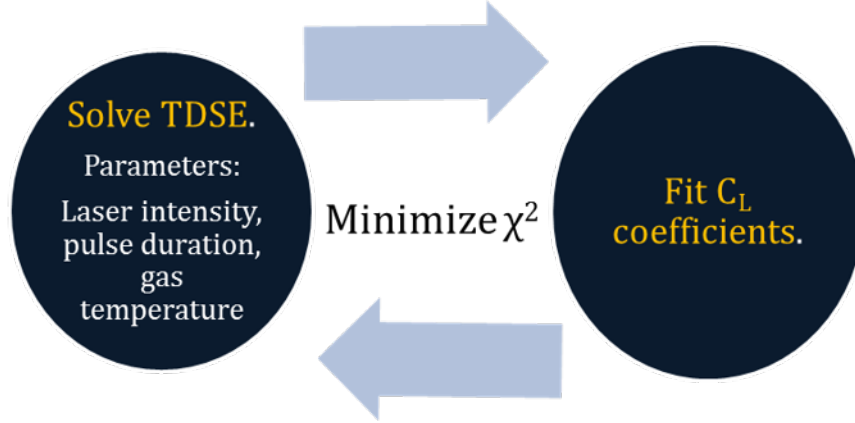


Figure 2.10: ORRCS schematics showing the multiple iterations of the fitting procedure with different input parameters starting from the TDSE till the χ^2 converges to the minimum.

Since we can calculate the axis distribution moment $\langle P_L(\cos(\theta)) \rangle$ after solving the time dependent Schrödinger's equation (see Sec. 2.2.4) for each time delay t we have the axis distribution moments that then can be inserted in the Eqn. 2.47 to solve for C_L using linear regression (see Fig. 2.11). We truncate the series in L_{max} by looking at the fidelity of the fit.

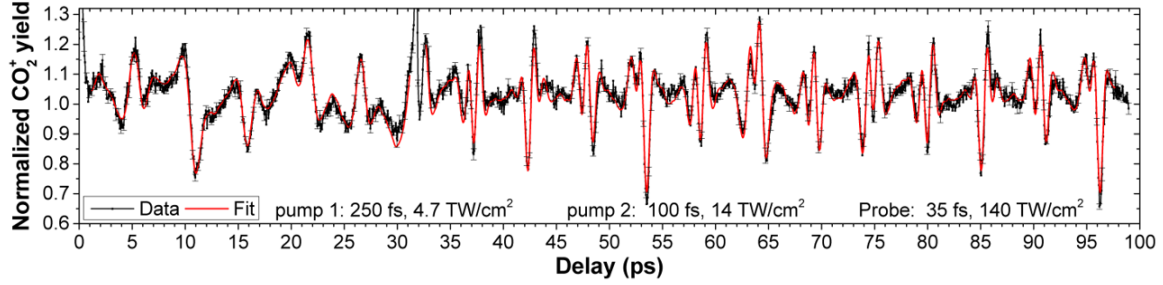


Figure 2.11: Application of ORRCS in strong field ionization of CO_2 ⁶. The yield of CO_2^+ is fitted using the ORRCS procedure, the image is taken from Huynh Van Sa Lam's thesis⁶.

For calculating the observable $\langle P_L(\cos(\theta)) \rangle$ in the Hund's basis set (b), we used the uncoupled basis set $|N, S; M_N, M_S\rangle$. The uncoupled space allows the observable to act in the $|N, M_N\rangle$ space leaving out $|S, M_S\rangle$ as a product. It works out since there is no physical meaning for the spin in the real space made up of the angle θ . The yield is written down as series of the calculated observable $Y(t) = \sum_L C_L \langle P_L(\cos(\theta)) \rangle(t)$ and apply the fitting procedure, we calculate the series of observable in uncouple basis $|N, S; M_N, M_S\rangle$. The time evolution of wave-functions are available in $|J, M_J\rangle$ so we do a basis transformation again from coupled to the uncoupled basis using the inverse of the transform similar in Eqn. 2.42. In our working code, we have built a matrix operator following with $\langle N, S; M_N, M_S | J, M_J \rangle$ values say $\mathbf{T}$ and we just invert the matrix $\mathbf{T}$ to $\mathbf{T}^{-1}$ to go back and forth, and hence the observable represented $\mathbf{O}$ will be transformed to appropriate space with $\mathbf{T}^{-1}\mathbf{O}\mathbf{T}$ or vice-versa accordingly to the desired space. The results acquired after this procedure will be shown in Chapter 3.

2.2.6 Wave-packet dynamics after strong-field ionization

In this section, I will introduce the rich dynamics induced by the strong field in the low-lying cationic states of the diatomic molecules, specifically the work done on O_2^+ and N_2^+ . This discussion will be relevant to the work done at Chapters 4 and 5. The understanding of the SFI produce cations and the inferences come from the theoretical and computational studies done by Magrakvelidze *et al.*⁸⁷, Xue *et al.*⁴, Yao *et al.*⁷ and Xu *et al.*⁸⁸. In case of N_2^+ , the studies are driven by attempts in understanding the phenomenon called air-lasing⁸⁹

where lasing of 391 nm light occurs⁹⁰ and in case of O_2^+ , it is to understand the convoluted strong field driven dissociative ionization pathways^{65;91–93}. Here I will briefly discuss the background and theoretical methods that were developed to understand these processes.

Magrakvelidze *et al.*⁸⁷ did quantum simulation to interpret the dynamics involved in the strong-field dissociative ionization experiment done by De *et al.*⁶⁵. Following this work, Xue *et al.*⁴ have pointed out discrepancies in the experimental data and the simulation and in the attempts to understand these discrepancies Xue *et al.*⁴ have used a channel-coupled TDSE (CCTDSE) method. Xue *et al.* were able to explain the discrepancies in the experimental data acquired by De *et al.*⁶⁵ and also were able to reproduce the data from and Corlin *et al.*⁹⁴ which was an XUV pump (Attosecond-Pulse-Train) and IR probe experiment. A similar method has been used by Yao *et al.*⁷ and Xu *et al.*⁸⁸ to explain their proposed mechanism of air-lasing subsequent to strong-field ionization in N_2^+ ^{7;88}.

In this method, the initial population in the low lying electronic states are considered to be the ones predicted by the strong-field approximation SFA⁹⁵ and the vibrational populations were determined by the Franck-Condon transition from neutral nitrogen molecules to molecular cations in the corresponding electronic states. But Yao *et al.*⁷ use an ad-hoc percentage of 20 % of population in both $A^2\Pi_u$ state and $B^2\Sigma_u$ state, and 60 % for $X^2\Sigma_u$ as initial states for solving the CCTDSE model. Once the initial populations are decided in the low-lying electronic states of interest (in case of N_2^+ [$X^2\Sigma_g$, $A^2\Pi_u$ and $B^2\Sigma_u$] and in case of O_2^+ [$a^4\Pi_u$, $b^2\Sigma_g^-$ and $f^4\Pi_g$]) CCTDSE is solved for these channels. As described by Xue *et al.*⁴, the CCTDSE can be written as the following set of equations, the CCTDSE can be written as the following set of equations,

$$i\frac{\partial}{\partial t} \begin{bmatrix} \chi_1 \\ \chi_2 \\ \vdots \end{bmatrix} = \begin{bmatrix} T_R + V_1(R) & E(t).d_{12} & \dots \\ E(t).d_{21} & T_R + V_2(R) & \dots \\ \vdots & \vdots & \ddots \end{bmatrix} \times \begin{bmatrix} \chi_1 \\ \chi_2 \\ \vdots \end{bmatrix}, \quad (2.49)$$

$\chi_i(R, t)$ are the radial wave functions of the i^{th} Born-Oppenheimer electronic states, $V_i(R)$

represents the adiabatic Born-Oppenheimer potential for channel i , d_{ij} signifies the dipole coupling between channels i and j , T_R denotes the nuclear kinetic energy operator and $E(t)$ represents the vector of the laser electric field. Subsequently, the wave-function was propagated until the end of the pump pulse to include the resonant-coupling effect, considering each molecular alignment angle in relation to the laser's polarization as SFI is angle-dependent. In work by Xu *et al.*⁸⁸ and Yao *et al.*⁷, the ionization starts from peak of the pulse and the wave-function propagation described here happens after it (see Fig. 2.12).

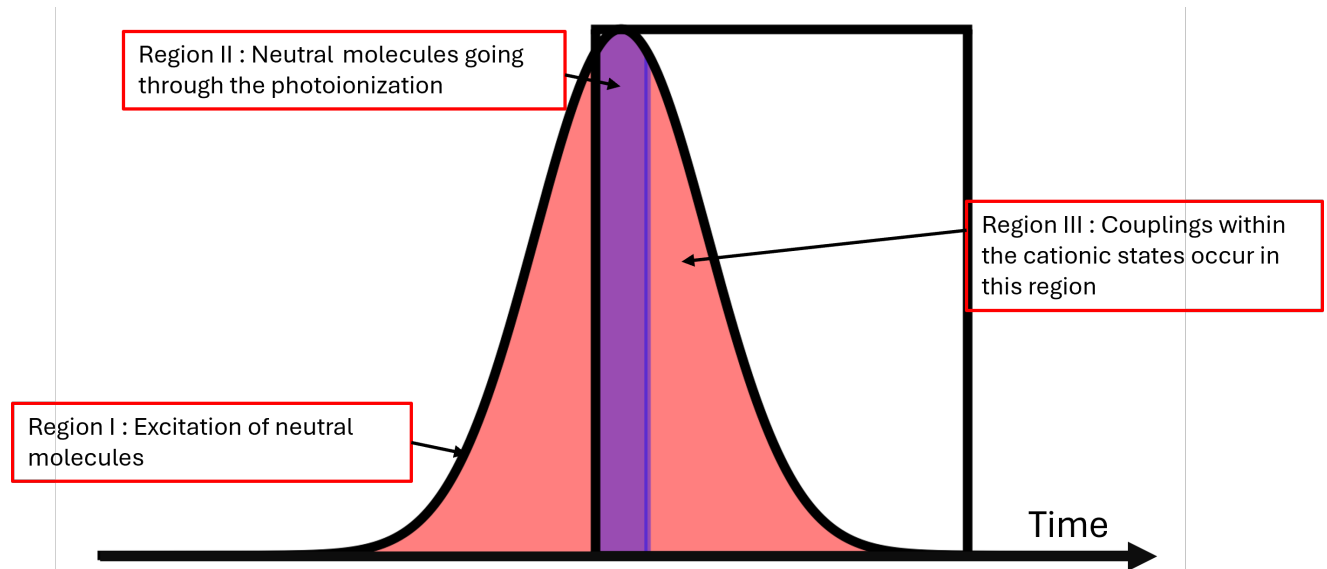


Figure 2.12: *Schematic diagram of the pumping mechanism in the 800 nm laser field. In region I photo-ionization is assumed to be weak, near the the peak of the pulse (region II) tunneling ionization has the maximum differential cross-section, populating the low-lying electronic states and in the tail of the pulse (region III) resonant coupling happens. This schematic is adapted from Yao et al.⁷.*

Both the studies of O_2^+ and N_2^+ have pointed out the importance of population redistribution that occurs due the the resonant couplings in the optical field post strong-field ionization. In Chapters 4 and 5 we will see that our experimental observation supports this inference.

Chapter 3

Strong-field ionization of the triplet ground state of O₂

Using strong-field ionization as a probe, we observe highly non-periodic evolution of the spin-rotation wave packet launched by a non-ionizing femtosecond pulse in oxygen. The non-periodicity is readily apparent only in rotationally cold molecules that are pumped with a weak alignment pulse. We show that this behavior is a consequence of the spin-rotation and the spin-spin couplings in the triplet ground state of the neutral molecule. A model that includes these couplings in the field-free Hamiltonian but in neither the alignment nor the ionization step explains most of the observed dynamics, suggesting that both processes do not depend explicitly on the electronic spin. We also show that the angle dependence of strong-field ionization can be retrieved from the delay-dependent even when coupling to spin complicates rotational dynamics.

3.1 Introduction

Laser-induced rotational dynamics following impulsive alignment of linear molecules have been investigated extensively for more than two decades^{43;44;46;96–101}. In impulsive alignment, the rotational wave packet can be well described by the time-dependent Schrödinger equation

(TDSE) for rigid rotors⁹⁷. For linear molecules, typically, the induced rotational wave packets are periodic because rotational energy levels are regularly spaced^{45;99}. Such wave packets have been used extensively to study the angle dependence of strong-field ionization (SFI) of molecules, either by scanning the angle between the alignment axis and the polarization of the ionizing pulse or by analyzing the delay dependence of the ionization rate due to the temporal evolution of the rotational wave packet^{2;102–105}.

However, the coupling of rotational motion to other degrees of freedom can introduce non-periodicity in the wave packet. The simplest example is the centrifugal distortion of molecules in high rotational angular momentum states. Although it is often necessary to include the effects of this distortion in modeling the rotational wave packet¹⁰⁶, it is assumed that the angle-dependent ionization rate is not distorted by the small change in the internuclear separation that results from this distortion. The non-periodicity introduced by the hyperfine coupling between the electric quadrupole moments of the atomic nuclei and the gradient of the electric field created by the electrons in molecular iodine⁵² is another example where rotational dynamics is weakly perturbed. In contrast, the delay-dependent high-harmonic yield of impulsively aligned NO, which was attributed to the spin-orbit coupling in the low-lying $^2\Pi$ states, is strongly modulated due to the role of spin dynamics in the high harmonic generation process^{53;54}.

Here we report non-periodic revivals of strong-field ionization of oxygen, which is an open-shell molecule with two unpaired π electrons in the $X^3\Sigma_g^-$ electronic ground state. The unquenched total electronic spin angular momentum, $S = 1$, should lead to peculiar rotational dynamics compared to closed-shell molecules in $^1\Sigma$ ground states such as N_2 and CO_2 ^{2;107–109}. Recently, a detail study of rotational wave packets expected to be produced by impulsive alignment in triplet oxygen has been investigated theoretically⁸⁵. However, in most past studies^{102;108–118}, these peculiar dynamics were not observed, and O_2 could be approximated as a spinless molecule. In this chapter, we show that rotational dynamics in ground-state O_2 can be highly non-periodic when the rotational temperature is kept low and the pump is weak enough to limit the rotational wave packet to small values of rotational angular momentum. We impulsively align cold O_2 molecules with the pump and then

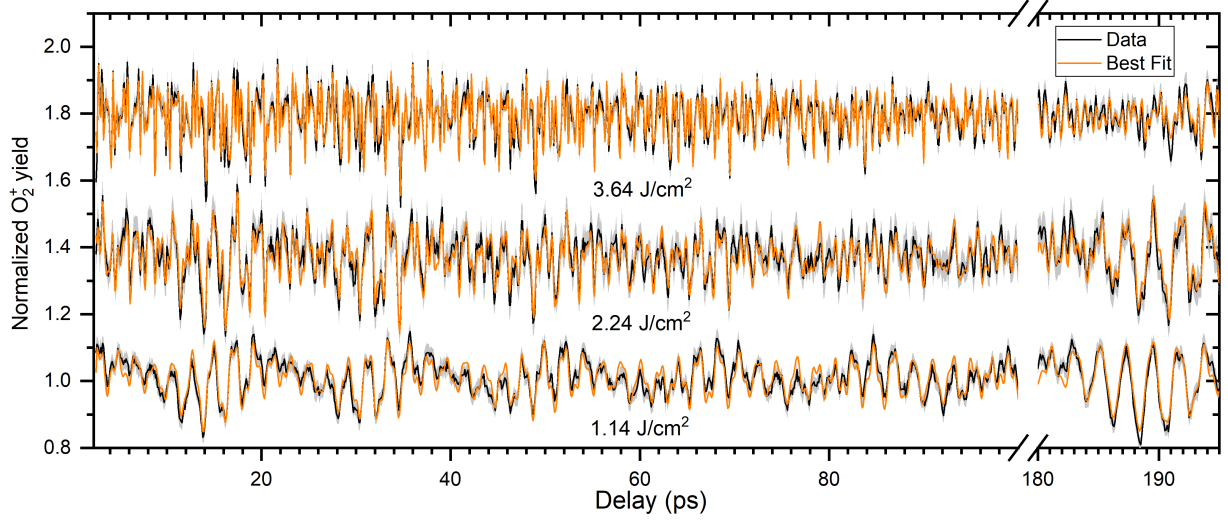


Figure 3.1: Normalized delay-dependent O_2^+ yield for different pump intensities (black lines) and their corresponding best fits (orange/gray lines). The probe is the same in all cases with intensity of 260 TW/cm^2 . For clarity, the data and fits for 2.24 and 3.64 J/cm^2 pump fluences are shifted vertically by 0.35 and 0.75 units, respectively. The pump fluences are estimated from the fits are shown below the corresponding plot lines in the graphs. Statistical error estimates ($\pm 3\sigma$) for the data are shown as light-gray shaded bands. Data near the end of the scan is shown on an expanded horizontal scale to show detail. The strong nonperiodic behavior is a consequence of the spin-rotation and the spin-spin couplings, as discussed in the text.

ionize them using a strong-field probe. We show that the observed nonperiodic behavior is a consequence of spin-rotation and spin-spin couplings in the molecule. We model the rotational dynamics by solving the TDSE using an effective Hamiltonian that includes these couplings. We also use a time-domain approach called ORRCS (Orientation Resolution through Rotational Coherence Spectroscopy)^{1;2} to retrieve the angle-dependent ionization rate. This method has been used to retrieve the angle dependence of SFI^{1;2;105;119}, high harmonic generation^{120;121}, and photoelectron¹²² and photofragment momentum distributions². We compare our retrieval result with previous SFI measurement¹⁰² and MO-ADK theory^{55;95}.

3.2 Experimental setup

The experimental setup is similar to the one reported in Ref.². A Ti:Sapphire laser produces pulses at a 1 kHz repetition rate with ~ 40 fs pulse duration and 1.2 mJ pulse energy at a central wavelength of 800 nm. We split the laser output into alignment and ionizing pulses and recombine them after a computer-controlled delay is introduced between them. The laser compressor gratings are adjusted to get the shortest pulse duration for the ionizing probe, while the alignment pulse is stretched to ~ 200 fs using SF11 glass. Both pulses have the same linear polarization in the plane of the detector of a velocity map imaging spectrometer⁷⁴. An Even-Lavie valve⁷⁰, operated with a (0.5%) oxygen in helium at a total pressure of 900 psi, generates a rotationally cold ($T_{rot} \approx 2$ K) molecular beam target for this experiment.

After the pulses interact with the molecules, we count the number of O_2^+ ions using a velocity map imaging spectrometer equipped with a microchannel plate (MCP) and a fast P47 phosphor screen. We select O_2^+ ions by gating the MCP so that it is active only when these ions reach it and image the phosphor using 1000 fps camera (Basler A504k). We centroid and count hits in the image for every laser shot. To avoid any saturation of the measured signal, we use the spectrometer out of focus and record data low count rates (≈ 1 ion per shot).

In order to improve the signal-to-noise ratio, we mechanically chop the alignment beam at 250 Hz, alternately blocking and transmitting pairs of adjacent pulses. The Even-Lavie valve is operated at 500 Hz, so that every alternate pulse in the laser pulse train interacts with the molecular beam. By synchronizing the operation of the chopper and the gas jet using digital delay generators, we create four different combinations of pump, probe, and gas: pump-probe-gas, probe-gas, pump-probe, and probe alone. We label each laser shot with one of these four types and use this information to correct for the fluctuations in laser intensity and gas density. The corrected delay-dependent signal that we use for further analysis is calculated as

$$Y(t) = \frac{Y[\text{Probe, Pump, Gas}] - Y[\text{Probe, Pump}]}{Y[\text{Probe, Gas}] - Y[\text{Probe}]}, \quad (3.1)$$

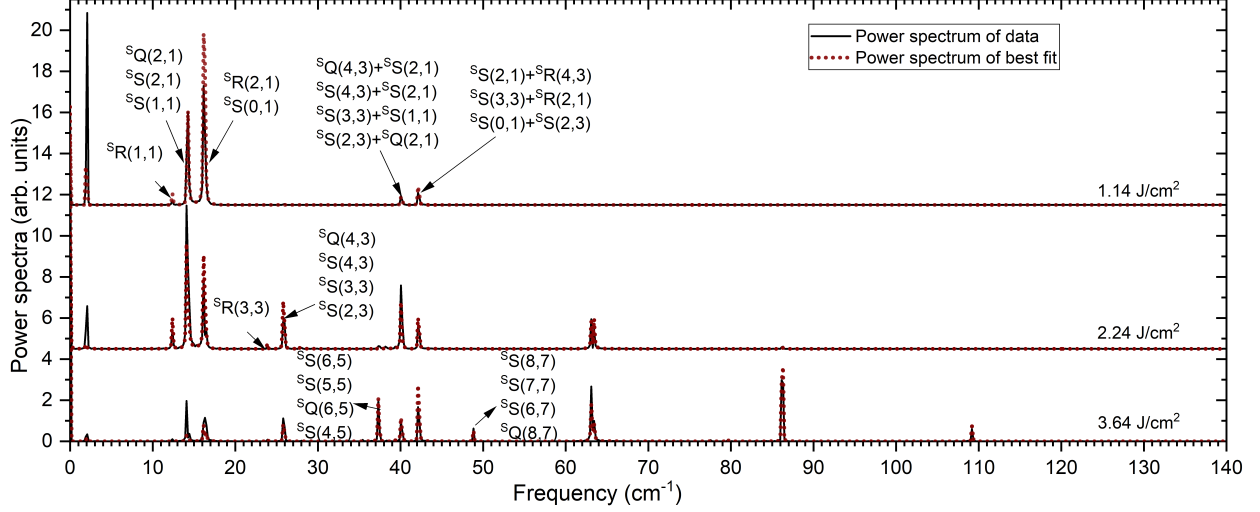


Figure 3.2: Fourier spectra of the delay-dependent data (solid) and the best fits (dotted) shown in Fig. 3.1. We have vertically shifted the spectra corresponding to 2.24 J/cm² by 4.5 units and the one corresponding to 1.14 J/cm² by 11.5 units. See text for details of spectroscopic notation and discussion on transition lines.

where Y is the count of O₂⁺ ions, and t is the pump-probe delay. Delay scans are repeated multiple times and averaged to minimize the effect of slow drifts in experimental conditions.

The data from three such scans, with different pump pulse energies but otherwise identical conditions, are shown in Fig. 3.1. In each case, the probe intensity is estimated to be 260 TW/cm² and the pump intensities are $\sim 2, 4$ and 8 TW/cm². The data clearly show not only the non-periodicity of the wave packets, but also that the shape of the revival pattern changes considerably with the intensity of the alignment pulse. The fits to the data shown in Fig. 3.1 are based on a model discussed below.

3.3 Model and analysis

Compared to the rigid-rotor model used in previous studies^{2;46;96–98}, in this work, we include the spin-rotation and the spin-spin couplings in the ground state oxygen molecule. The effective field-free Hamiltonian H_0 can be written as

$$H_0 = BN^2 - DN^4 + \frac{2}{3}\lambda(3S_z^2 - \mathbf{S}^2) + \gamma\mathbf{N} \cdot \mathbf{S}. \quad (3.2)$$

The first two terms describe the rotational kinetic energy of molecules, where $B = 1.4376844 \text{ cm}^{-1}$ is the rotational constant, $D = 4.87 \times 10^{-6} \text{ cm}^{-1}$ is the centrifugal distortion, and $\mathbf{N}$ is the rotational angular momentum. The third term describes the spin-spin coupling, where $\mathbf{S}$ is the electronic spin angular momentum, S_z is its projection on the internuclear axis, and $\lambda = 1.98476 \text{ cm}^{-1}$ is the spin-spin coupling constant. The last term describes the spin-rotation coupling where $\gamma = -0.0084298 \text{ cm}^{-1}$ is the spin-rotation coupling constant. The spectroscopic constants were taken from Ref.⁸¹. This effective Hamiltonian can successfully reproduce the rotational Raman spectra of O_2 ^{123–128}. Sonoda *et al.*⁸⁵ included neither the centrifugal distortion term nor the off-diagonal terms of the spin-spin coupling in their calculation of spin-dependent dynamics to 20 ps; we keep both to ensure good agreement between measured and modeled quantum beat frequencies for our 200 ps scans¹²⁸.

The interaction between molecules and the alignment pulse can be written as⁹⁷

$$H_{int}(t) = -\frac{1}{4}\Delta\alpha I(t) \cos^2 \theta, \quad (3.3)$$

where $\Delta\alpha = 7.13$ atomic units ($1 \text{ au} = 1.4818 \times 10^{-25} \text{ cm}^3$)¹²⁹ is the polarizability anisotropy, I is the laser intensity, and θ is the angle between the molecular axis and the laser polarization. This form of the interaction Hamiltonian implicitly assumes that impulsive alignment is independent of spin. The effective total Hamiltonian is then $H_{tot} = H_0 + H_{int}$. We model the measured delay-dependent yield $Y(t)$ as a convolution of the molecular-frame angle-dependent yield, $S(\theta)$, and the delay-dependent molecular axis distribution after the pump pulse. Expanding the unknown $S(\theta)$ in a Legendre polynomial basis with coefficients C_L leads to

$$Y(t) = \sum_L C_L \langle P_L(\cos \theta) \rangle(t), \quad (3.4)$$

where $\langle P_L(\cos \theta) \rangle(t)$ are axis distribution moments—the expectation values of the Legendre polynomials averaged over the thermal distribution of initial states. As described in^{1;2}, we evaluate $\langle P_L(\cos(\theta)) \rangle(t)$ from TDSE solutions calculated on a grid of laser intensities, pulse durations and rotational temperatures.

We then use linear regression to fit $Y(t)$ to the model described by Eq. (3.4) over this grid of parameters, and the parameter set that produces the smallest residual sum-of-squares gives us our best estimate of the spin-rotation wave packet. Simultaneously, we also obtain the angle-dependent yield from the C_L coefficients, as in Refs. 1;2. This model assumes that the electron spin plays no explicit role in strong-field ionization; indeed, in theoretical treatments of strong-field ionization electron spin is usually either discounted¹³⁰ or not considered at all^{55;131} because the optical field does not couple effectively with the spin.

Figure 3.2 shows Fourier spectra of the data and fits shown in Fig. 3.1. These spectra show incommensurate frequencies, as expected from the nonperiodic behavior in the time domain. Each data set spans 2.5 ps to 196.4 ps in pump-probe delay with a step size of 0.1 ps, sufficient to sample the time evolution of the rotational wave packets and to provide a frequency step size of $\approx 0.172 \text{ cm}^{-1}$. The insets in both figures provide pump fluences estimated from the fits.

3.4 Results and discussion

Comparing with rotational Raman spectrum of O_2 ¹³², we can assign known transitions to the spectral lines in Fig. 3.2. Without the spin-rotation coupling, there is only one possible Raman transition between any two rotational states (say, the $^S S_0(1,3)$ transition between $N = 1$ and $N = 3$)¹. However, spin-rotation coupling splits each rotational state (N) into three states (with the total angular momentum $J = N, N \pm 1$); consequently, the $\Delta N = 2$ Raman line is split into six. With our experimental resolution, we can only resolve three lines that are labeled $S_-(N)$, $S_0(N)$ and $S_+(N)$ ¹³², where the subscript indicates the change in the spin quantum number S and N is the initial rotational angular momentum quantum number. For example, the $\approx 12 \text{ cm}^{-1}$ line is $S_-(1)$. It consists of a single Raman transition, $^S R(1,1)$. But the $S_0(1)$ line at $\approx 14 \text{ cm}^{-1}$ includes $^S Q(2,1)$, $^S S(2,1)$ and $^S S(1,1)$ transitions, and the $S_+(1)$ line at $\approx 16 \text{ cm}^{-1}$ includes $^S R(2,1)$ and $^S S(0,1)$. Unlike a conventional

¹The spectroscopic notation is $^{\Delta N} \Delta J(N'', J')$ for a transition from (J'', N'') to (J', N') . Letters used for the change in quantum numbers are; $S = +2$, $R = +1$ and $Q = 0$. For instance, $^S R(1,1)$ denotes the $(J' = 2, N' = 3) \leftarrow (J'' = 1, N'' = 1)$ transition.

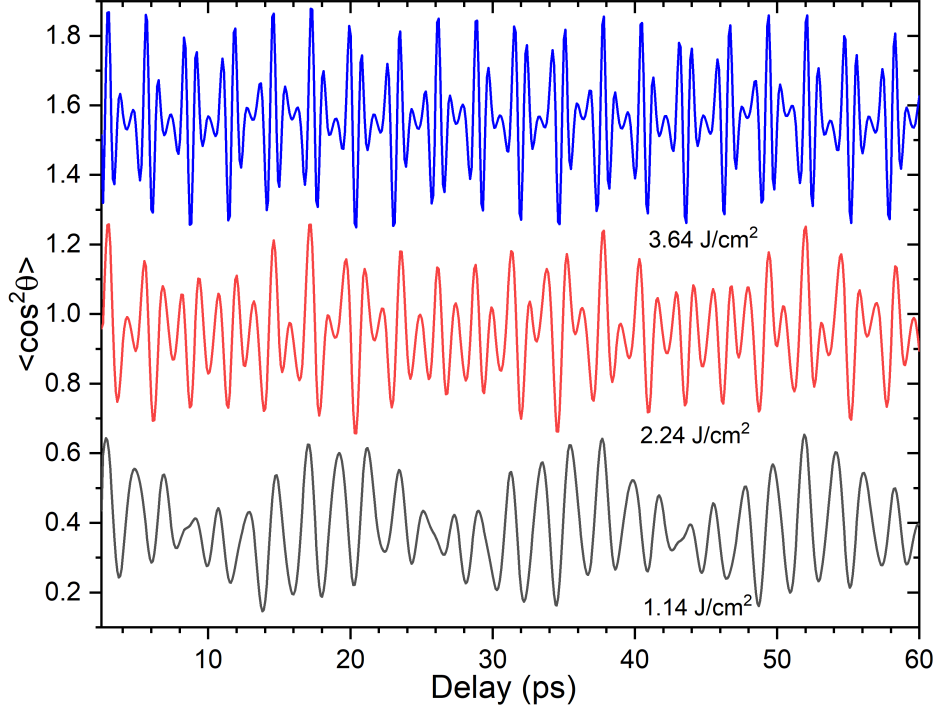


Figure 3.3: The expectation value of $\cos^2 \theta$ for spin-rotation wavepackets that best fit the data shown in Fig. 3.1. The plots for 2.24 J/cm^2 and 3.64 J/cm^2 fluences were shifted up by 0.5 and 1.1, respectively, for visual clarity.

rotational Raman spectrum, the data also shows lines corresponding to multiple Raman cycles (mostly $\Delta N = 4$), as expected in an impulsive alignment experiment⁹⁷. Each of these line also corresponds to multiple Raman excitation pathways. For instance, the $\approx 40 \text{ cm}^{-1}$ line comprises four possible excitation pathways that are shown in Fig. 3.2. Individual transitions that contribute to line at $> 60 \text{ cm}^{-1}$ are not identified in fig. 3.2.

Our data also shows a prominent 2 cm^{-1} line, which corresponds to $\Delta N = 0$ and $\Delta J = 1$ “pure spin” transitions^{133;134}, in which the spin vector $\vec{S}$ is reoriented relative to the rotational angular momentum vector $\vec{N}$. The presence of this line suggests that both the pump and the probe processes are sensitive to electronic spin. But neither the pump nor the probe step needs to be explicitly dependent on spin for the pure spin line to appear in the FFT spectrum—the dependence of both on molecular orientation and of the eigenenergies on spin and rotation is sufficient. Indeed, our model for the pump excitation (Eq. (3.3)) depends only on the angle between the molecular axis and the laser polarization vector, but the expectation

values of $P_L(\cos \theta)$ that comprise the fit show the pure spin line in FFT spectrum.

As the pump intensity is increased, the Fourier spectrum (Fig. 3.2) shows greater contributions from $\Delta N > 2$ coherences. In oxygen, the spin-rotation coupling is only important for small values of angular momentum¹³². This is consistent with Eq. (3.2), where rotation, spin-rotation and spin-spin terms scale as N^2 , N^1 , and N^0 , respectively. In our experiment using a cold molecular beam, almost all the molecules are initially in the lowest rotational state ($N = 1$, since $N = 0$ and all even N states are forbidden by nuclear spin statistics). Moreover, by keeping the pump fluence low, we keep the rotational wave packet limited to small values of N . Under these conditions, the dynamics are quite different from the simple periodic behavior expected from a rigid linear rotor. If the initial temperature of the gas sample is high, or the alignment pump pulse is strong, the rotational wave packet will be dominated by high- N states and the effect of spin-rotation and spin-spin couplings will be difficult to discern. The effect of the pump fluence can be seen in Fig. 3.3, in which the expectation values of $\cos^2 \theta$ from the simulations are plotted. Only at the highest fluence does the revival pattern resemble the structure familiar from spinless diatomic molecules. For these reasons, earlier experiments of the SFI of oxygen were not sensitive to the triplet nature of its ground state^{108;114;115;118}.

Figure 3.4 shows the angle-dependent ionization rates that we retrieve from the fits. The axis distribution moment of order L in Eq. (3.4) arises from transitions with $\Delta N = L$. For all three data sets, we truncate the series expansion in Eq. (3.4) at $L = 4$ since the $\Delta N = 6$ contribution is very weak in all three cases, as can be seen in the Fourier spectra of the data, for details see^{1;2}. The extracted ionization rates in Fig. 3.4 are in reasonable agreement with MO-ADK calculations and the measurement by Pavičić *et al.*¹⁰².

However, as can be seen in Fig. 3.2, our model accounts very well for the frequencies observed in the experiment, but for not their amplitudes. In our measurement, the average uncertainty of the data is about 1%. For other linear molecules, such as CO₂, the OR-RCS procedure provides excellent fits with the reduced chi-squared $\chi_{\text{red}}^2 \approx 1$ ², indicating a discrepancy between data and fit on the order of the experimental uncertainty. In this work, our fits are not as good as reported before² with $\chi_{\text{red}}^2 \approx 5 - 10$. The mismatch can

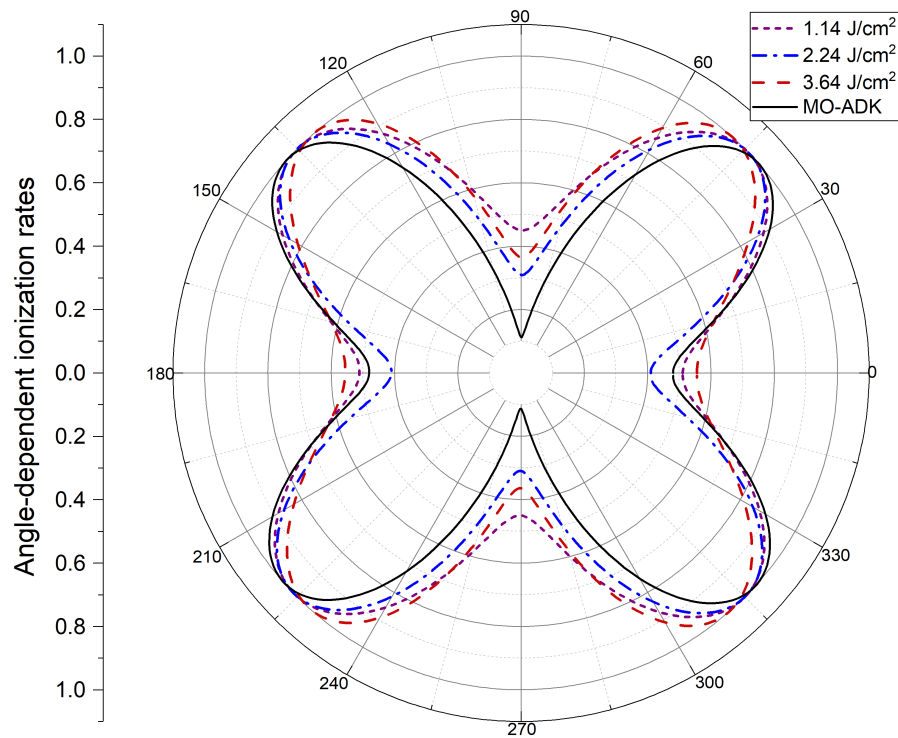


Figure 3.4: *Angle-dependent ionization rates retrieved from data shown in Fig. 3.1 and calculated using MO-ADK. In each case, the angle-dependent ionization rate is normalized to its maximum value.*

come from two assumptions that we have made in our model: that the initial distribution of molecules is thermal and that SFI does not depend explicitly on the spin. We believe that a non-thermal distribution of initial states is the reason for the mismatch. Previous studies on oxygen seeded in a helium jet^{135–137} have found nonthermal distributions of rotational states, suggesting that this is the case in our jet as well. Our setup provides cold molecules at roughly the same temperature as the experiments on O₂ performed by Aquilanti *et al.*, at about 1.8 K¹³⁵. Although better characterization of the initial state distribution can be expected to improve the fits and lead to a more consistent determination of angle-dependent ionization rate, these measurements demonstrate that the ORRCS method can be used to retrieve the dependence of ultrafast optical processes on molecular alignment even in the presence of coupling of rotations to other degrees of freedom.

3.5 Conclusion

We have measured non-periodic evolution of the SFI yield after impulsive alignment of rotationally cold oxygen molecules in a pump-probe experiment. This behavior is a consequence of the spin-rotation and the spin-spin couplings in the triplet ground state of the molecule. Although both rotational and Raman spectroscopy of O_2 are well studied and understood, no signature of this structure has been measured in the SFI experiments to the best of our knowledge. The most important reason for this situation is that spin-spin and spin-rotation coupling terms do not scale up with rotational quantum number as rapidly as the rotational energy. Thus, the effect of these couplings is obscured in typical impulsive alignment experiments that use higher initial temperatures and stronger pump pulses. An effective Hamiltonian that includes these couplings accounts for all the frequencies seen in the FFT of the delay-scan data, but it does not fully represent the observed dynamics. This discrepancy is likely to be due to a non-thermal population distribution in our supersonic jet.

High-resolution FFT spectroscopy reveals couplings between rotational motion and other degrees of freedom in molecules. Although oxygen is unusual in having a triplet ground state, coupling of rotation to orbital and spin angular momenta is commonplace in excited states of molecules. Since the rotational constants depend not only on the electronic state but also on individual vibrational levels, FFT spectroscopy of momentum distributions also allows unambiguous identification of long-lived coherences excited by the pump pulse. Although neither the pump nor the probe processes are expected to be explicitly spin-dependent in our experiment, we can nevertheless probe spin dynamics due to the inherent coupling of spin and rotation in the molecule. Such measurements in excited and ionic states of diatomic molecules can be expected to provide us with highly detailed information about the nature of pump-induced wave packets. Strong-field ultrahigh-resolution FFT spectroscopy has been used to measure the rovibrational spectra of D_2^+ ¹³⁸ and spin-orbit splitting in rare gas atoms¹³⁹. Our results show that such measurements not only yield spectroscopic information about the states populated coherently by the pump pulse, but also help characterize the interaction

of the molecule with the probe pulse.

Chapter 4

High-resolution FFT spectroscopy of spin-rotation wavepackets in N_2^+ following strong-field ionization

When nitrogen molecules are ionized by femtosecond pulses at 800 nm, post-ionization coupling launches wavepackets in several low-lying cationic states. We probe these bound-state wave packets using a dissociative third harmonic probe and use FFT spectroscopy to identify the states involved with rotational resolution. We find broad rotational excitation in the three lowest cationic states. The coupling of spin and electronic angular momentum to rotational angular momentum is also apparent over the 100 ps scan. We have found the dissociative pathways and the resonance enhance pathway involved in the dissociation process using the rotational coherence and also found the type of transition using the delay-dependent angular distribution.

4.1 Introduction

Several experimental demonstrations (higher-harmonic generation (HHG)^{21;120}, above-threshold ionization^{19;20;140}, laser-induced electron diffraction¹⁴¹ and non-sequential double ioniza-

tion¹⁴²) and theoretical models (Molecular Orbital Ammosov-Delone-Krainov (MO-ADK)^{55;143}, Molecular Orbital improved Perelomov-Popov-Terent'ev (MO-PPT)¹⁴⁴) have provided tools to understand strong-field ionization (SFI) in atoms and small molecules. The studies show that ionization rate in SFI decreases exponentially as the ionization potential of the state increases. Therefore, the probability of finding the cation in the ground state dominates among other low-lying cationic states post-SFI¹⁴⁵. Nevertheless, the populations of low-lying cationic states following the laser pulse are frequently ambiguous, as the newly formed ionic states may undergo additional coupling induced by the laser. One fascinating example is the observation of air (78 % N₂ and 21 % O₂) lasing. The explanation for this lasing process is the stimulated emission between the X $\leftarrow$ B state of N₂⁺ (390 nm). Recently, this phenomenon has gained popularity as many studies^{7;14;57-64} have attempted to explain the population inversion after SFI. This article explores the rotational wave packet in the excited states of N₂⁺ produced in a strong field-induced process post-SFI. We observe the rotational population of the cation in all the relevant electronic states of air lasing: X, A, and B. Our observation shows a strong alignment of the N₂⁺ excited states by the pump pulse. This observation supports the explanation provided by Lytova *et al.*^{62;63} for air lasing.

Recent studies^{4;7;93;145} have modeled the population redistribution after SFI in the low-lying cationic states using dipole coupling among these states. In particular, for N₂⁺ (X, A, and B) states Yao *et al.*⁷ have pointed out that near resonant dipole transition induced by the strong IR pump post-ionization plays a vital role in population redistribution in these low-lying states. Our measurement shows the evidence and reveals the significance of near resonance effects in the strong-field-induced process.

The dissociative photoionization of N₂ plays a significant role in various environments, including the Earth's atmosphere^{146;147} and the interstellar medium^{148;149}. The intricate dissociative pathways involved in the formation of N⁺ + N photo-products from N₂⁺ ions^{8;9;150} was revealed using a Vacuum ultraviolet(VUV) light source directly accessing the states of N₂⁺. In contrast, we use SFI to access the N₂⁺ ionic states and probe using a mid-UV (264 nm) source. Our analysis combines rotational coherent spectroscopy (RCS) with the kinetic energy release (KER) of the photofragment N⁺. We are able to assign the major

photodissociation channels that result in $\text{N}^+ + \text{N}$ photo-products. We show the crucial role played by 1+1 resonance in few photon photodissociation processes. Furthermore, we observed that dissociative pathways arising from different vibrational states of a low-lying electronic state, which was excited by the pump, exhibited notable differences.

The previous works on ground state molecular system of NO^{53;151} and O₂^{3;85} have demonstrated the necessity of incorporating multiplet energy splittings in rotational energies when analyzing the rotational dynamics within the electronic state multiplet. The role of spin-rotation coupling is evident in this work in the delay-dependent feature of ($\Omega = 1/2$) and ($\Omega = 3/2$) states of A ² Π_u . We observe clear separation in alignment peaks of ($\Omega = 1/2$) and ($\Omega = 3/2$) states, giving rise to a non-periodic delay-dependent dynamics³. Additionally, we have identified a chirping behavior in the spin-rotation wavepacket of ($\Omega = 1/2$) state. Our investigation led to the importance of spin-orbit coupling to create the chirping effect.

4.2 Experimental setup

The experimental setup is similar to the one reported in¹⁵², where we use a 790 nm pump and a third harmonic probe pulse. We perform this experiment using a HITS laser with a 1 kHz repetition rate, 35 fs pulse duration, and 2.6 mJ pulse energy at a central wavelength of 790 nm. A 70-30 beamsplitter splits the laser output into a (30 %) pump and a (70 %) probe arm. The 30 % arm(790 nm) ionizes and aligns the molecules. The remaining 70 % arm was up-converted from the fundamental (790 nm) to a third harmonic (264 nm) using the same optical setup described by Lam *et al.*¹⁵². The pump arm generates the aligned molecular ions, and the UV arm probes the aligned molecular ions through dissociation. The dissociation channel observed is the N^+ ion partnered with a neutral N coming from N_2^+ . We established this working condition¹⁵² using a substantial IR pump intensity 2×10^{14} W/cm² that can generate N^+ ion alone and a weak intensity UV probe 1×10^{12} W/cm² that does not dissociate the neutral molecule alone. The weak-intensity UV probe ensures a few-photon dissociation of the molecular ion. The two arms are recombined using a separator that reflects the third harmonics (264 nm) and transmits the fundamental (790 nm) before

entering the vacuum chamber. Both the beams are focused using a 20 cm two-color dielectric focusing mirror in the interaction region. The probe arm goes through a computer-controlled long delay stage, which will delay the UV pulses. The laser compressor gratings are adjusted for optimum output power from the third harmonic setup with a pulse duration of ~ 120 fs. At the same time, the ionization-alignment pump has a pulse duration of about ~ 40 fs. Both pulses enter the vacuum chamber through a Brewster-angled Calcium Fluoride window; this ensures a clean linear polarization for both the pulses parallel to the plane of the detector, and reduces any possible noise from scattered UV pulse. We use Even-Lavie valve⁷⁰ to generate the molecular beam target, operated with pure nitrogen gas at a total pressure of ~ 100 psi. The estimated rotational temperature of the pure nitrogen gas at the interaction region is ~ 10 K. We imaged the N^+ ions from the photodissociation of N_2^+ using a velocity map imaging spectrometer⁷⁴ equipped with a microchannel plate (MCP) and a fast phosphor screen (P47). We select N^+ ions by gating the MCP. The gate signal with N^+ ion's arrival time and gate width was fed into a high voltage switch from a delay generator, allowing the MCP detector to be active only when N^+ ions hit the MCP. We count each hit image from the phosphor for every laser shot using a 1000-frames-per-second camera (Basler A504k). We also implemented background subtraction, improving the signal-to-noise ratio. The background subtraction is done by mechanically chopping the 264 nm beam at 250 Hz and alternately blocking and transmitting adjacent pulses. The Even-Lavie valve is operated at 500 Hz, so every alternate pulse in the laser pulse train interacts with the molecular beam. We synchronized the chopper and gas jet operation using digital delay generators. This operation creates four combinations of pump, probe, and gas: pump-probe-gas, probe-gas, pump-probe, and probe alone. We label each laser shot with one of these four types and use this information to correct the fluctuations in laser intensity and gas density.

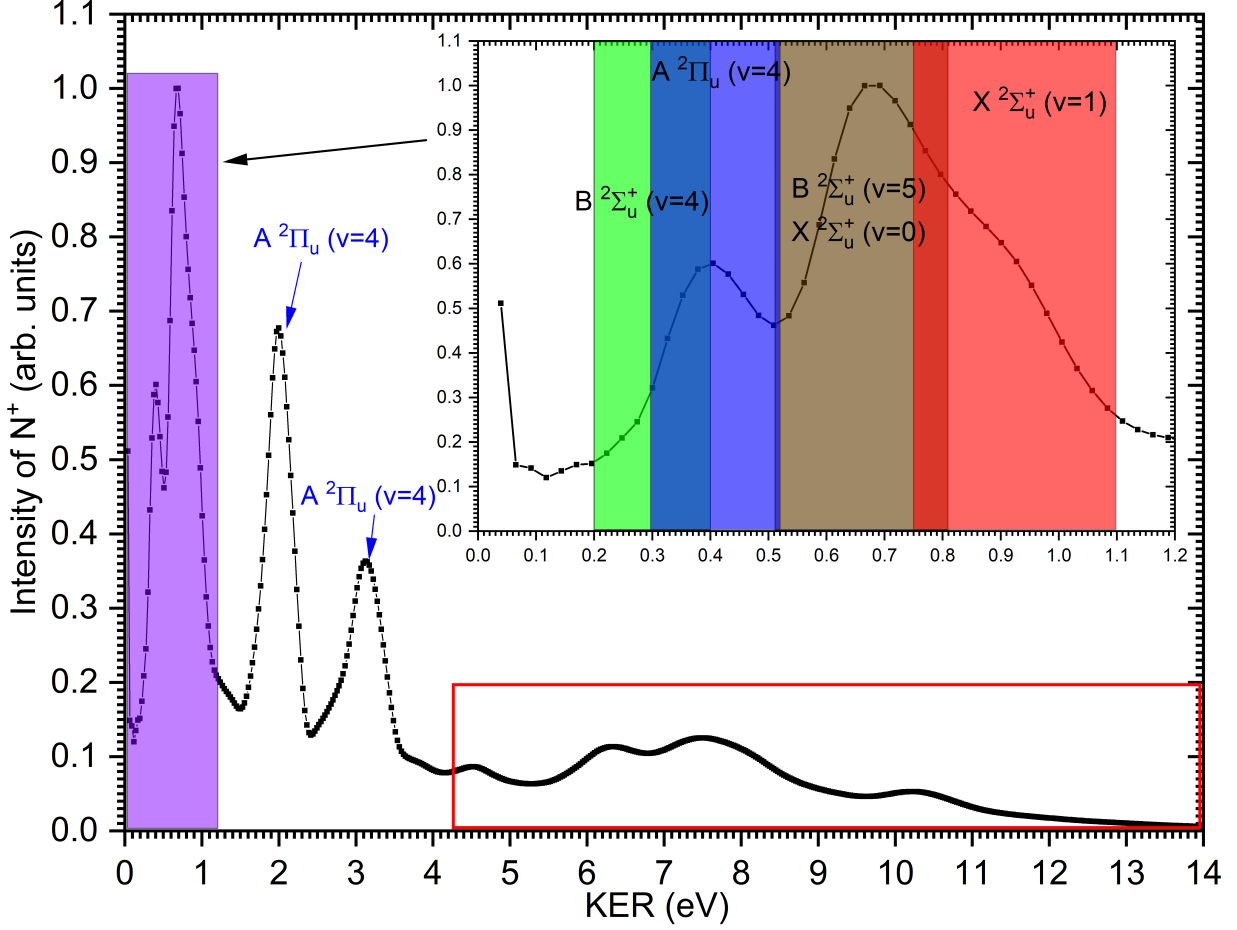


Figure 4.1: Angle and delay integrated KER distribution. The identified electronic states are shown in the graph and the inset shows the zoom-in version of the 0-1.2 eV ranges of the distribution as most of the identified states are densely observed in this energy range. The rectangular box shows the high energy band and the contribution of this band comes from pump alone see in the text.

4.3 Analysis

We employed a two-step process as described to unpack the information from the data. Each delay-dependent 2D images is normalized using the following formula¹⁵²,

$$M(t) = \frac{M[\text{Probe, Pump, Gas}](t) - M[\text{Probe, Pump}](t)}{Y[\text{Probe, Gas}](t) - Y[\text{Probe}](t)}, \quad (4.1)$$

where M is the 2D image and Y is the count of N^+ ions for the particular combination at each delay, and t is the pump-probe delay. A total of 24 delay scans were repeated and

averaged to minimize the effect of slow drifts in experimental conditions.

The first step is to perform Abel-inversion using pBasex⁷⁷ on the normalized and averaged raw images, generating best-fit and error images. Feeding the average and error images into our pBasex code with error propagation developed by Lam *et al.*¹⁵², we acquired the coefficient $C_{k_0,L}(t)$ with error for each delay. The $C_{k_0,L}(t)$ coefficients are acquired from the inverted slice after performing Abel-inversion to 2D raw images. Mathematically, it is described by the following equation,

$$M(\vec{k}, t) = \sum_{k_0 L} C_{k_0 L}(t) e^{-\frac{(k-k_0)^2}{2\sigma}} P_L(\cos \theta), \quad (4.2)$$

We also used the error in coefficient $C_{k_0,L}(t)$ to propagate our error estimate in this work further. We assumed the error in the coefficient to be Gaussian-distributed and generated 100 samples of coefficients to achieve the error estimate. The acquired delay-dependent coefficients $C_{k_0,L}(t)$ are Fourier transformed to get the quantum beats. Similar quantum beat analysis using a VMI spectrometer has been carried out for Xe atom by Forbes *et al.*¹⁵³. We have 3D $C_{k_0,L}(\omega)$ with kinetic energy release, L moment-dependent, and quantum beat (QB) spectra. This work will discuss the results only from the first moments $L = 0$ even though we have higher order moments of L, it will be referred as $\langle P_0 \rangle(t)$ in the following sections. The 2D plot shown in Fig. 4.2 is a slice from the 3D stack limiting to $L = 0$.

Long delay scan results in a high-resolution QB spectrum (sub-cm^{-1}) in the frequency domain, allowing unambiguous identification of electronic, vibrational, and rotational states populated by the pump pulse. The 2000 sample points in the time domain should give us 2000 points in the frequency domain. However, we have increased the frequency points by zero-padding the data such that we have 2^N points with $N = 14$, thus increasing the frequency resolution but not the absolute resolution of the data. The data presented is windowed and zero padded and we have used the Hanning window for the data presented in Fig. 4.2.

We can calculate the Raman lines with a sufficient spectroscopic constant for the Dunham equation¹⁵⁴ available experimentally verified and theoretically calculated. The rotational and

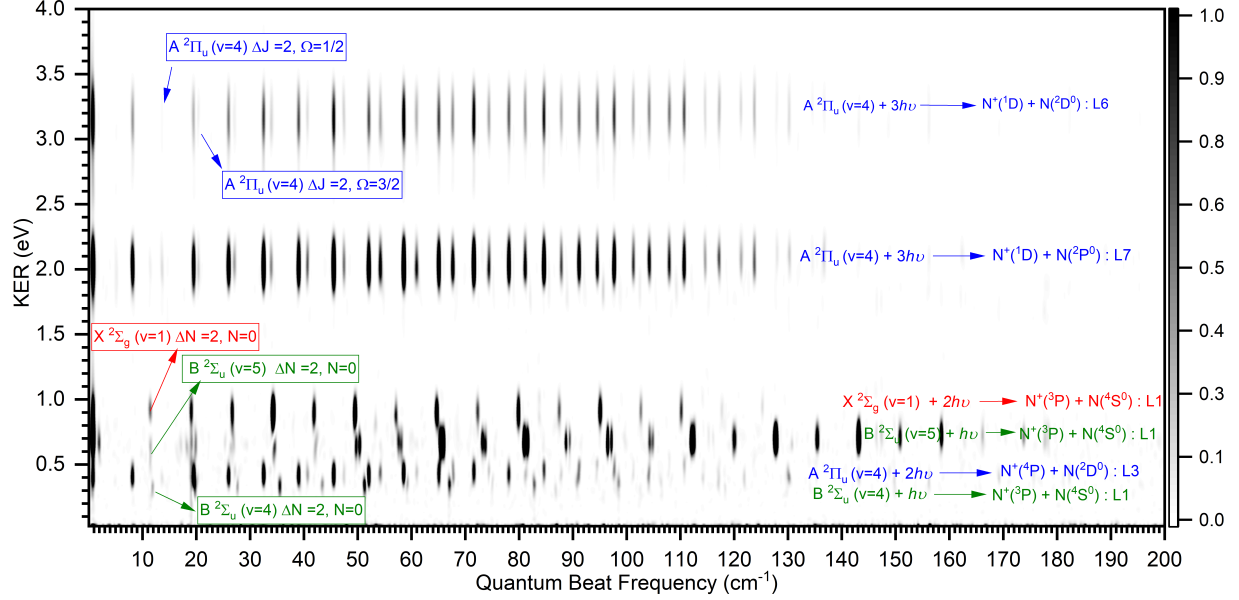


Figure 4.2: The 2D KER-FFT plot for $L = 0$ coefficients with KER range from 0 to 4 eV and the QB frequency from 0 to 200 cm^{-1} . States identified with the Raman lines are marked along with dissociation channels and the required number (264 nm) photon for achieving the KER, read discussion for details.

centrifugal distortion constants are unique for each electronic and vibrational manifold of the state; therefore, we get an identification in all manifolds of the state. We then compare the measured QB frequencies with Raman spectra calculated using Dunham equations. See appendix A. As depicted in Fig. 4.2, the observed Raman lines form a series rather than a singular peak or transition. Hence these multiple lines may not originate from the same Raman series. To eliminate this ambiguity, we integrate over a KER range and overlap the calculated Raman series of lines with the observed lines in the 1D plot to identify the state, see Fig. 4.4(a). The calculated Raman lines for different electronic and vibrational lines are run through the 1D map until we match the observed lines. The criterion for a suitable match is that the whole measured series overlaps with the series of calculated Raman lines, and the difference between the calculated and measured peaks is well within the resolution of the scan, i.e., 0.32 cm^{-1} . Thus, we can almost always unambiguously match the observed QB series to a vibronic level.

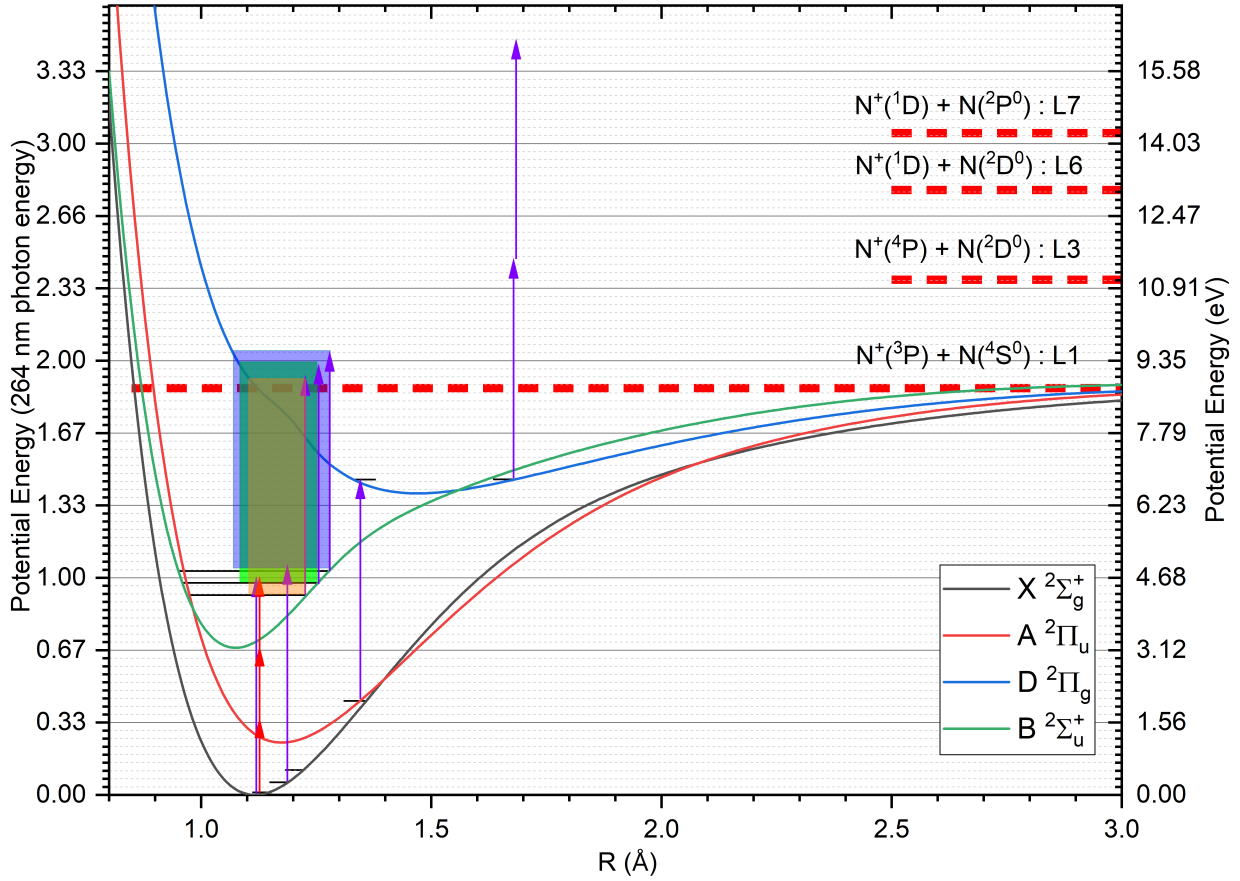


Figure 4.3: The relevant potential curves showing the low-lying states of N_2^+ . Purple arrows denotes the 264 nm probe and it highlights the possible dissociation pathways. The red arrows denotes the 790 nm pump. Here the near-resonant pathways between different vibrational states of these low-lying states are identified. L1, L3, L6 and L7 are the dissociation levels as per^{8;9} (see appendix C). These potential energy curves are recovered from¹⁰.

4.4 Results and discussion

The experiment is performed with an intense 790 nm beam of $\sim 200 \text{ TW/cm}^2$ as a pump to ionize and align, followed by a weak UV probe of $\sim 1 \text{ TW/cm}^2$ to dissociate the N_2^+ ions. In Fig. 4.1, we do not see N^+ ions from the probe only, and most of the ions are already generated only when the pump is present. In Fig. 4.1, the region of interest lies in the low KER spectrum, which is coming from the dissociation of $N_2^+ \rightarrow N^+ + N$, and the high-energy KER region marked by the rectangular box is already dissociated only by the

pump only. The high-energy KER band is delay-independent and does not have coherences. The peaks around 6.5, 7.5, and 10.5 eV corresponds to coulomb explosion of N_2 into $N^+ + N^+$ and KER positions matches with the calculation shown in work done by Yuen and Lin¹⁵⁵ and previously measured data¹⁵⁶.

With a 100 ps long scan and 50 fs delay steps, the FFT spectrum has a resolution of 0.32 cm^{-1} and a Nyquist frequency of 333.56 cm^{-1} . We found excellent agreement between QB frequencies and Raman spectra—identifying the ionic states populated after the strong-field ionization by the IR pump pulse. We observe broad rotational wave packets in X, A, and B states of N_2^+ ion core; see Fig. 4.2 in the 0-4 eV KER region of spectra. As we can see from $\langle P_0 \rangle$ in Fig. 4.2, most of the lines are coming from $\Delta J = 2$ (A state representation) or $\Delta N = 2$ (X and B state representation). Each line is a $\Delta J = 2$ coherence between two rotational states on a specific vibrational and electronic state. In the KER-FFT spectrum, we have identified the dissociation channels corresponding to KER for each specific vibrational and electronic level. In the time domain, see Fig. 4.5(a),(c) and 4.6, we also observe revival structures corresponding to these lines, indicating that we could align the low-lying ionic state with the IR pump. The following discussion will be about these three low-lying states, with each section focusing on each state.

4.4.1 B $^2\Sigma_u^+$

As shown in the angle and delay integrated KER plot, see the inset of Fig. 4.1 the two KER range 200-400 meV and 500-800 meV band belongs to the B $^2\Sigma_u^+$ $v=4$ and $v=5$ respectively. This assignment is done by comparing the calculated Raman lines; we have identified that the lower KER band comes from $v = 4$, $\Delta N = 2$ and the higher KER from $v = 5$, $\Delta J = 2$ as shown in the KER-FFT of $\langle P_0 \rangle$, see Fig. 4.2.

According to the KER, both the vibrational level of B $^2\Sigma_u^+$ ($v = 4$ and $v = 5$) matches with L1 ($^3P(N^+) + ^4S_0(N)$) dissociation asymptotes by absorbing a single photon of the third harmonic probe see Fig. 4.1. The separation in KER between the two bands B $^2\Sigma_u^+$ is ~ 300 meV, which is close to the vibrational level separation of B $^2\Sigma_u^+$ $\Delta E_{v,v+1}$ at $v = 4$, hence

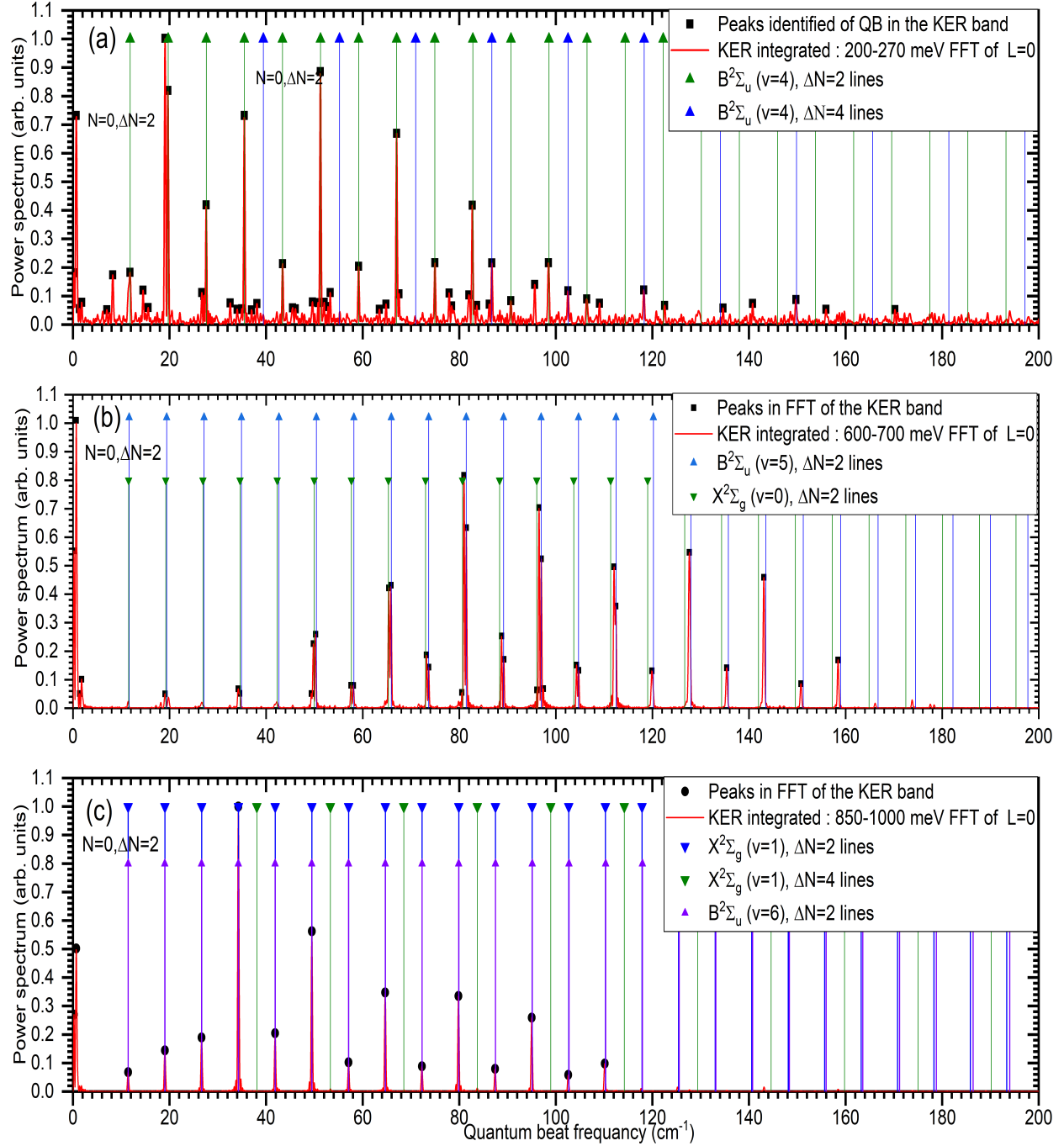


Figure 4.4: Plots of $FFT[C_0(t)]$ with the states and integrated KER range shown in the inset. The peaks are highlighted with black square dots to easily identify the overlap with the calculated Raman lines.

both channels come from the same dissociation asymptotes. All the possible electronic states that can give the L1 dissociation limit are calculated by Liu *et al.*¹⁰ using icMRCI + Q/56 + CV + DK calculations. To deduce the dissociative state, we assume dipole coupling from the B $^2\Sigma_u^+$ ($v = 4$ and $v = 5$) to the dissociative states provided by Liu *et al.*¹⁰ using a single photon of 264 nm. From B $^2\Sigma_u^+$, the single photon dipole allowed states according to the symmetry are: X $^2\Sigma_g^+$ and $^2\Pi_g$. Even though it is possible to couple the quartet and sextet states as they are not dipole-allowed, the transition probability must be small compared to the dipole-allowed states, hence less likely candidates for B $^2\Sigma_u^+$ state to dissociate through them. Among the dipole-allowed electronic states, the more likely dissociative state is $^2\Pi_g$ since it is more repulsive in the Frank-Condon region, compared to X $^2\Sigma_g^+$.

With the given intensity of the pump pulse (~ 200 TW/cm²), a direct multi-photon ionization could knock an electron out of N₂ with 12 photons of IR putting the N₂⁺ ionic core in B $^2\Sigma_u^+$ $v = 0$ state and 13 photons will put it on $v = 5$. For direct ionization from ground state X $^1\Sigma_g^+$ ($v = 0$) to B $^2\Sigma_u^+$ ($v = 5$) Frank-Condon factors¹⁵⁷ will suggest that the population should be small. Furthermore, there could be resonances in the pathways for multi-photon ionization, which could significantly alter the expected populations. Since the IR pump intensity is ~ 200 TW/cm², tunneling ionization is significant at such intensities for 800 nm wavelength, and this tunneling ionization is understood using SFA⁵⁵. According to the estimate predicted by SFA, the population will be mostly in the ground state of N₂⁺ ionic (X $^2\Sigma_g^+$) just after the peak of the pulse. In attempts to explain the air-lasing phenomena, Xu *et al.*,⁸⁸ and Yao *et al.*⁷ have considered population redistribution occurring in the low-lying states in the second half of the IR pulse. Yao *et al.*⁷ calculated with an 800 nm and a ~ 40 fs pulse, the population redistribution in X, A, and B states resulting from dipole coupling. The estimated population at the end of the pulse in B $^2\Sigma_u^+$ mainly was in $v = 0$ and $v = 4$. Following the redistribution model with dipole coupling, even with a population significantly more in the ionic ground state (X $^2\Sigma_g^+$), we should have an enhancement in $v = 5$ region due to the three-photon near-resonant excitation with our ~ 790 nm pulse which has a bandwidth of ~ 120 meV. B $^2\Sigma_u^+$ ($v = 4$) and ($v = 6$) will also gain some population as well with the tail of bandwidth in 1+1+1 three-photon near-resonant excitation. To clarify

that we have near three photon resonance, we can compare the QB of B $^2\Sigma_u^+$ ($v = 4$) and ($v = 5$) in $\langle P_0 \rangle$ see Fig. 4.4(a) and (b).

In contrast to air-lasing experiments and calculations, our measurement — see Fig. 4.2 does not show the expected population in B $^2\Sigma_u^+$ ($v = 0$). The reason for this absence is that the third harmonic probe has to drive the photodissociation with two photons [see Fig. 4.1. However for B $^2\Sigma_u^+$ $v = 4$ and $v = 5$, a single photon is sufficient for dissociation. Hence the photodissociation from $v = 4$ and $v = 5$ is dominant compared to photodissociation from $v = 0$. With a single 264 nm photon, from B $^2\Sigma_u^+$ ($v = 0$) there is no dipole-allowed electronic bound state to go through a 1+1 resonance enhanced photodissociation either. The KER band from 850 meV to 1000 meV (see Fig. 4.2) could be from B $^2\Sigma_u^+$ $v = 6$ since the $\Delta N = 2$ Raman lines from X $^2\Sigma_g^+$ $v = 0$ and B $^2\Sigma_u^+$ $v = 6$ are not distinguishable with 0.32 cm^{-1} resolution and with the pathway shown in Fig. 4.1 the KER will be same. However, we will rule this possibility out in our discussion see Sec. 4.4.4. The absence of $v = 6$ and any vibrational level above $v > 6$ is caused by inefficient excitation in the IR pump and low Frank-Condon factor from X $^2\Sigma_g^+$ $v = 0$, and $v = 1$. The quick fade and short span rotational coherences in $v = 4$ can be because the three-photon resonance is nearest to $v = 5$, and the excitation is only happening at the tail of the pulse.

4.4.2 A $^2\Pi_u$

In the $\langle P_0 \rangle$ KER-FFT spectrum (see Fig. 4.2), we observed dominant Raman lines over different ranges of KER (0.300-0.500, 1.8-2.2 and 2.9-3.4 eV) with same quantum beat frequencies. We have identified that all the Raman lines from these KER bands come from the same vibrational level of A $^2\Pi_u$ $v = 4$. In the low KER region around 0.300-0.500 eV, there is some overlap in the KER band of B $^2\Sigma_u^+$ $v = 4$.

With 11 and 12 photons of 790 nm, the pump pulse can ionize directly to $v = 2$, and $v = 10$ of A $^2\Pi_u$ with $v = 2$ being the dominant considering the Frank-Condon factor¹⁵⁷. Now, examining ionization with SFA approximation followed by population redistribution in the tail of the pulse, we should get a population around $v = 2$, $v = 3$, and $v = 4$. From

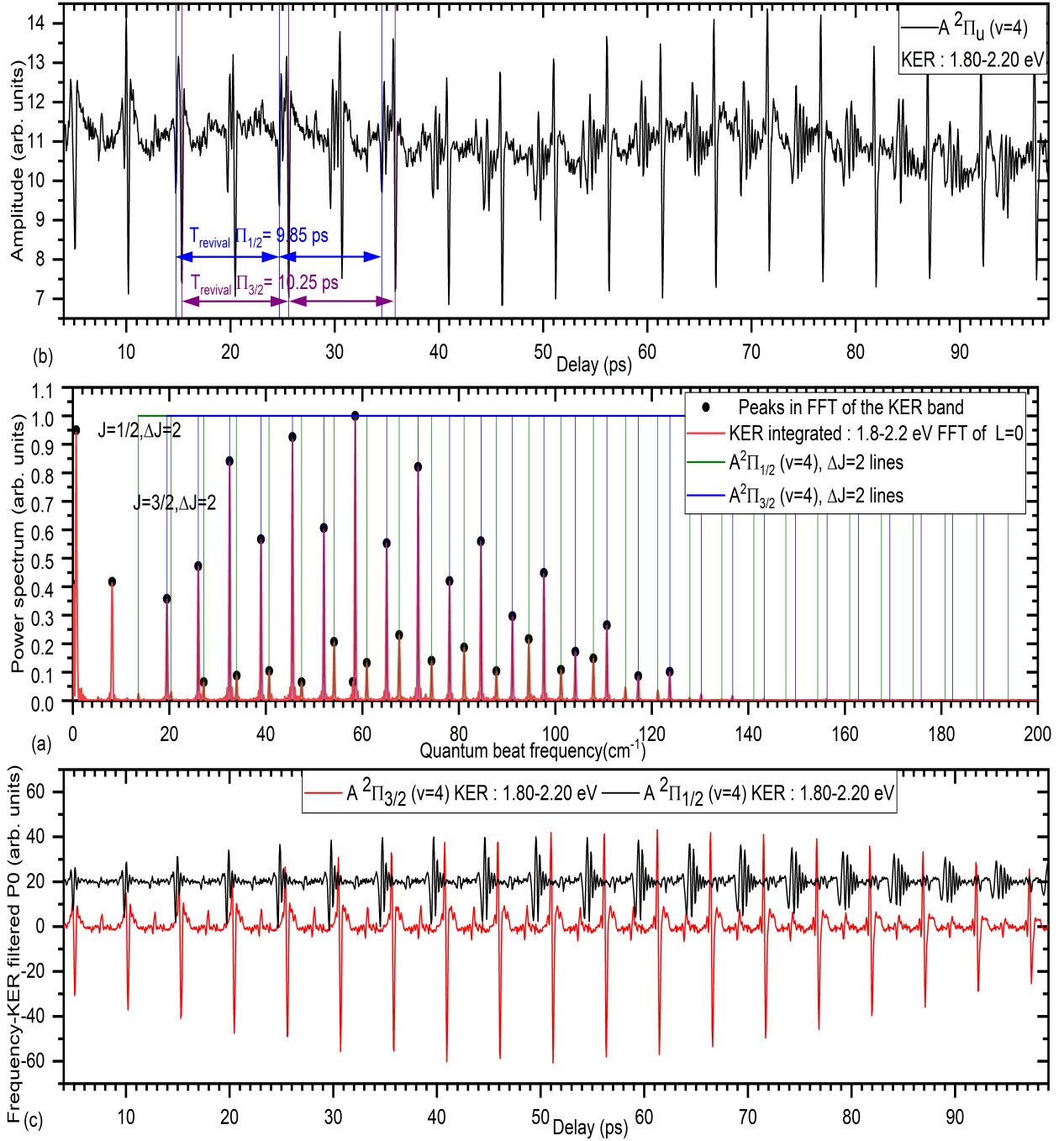


Figure 4.5: (a) KER integrated delay dependence of the $A^2\Pi_u (v=4)$ channel integrated over 1.8-2.2 eV. As shown in the (b), the consecutive QB separation for F_1 and F_2 corresponds to the half revival in the delay dependence. (b) FFT of the $A^2\Pi_u (v=4)$ channel integrated over 1.8-2.2 eV. The peaks are shown in red dots as per the peak finding algorithm and drop down line on it is the calculated $\Delta J = 2$ frequencies using the energy equation for $A^2\Pi_{3/2} (F_1)$ and $A^2\Pi_{1/2} (F_2)$, shown by the blue and purple drop down lines respectively. (c) Frequency and KER (1.8-2.2 eV) filtered delay dependent yield of $A^2\Pi_{3/2} (F_1)$ and $A^2\Pi_{1/2} (F_2)$. The inset shows red curve belongs to $A^2\Pi_{3/2} (F_1)$ and the black curve belongs to $A^2\Pi_{1/2} (F_2)$. An offset of 20 units is added to the delay dependent yield of $A^2\Pi_{1/2} (F_2)$.

the ground state $X \ ^2\Sigma_g^+$, there will be one-photon near resonant excitation to $A \ ^2\Pi_u$. These transitions¹⁵⁷ are $X \ ^2\Sigma_g^+ (v = 0) \rightarrow A \ ^2\Pi_u (v = 2)$, $X \ ^2\Sigma_g^+ (v = 1) \rightarrow A \ ^2\Pi_u (v = 3)$ and $X \ ^2\Sigma_g^+ (v = 2) \rightarrow A \ ^2\Pi_u v = 4$ at 787, 810 and 835 nm respectively. The pump pulse covers these wavelengths. Hence the pump should be able to populate $A \ ^2\Pi_u v = 2, v = 3$, and $v = 4$ efficiently.

The lack of any vibrational levels other than $v = 4$ from the spectra is surprising since we expect at least $v = 2$ and $v = 3$ levels to be present in A state spectra. We have identified there is a resonant transition between $A \ ^2\Pi_u (v = 4) \rightarrow D \ ^2\Pi_g (v = 3)$ with 264 nm wavelength photons from Table 45 in Lofthus and Krupenie work¹⁵⁷. Due to this resonance, the probe has a high selectivity to photodissociate ($v = 4$) only with a 1+1 resonant enhanced photodissociation process. The probe also cannot excite multiple vibrational levels since it has a small bandwidth of ~ 40 meV, whereas the energy separation between the A state vibrational levels ~ 220 meV around $A \ ^2\Pi_u (v = 4)$. Therefore, the dominance of the $v = 4$ level is likely due to the 1+1 resonant enhanced photodissociation process.

From the $A \ ^2\Pi_u (v = 4)$ state dissociates to L1 ($^3P(N^+) + ^4S_0(N)$) and L3 ($^3P(N^+) + ^2D_0(N)$) dissociative asymptotes — check table C.1 in appendix C by absorbing one more UV photon from $D \ ^2\Pi_g (v = 3)$, see Fig. 4.3. The N_2^+ ions dissociating to L1 match up with the highest KER band 2.9-3.4 eV, though this KER band could also be generated by absorbing three UV photons from $A \ ^2\Pi_u (v = 4)$ through $D \ ^2\Pi_g (v = 3)$ and one more resonance state to L6 ($^1D(N^+) + ^2D_0(N)$) generating this band. The ones from L3 have the lowest KER band (0.3-0.5 eV). For $A \ ^2\Pi_u (v = 4)$ to dissociate to the L3 asymptote, the second photon of UV has to be absorbed at the right turning point of $D \ ^2\Pi_g (v = 3)$, see the potential energy curves Fig. 4.3. Energetically, it would be impossible to dissociate $A \ ^2\Pi_u (v = 4)$ state from the L3 asymptote with two UV photons from the bond length of around 1.3 Å. From the dissociating states calculated by Martin *et al.*⁸ and Aoto *et al.*⁹, we found the only possible candidate for the middle KER band of $A \ ^2\Pi_u (v = 4)$ state with 1.8-2.2 eV to be the L7 asymptote. By exciting $D \ ^2\Pi_g (v = 3)$ with two UV photons, N^+ ions can have KER of 1.8-2.2 eV dissociating from the L7 dissociation asymptote. A three-photon process with a UV probe with the estimated intensity of ~ 1 TW/cm² is unlikely. We suspect

that another unidentified intermediate resonance is responsible for the strong signal in this channel. Because of this resonance the KER band at 2.9-3.4 eV is also likely coming from L6 with three photons of UV from A $^2\Pi_u$ ($v = 4$).

Out of the 12 dissociative states calculated in¹⁰ for the L1 asymptote, the dipole-allowed state from D $^2\Pi_g$ are A $^2\Pi_u$ and B $^2\Sigma_u^+$. As seen from the potential energy curve (see Fig. 4.2), through photon absorption D $^2\Pi_g$ can only transfer population to B $^2\Sigma_u^+$ at larger bond length than equilibrium bond length (greater than ~ 1.55 Å). So, the second photon absorption for dissociation likely occurs at the right turning point of D $^2\Pi_g$. Similarly, there are 36 dissociative states with L3 asymptote calculated by¹⁰, out of which the dipole-allowed states are 2 $^2\Pi_u$, 3 $^2\Pi_u$, 2 $^2\Sigma_u^+$, 3 $^2\Sigma_u^+$, $^2\Sigma_u^-$, $^2\Delta_u$ and 2 $^2\Delta_u$. As for dissociation states from the L6 and L7 asymptote, there could be more possible pathways as it could have many more dissociative states in the higher energy. Nevertheless, from potential energy calculation from⁹ and⁸, we can deduce that the only energetically possible when the two photons are absorbed at the right turning point of D $^2\Pi_g$ ($v = 3$) around 1.7 Å and the possible dipole allowed state is 7 $^2\Sigma_g^+$.

4.4.3 X $^2\Sigma_g^+$

According to SFA calculations, most populations after the peak of the pump pulse should be in X $^2\Sigma_g^+$ ¹⁴⁴. Along with SFA calculation, Xu *et al.*⁸⁸ uses the Franck-Condon approximation that assumes the initial nuclear wave function mirrors that of the vibrational ground state of N₂. The Frank-Condon factor as per^{157;158} the X $^2\Sigma_g^+$ ($v = 0$) should be most favoured after the SFI. Now, following the population redistribution scheme, the vibrational levels of X $^2\Sigma_g^+$ will be redistributed see in the reference^{7;88;145}. In our KER-FFT measurement, see Fig. 4.2 we have identified $^2\Sigma_g^+ v = 0$ and $v = 1$ with KER of ~ 500 meV - 600 meV band and ~ 800 meV - 1000 meV respectively dissociating from L1 asymptote with 2 UV-photons. With this, we would not expect the poor visibility of $v = 0$ coherences in our observation. Population depletion could be a contributing reason for the low visibility of X $^2\Sigma_g^+ v = 0$. We have already identified X $^2\Sigma_g^+ v = 0 \rightarrow$ B $^2\Sigma_u^+$ ($v = 5$) and $^2\Sigma_g^+ v = 0 \rightarrow$ A $^2\Pi_u$ ($v = 2$)

to be a near three-photon resonance excitation and a near 1-photon resonance excitation respectively in the IR pump see the pathways in Fig. 4.3. Similar near resonances excitation in the pump is identified for $^2\Sigma_g^+ v = 1$ to B $^2\Sigma_u^+$ ($v = 6$) and A $^2\Pi_u$ ($v = 3$), see Fig. 4.3. However, our measurement suggests the population depletion effect is less with ($v = 1$). We also need to consider the the Frank-Condon factors between X $^2\Sigma_g^+$ ($v = 1$) and B $^2\Sigma_u^+$ ($v = 6$) is very low X $^2\Sigma_g^+$ ($v = 1$) and A $^2\Pi_u$ ($v = 3$) X $^2\Sigma_g^+$ ($v = 0$) and A $^2\Pi_u$ ($v = 2$) are comparable and later is bigger by a factor of ~ 2 ¹⁵⁷.

The potential dissociative states through L1 asymptote based on Liu *et al.*¹⁰ calculation and considering only dipole transitions of two UV photons from X $^2\Sigma_g^+$ is D $^2\Pi_g$. Another possible explanation for the diminished ($v = 0$) could be that the direct 2-UV photodissociation through L1 from X $^2\Sigma_g^+$ ($v = 0$) $\rightarrow$ D $^2\Pi_g$ is less likely compared to the X $^2\Sigma_g^+$ ($v = 1$) $\rightarrow$ D $^2\Pi_g$ is low compared to the dissociation through the right turning point of ($v = 1$), as the wavefunction overlap increases. With the spectroscopic parameters ω_e , $\omega_e x_e$ and $\omega_e y_e$ in¹⁰, the X $^2\Sigma_g^+$ $v = 0 \rightarrow$ B $^2\Sigma_u^+$ $v = 5$ and X $^2\Sigma_g^+$ $v = 1 \rightarrow$ B $^2\Sigma_u^+$ $v = 6$ transitions resonance wavelengths are 268.1 nm and 267.3 nm respectively. The probe pulse has a bandwidth of ~ 2 nm with a peak at 264 nm, the UV photodissociation process is off-resonant with X $^2\Sigma_g^+$ $v = 1 \rightarrow$ B $^2\Sigma_u^+$ $v = 6$ is closer to the peak of 264 nm.

4.4.4 Dissociative pathways

As discussed in the previous section, we can have many possible dissociation channels for the higher dissociation asymptotes (L3 and L7). This section will focus on the dissociation pathways of X, and B states to L1 dissociation asymptote and A state to L3 dissociation asymptote. The photo-dissociation fragments display spatial anisotropy when a linearly polarized light beam breaks apart a molecule⁸³. In a parallel-type transition (where μ is parallel to the inter-nuclear axis), $I(\theta)$ is proportional to $\cos^2(\theta)$, while in a perpendicular-type transition (where μ is perpendicular to the inter-nuclear axis), $I(\theta)$ is proportional to $\sin^2(\theta)$. The angle θ is the Lab-frame polar angle about the laser polarization axis similar

to the definition in ^{2;152}. From ^{2;83}, shown for 1-photon transition,

$$I(\theta, t) = \sigma(t)(1 + \beta(t)P_2(\cos(\theta))) \quad (4.3)$$

$$\sigma(t) \propto \langle P_0 \rangle (t) \quad (4.4)$$

$$\beta(t) \propto \langle P_2 \rangle (t). \quad (4.5)$$

After SFI by a linearly polarized light, we can assume the molecular ion to be along the laser polarization axis, and $\langle P_0 \rangle (t)$ observable in Fig. 4.6(a),(b) and (c), represents the aligned molecular ions in the molecular axis. This is analogous to the zeroth-order axis distribution moments discussed in the ^{122;152;159}, which contains molecular alignment information and higher-order axis distribution moments describe the nature of ionization-the dipole transition involved during the ionization. Therefore, the observable $\langle P_2 \rangle (t)$ in Fig. 4.6(a),(b), and (c) contains the information of dipole transition involved in the dissociation from the bound to the continuum state. The ratio of $\langle P_2 \rangle$ and $\langle P_0 \rangle$ is proportional to the Beta parameter. Therefore, from the phase shift observed between $\langle P_2 \rangle (t)$ and $\langle P_0 \rangle (t)$, we can deduce the type of transition involved in the photodissociation.

From Fig. 4.6 (c), the $\langle P_0 \rangle (t)$ and $\langle P_2 \rangle (t)$ of B $^2\Sigma_u^+$ ($v = 4$), we observe an out-of-phase between the two observable because the photodissociation process in this case is a perpendicular-type transition, ($^2\Sigma_u^+ (v = 4) \xrightarrow{\perp} D \ ^2\Pi_g$) as Σ changes to Π with one photon of 264nm probe. In the KER range of 850-1000 meV just from the Raman lines, we cannot distinguish the contribution of X $^2\Sigma_g^+$ ($v=1$) and B $^2\Sigma_u^+$ ($v=6$) in the dissociation channel as the lines are overlap see Fig. 4.4 (c). In this case, there is a 90°-phase shift between $\langle P_0 \rangle (t)$ and $\langle P_2 \rangle (t)$ (see Fig. 4.6 (a)), suggesting that the photodissociation process is a mixed-type transition. Therefore, the dominant contribution is coming from X $^2\Sigma_g^+$ ($v=1$) $\xrightarrow{\parallel}$ B $^2\Sigma_u^+$ ($v=6$) $\xrightarrow{\perp}$ D $^2\Pi_g$. If the B $^2\Sigma_u^+$ ($v=6$) $\xrightarrow{\perp}$ D $^2\Pi_g$ was dominant in the photodissociation process, the $\langle P_0 \rangle (t)$ and $\langle P_2 \rangle (t)$ should have been out-of-phase similar to $^2\Sigma_u^+ (v = 4)$ case in Fig. 4.6 (c). Similar to B $^2\Sigma_u^+$ ($v = 4$) we would expect the photodissociation from B $^2\Sigma_u^+$ ($v = 5$) to have a perpendicular-type transtion following the same pathway B $^2\Sigma_u^+ (v = 5) \xrightarrow{\perp}$

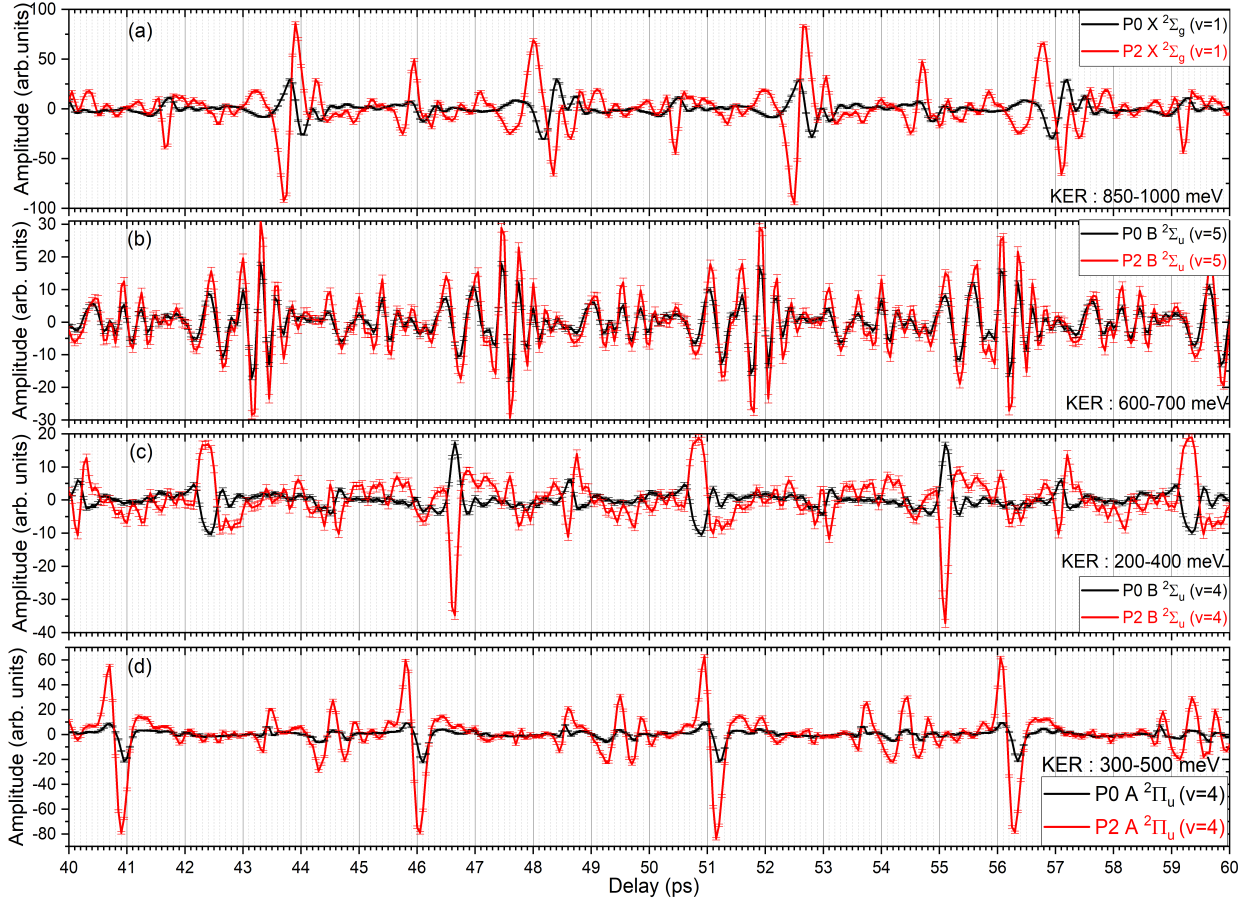


Figure 4.6: Frequency and KER filtered $\langle P_0 \rangle(t)$ and $\langle P_2 \rangle(t)$ delay-dependent intensity of (a) $X^2\Sigma_g^+(v=1)$ (b) $B^2\Sigma_u^+(v=5)$ (c) $B^2\Sigma_u^+(v=5)$ and (d) $A^2\Pi_u$. The black curves are $\langle P_0 \rangle(t)$ and the red curves are $\langle P_2 \rangle(t)$. All the delay axis are from 40 to 60 ps. $X^2\Sigma_g^+(v=1)$ (b) $B^2\Sigma_u^+(v=5)$ (c) $B^2\Sigma_u^+(v=5)$ are dissociating to L1 asymptote whereas (d) $A^2\Pi_u$ is dissociating to L3 asymptote. The inset text and the legends shows the state for which frequency filter and KER band filter was applied.

D $^2\Pi_g$ with one 264 nm photon. Surprisingly, there is no phase shift between $\langle P_0 \rangle(t)$ and $\langle P_2 \rangle(t)$ in the KER region of 600-700 meV (see Fig. 4.6 (b)), which corresponds to the B $^2\Sigma_u^+$ ($v = 5$) implying a parallel-type transition. This is probably because B $^2\Sigma_u^+$ ($v = 5$) dissociates to a continuum state of $X^2\Sigma_g^+$ as there is no dissociative state available with L1 asymptote will dissociate with a parallel-type transition from B $^2\Sigma_u^+$.

4.4.5 Spin-orbit coupling effect in A $^2\Pi_u$ ($v = 4$)

Since A state is a doublet pi, the value of the projection of total electronic orbital angular momentum on the inter-nuclear axis is one ($\Lambda = \pm 1$). The spin-orbit coupling constant is significantly larger than rotational constant B (1.74 cm^{-1}) in the A (-74.6 cm^{-1}) $^2\Pi_u$, and under these conditions, the azimuthal electronic orbital momentum(Λ) gets coupled to azimuthal spin angular momentum (Σ) and the angular momentum coupling of A $^2\Pi_u$ state is described with Hund's case (a)⁸¹. The energy eigenfunction for such systems is written as a linear combination of parity conserved wavefunction $|J, \Omega, \pm\rangle$, where $|J, \Omega, \pm\rangle = \frac{1}{\sqrt{2}}(|\Lambda\rangle |S = 1/2, \Sigma = 1/2\rangle |J, \Omega = \Lambda + \Sigma\rangle \pm (-1)^{(J-S)} |\Lambda\rangle |S = 1/2, \Sigma = -1/2\rangle |J, \Omega = \Lambda + \Sigma\rangle)$, (for $\Omega = 3/2$ and $1/2$ in this case) which is often known as F₁ and F₂ states⁸¹. In Fig. 4.2, the KER-FFT spectrum shows two series corresponding to the $\Omega = 3/2$ (F₁) and $\Omega = 1/2$ (F₂) states for all the KER bands of A $^2\Pi_u$. In our measurement (see Fig. 4.4(a)), the F₁ lines get more intense than the F₂ lines over large J values, and the intensity of F₂ and F₁ lines becomes comparable for $J = 19.5, \Delta J = 2$ for $\Omega = 3/2$ (F₁) and $J = 18.5, \Delta J = 2$ for $\Omega = 1/2$ (F₂).

From the delay-dependence shown in Fig. 4.5(a), we observe two different revival structures corresponding to the F₁ and F₂ lines in the frequency domain. The revival periods are ~ 9.35 ps and ~ 10.25 ps for $\Omega = 1/2$ (F₂) and $\Omega = 3/2$ (F₁) respectively. Because of the different periods, the two revival peaks drift apart at longer time delays, and the difference between the $\Omega = 1/2$ (F₂) and $\Omega = 3/2$ (F₁) in the time domain becomes visible. This can be understood in the frequency domain in the discussion below.

Firstly we take an FFT of the delay dependent data shown in Fig. 4.5(a) to acquire the

the QB shown in Fig. 4.5(b). Following the FFT, we identify the $\Omega = 1/2$ (F_2) and $\Omega = 3/2$ (F_1) in frequency domain. In the frequency domain we filter out a state either $\Omega = 1/2$ (F_2) and $\Omega = 3/2$ (F_1) by making all the other frequency set to DC background and selecting only the corresponding QB series by putting a rectangular window around it. Then we take the inverse FFT to acquire the Fourier filtered time-dependent signal shown in Fig. 4.5(c).

In Fig. 4.5(c) we see that there is repetitive fast oscillating feature which only appear $\Omega = 1/2$ (F_2) but not in the $\Omega = 3/2$ (F_1) delay-dependence yield. This fast oscillating feature in $\Omega = 1/2$ (F_2) shows a drift in phase as which can be seen by comparing the every half revival whereas in the $\Omega = 1/2$ (F_2) this drift in phase after every half revival is not present. Both the fast oscillating "chirp" and phase shift feature is seen only in $\Omega = 1/2$ (F_2) state. To clarify the observed distinction which present solely in $\Omega = 1/2$ (F_2) and absent in $\Omega = 3/2$ (F_1), we focus exclusively on the time evolution within the field-free region shown in Fig. 4.5(a) and the field-free evolution phase dictates time evolution in the rotational wavepacket which is $\Delta E_{J+2,J} \times t$, where t is the time delay. We will only consider $\Delta J = 2$ transitions as they dominate our observation.

This odd behavior of $\Omega = 1/2$ (F_2) is best understood in frequency domain. Using Eq. A.2 and A.3 we acquired the Raman lines for both $\Omega = 1/2$ (F_2) and $\Omega = 3/2$ (F_1) and we assume that $\Delta E_{J+2,J}$ as a linear function of J which can be written as $\Delta E_{J+2,J}(J) = a_1 + b_1 J$. In terms of frequency combs vernacular, $f_m = m f_{rep} + f_0$ where f_0 is comb offset-here it is a_1 , f_{rep} is the repetition rate-here it is the coefficient b_1 and J represent the comb index which is the m . We can determine the carrier-envelope offset frequency (f_0) for both $\Omega = 1/2$ (F_2) and $\Omega = 3/2$ (F_1) (10.8 cm^{-1} and 9.7 cm^{-1} respectively), due to this difference in carrier-envelope offset we do see the drift in time domain.

To check the most contributing parameter among A , D , and A_D in making $\Delta E_{J+2,J}$ a quadratic function. By setting $A \rightarrow 0$ regardless of the D value the difference in the quadratic content of the $\Omega = 1/2$ (F_2) and $\Omega = 3/2$ (F_1) goes away. We look at the fit quality for the linear model by looking at the reduced χ^2 of the fit by setting D and A_D as fixed parameter and A as free parameter. This way, the least reduced χ^2 would mean low quadratic content in the model $\Delta E_{J+2,J}$ as a function of J . As shown in Fig. 4.7, the linear fit quality at

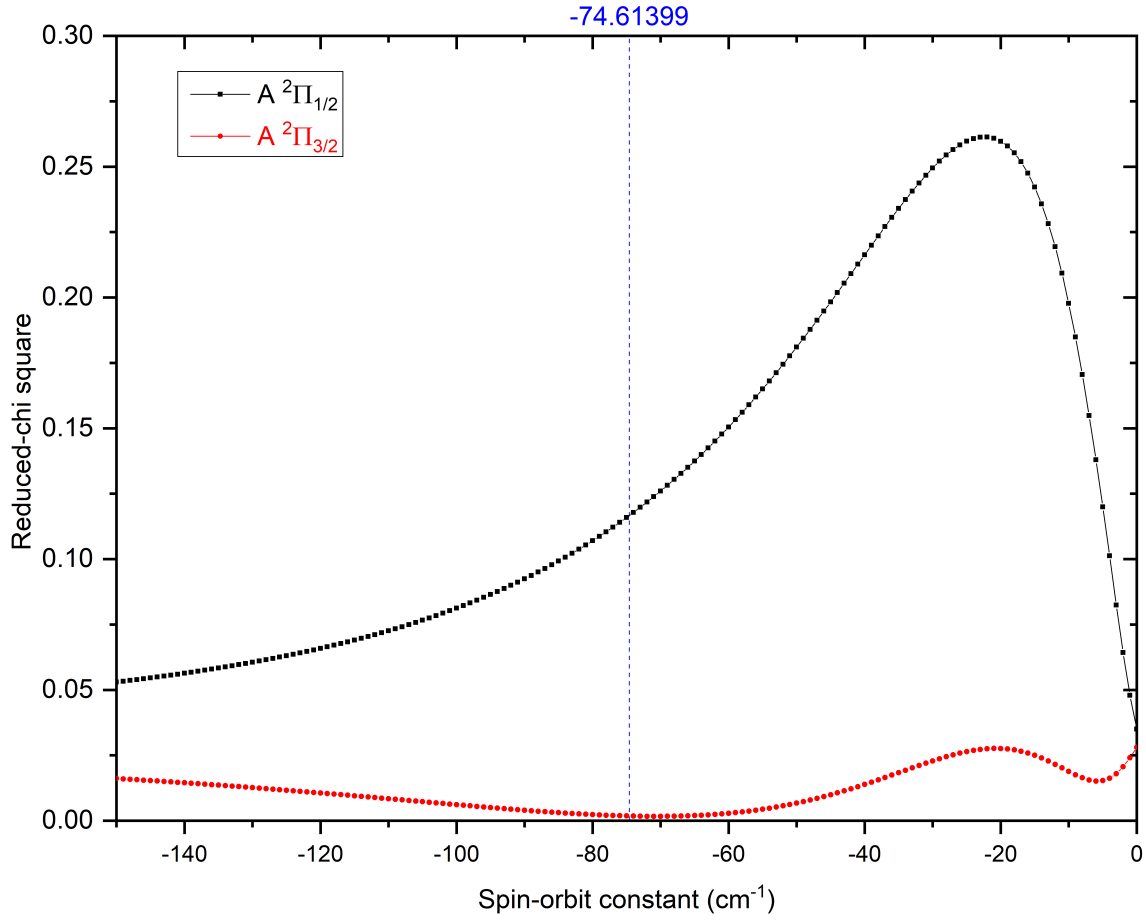


Figure 4.7: Reduced χ^2 of the linear model fit Vs spin-orbit interaction constant. The dotted blue line shows the spin-orbit interaction constant values for $A \ ^2\Pi_u$. As indicated in the inset the red and black curves correspond to reduced χ^2 values for $\Omega = 1/2$ (F_2) and $\Omega = 3/2$ (F_1) respectively.

$A = -74.6 \text{ cm}^{-1}$ is almost zero as compared to 0.05 for $\Omega = 3/2$ (F_1), showing the quadratic component in $\Omega = 1/2$ (F_2) is more at $A = -74.6 \text{ cm}^{-1}$.

Since we found that the linear model for $\Omega = 3/2$ (F_1) does not fit very well whereas it doesn't fit for $\Omega = 1/2$ (F_2). So we compare the quadratic coefficients of function $\Delta E_{J+2,J}(J) = a_2 + b_2 J + c_2 J^2$ for $\Omega = 3/2$ (F_1) and $\Omega = 1/2$ (F_2). The quadratic coefficients a_2 , b_2 and c_2 for $\Omega = 3/2$ (F_1) is 9.6 cm^{-1} , 6.5 cm^{-1} , and 0.0003 cm^{-1} respectively and for $\Omega = 1/2$ (F_2) is 10.1 cm^{-1} , 6.8 cm^{-1} , and 0.005 cm^{-1} respectively. Therefore the variation of $\Delta E_{J+2,J}$ with respect to J exhibits a more pronounced quadratic trend for $\Omega = 1/2$ (F_2) as c_2 is an order larger compared to that of $\Omega = 3/2$ (F_1). Hence, the chirp behavior in the time domain is attributed to the higher quadratic component in $\Delta E_{J+2,J}$ for $\Omega = 1/2$ (F_2).

4.5 Conclusion

In this experiment, we have achieved a broad coherent rotational wave packet for the low-lying states of N_2^+ . As shown earlier, we obtained a minimum of $J = 20$ with $\Delta J = 2$ for all observed states (X, A, and B) of N_2^+ following the process induced by the strong field of the molecular ion post-ionization. This demonstrates strong evidence of tightly aligned molecular ions induced by the strong field.

With this technique, we acquire a fine frequency resolution after doing long-delay scans (for this work it was 0.32 cm^{-1}). In this report, we present a clear identification of wavepackets that were coherently generated by the pump pulse in electronic, vibrational, and rotational states. As demonstrated above the identification is achieved by combining VMI and FFT spectroscopy which generates the KER-quantum beat spectrum. In conclusion, our analysis strongly supports the explanation provided in the previous study^{4;7;145} in for what happens post-SFI and how the population gets redistributed. We have also highlighted the importance of near-resonance effects in the process induced by strong fields.

Our investigation delved into the impact of the coupling between electronic and rotational angular momentum on the dynamics of low-lying molecular ion states under the influence

of a strong field. We demonstrated the dynamic in A $^2\Pi_u$ with $\Omega = 3/2$ and $\Omega = 1/2$, the spin, orbital, and rotational angular momentum gets coupled which leads to a non-periodic behavior in the delay-dependence of this state. We also identified a chirp behaviour in the time-domain of $\Omega = 1/2$ state which is unique for A $^2\Pi_u$ of N_2^+ due to the value of spin-orbit interaction and centrifugal constants. This finding gives a significant influence on the alignment-dependent effect involving A state. In the three-level scheme of air lasing, if the population inversion depends on alignment then this coupling of electronic and rotational angular momentum will play a crucial role.

With the state identification using the Raman lines, we distinguish the elusive dissociation pathways in a few-photon dissociation. Furthermore, we have emphasized the critical role played by the 1+1 resonant transition in the probe step. Our observation suggests that the intermediate resonant transition heavily influences the transition type observed in a photodissociation process, acting as a rate-limiting step. We have also found evidence of a fascinating dissociative pathway following SFI and a resonant probe driving a stimulated emission and a photodissociation.

Chapter 5

Strong-field induced rotational coherences in the cationic states of O₂

We investigate the wave packet that remains bound in the ground and excited cationic states of oxygen after strong-field ionization by an intense 800-nm pulse. A much weaker probe pulse (either 800 nm or 264 nm) is used to dissociate these still-bound cations. The momentum distribution of O⁺ is measured as a function of pump-probe delay, and then Fourier transformed to obtain kinetic-energy-dependent and rotational-state-resolved quantum beat spectra. The sub-cm⁻¹ resolution of the Fourier transform allows unambiguous identification of the electronic, vibrational and rotational states populated by the pump and then dissociated by the probe. Although tunnel ionization is expected to populate the lower-lying $a^4\Pi_u$ state more effectively than the $b^4\Sigma_g^-$ state, the Fourier spectrum shows only a weak wave packet in the former. All the strong lines in the 800 nm probe experiment are due to rotational states in the higher-lying b manifold. The experiment confirms the role of the resonant coupling between the two states by the 800 nm pulses [Xue *et al.*, Phys. Rev. A 97, 043409 (2018)]⁴ and reveals the importance of rovibrational excitation and predissociation in determining the momentum spectrum of the O⁺ fragments. The $X^2\Pi_g$ state, observed with the 264-nm probe pulse, shows the effect of spin-orbit and spin-rotation couplings and the importance of resonant coupling in the probe pulse.

5.1 Introduction

When molecules are ionized by intense ultrashort laser pulses, a range of electronic, vibrational and rotational states can be coherently populated in the cation either directly in the ionization step itself, or through efficient dipole coupling between various cationic states after ionization (see, for instance,⁷). These laser-induced coherent nuclear wave packets can be used to study properties of potential curves by measuring kinetic energy release (KER) distributions and observing their time-dependent oscillations^{65;94}.

The dissociation of O_2^+ ions driven by ultrafast laser pulses have been investigated by experiment and theory, where the primary mechanism is determined to be the coupling between the $a^4\Pi_u$ state and the weakly-repulsive metastable $f^4\Pi_g$ state^{87;91;94;160}. This mechanism can explain many experiments performed under various conditions, including XUV-pump-IR-probe experiments with neutral O_2 ^{94;160} and the single-IR-pulse experiment using “hot” O_2^+ ion beam⁹¹. However, in the IR-pump-IR-probe experiment by De *et al.*⁶⁵, the coupling between $a^4\Pi_u$ and $f^4\Pi_g$ states was used to explain most of the data, but there are notable discrepancies in the KER and quantum beat (QB) spectra. The simulated energy-dependent structure in the KER and the QB frequencies do not match with the observed ones.

Recently, Xue *et al.*⁴ have theoretically re-examined the experiment performed by De and coworkers⁶⁵. They identify the important contribution of the $b^4\Sigma_g^-$ state to the dissociation of O_2^+ . Although the $b^4\Sigma_g^-$ state is not dipole-coupled to the repulsive $f^4\Pi_g$ state, it is resonantly coupled to the $a^4\Pi_u$ state by a 800-nm photon. By taking into consideration the angle-dependent population redistribution between the $a^4\Pi_u$ and $b^4\Sigma_g^-$ states, Xue *et al.* can reproduce the energy-dependent structure and the quantum beat frequencies observed by De *et al.*⁶⁵, illustrating the importance of post-ionization population redistribution in understanding the dissociation dynamics.

In this work, we use a strong 800-nm pulse to ionize O_2 and then use a weak pulse (either 800 nm or 264 nm) to probe the wave packet that remains bound in excited cationic states. We measure the delay dependence of the momentum spectrum over multiple rotational peri-

ods, leading to a high-resolution QB spectrum using the Fourier transformation. Our results show a dominant contribution from rotational states of $b^4\Sigma_g^-$, corroborating the theoretical work by Xue *et al.*⁴. We also show the importance of the rovibrational excitation and the predissociation in determining the momentum spectrum of O^+ fragments.

5.2 Methodology

The experimental setup has been discussed in chapter 2 section 2.1.2 and is described only briefly here. We split the output of FLAME laser into the pump and the probe pulses, introduce a delay between the two, and recombine them on a dielectric beamsplitter. The probe pulse can either be the IR pulse or its third harmonic generated using BBO crystals. Both are then focused into a velocity map imaging (VMI) spectrometer⁷⁴ by a 20 cm focal length concave mirror. Both pulses have identical linear polarization, parallel to the detector plane. The pump has enough intensity ($\approx 3 \times 10^{14}$ W/cm²) to dissociate O_2 into O^+ , mostly from singly charged molecular ions. The probe is weaker (2×10^{13} W/cm² for 800 nm and 1.5×10^{12} W/cm² for 264 nm) and does not produce any O^+ signal. The laser pulses interact with rotationally cold molecules (estimated temperature is ≈ 2 K reported by Wangjam *et al.* in³) produced by supersonic expansion (0.5% O_2 in He at a total pressure of 900 psi) through an Even-Lavie valve¹⁶¹. The microchannel plate detector in the VMI spectrometer is gated to select O^+ ions, and the momentum distribution is recorded by imaging the phosphor screen with a 1000-fps camera and counting individual ion hits using a centroid-finding algorithm. The count rate of O^+ ions is kept at < 5 hits per shot to minimize detector saturation at small kinetic energy (KE). We vary the delay between the pump and the probe using a computer-controlled translation stage. In about 40 hours, we record 15 scans in total; each scan is 200 ps long with a step size of 50 fs (4000 delay points).

The data normalization and analysis done on the raw images is same as in chapter 4, and it well described there in section 4.3.

We use the Dunham expansion¹⁵⁴ with molecular constants from spectroscopic data^{10;162–168} to calculate the rotational energy levels and the Raman spectra (see Appendix A). We com-

pare the QB frequencies determined by the experiment with the expected positions of Raman lines to identify the rotational, vibronic, and electronic states involved in the dissociation dynamics. This data is provided in Appendix B.

5.3 Results and discussion: 800 nm Probe

5.3.1 Kinetic energy release

In this section, the probe pulse is ≈ 800 nm, 45 fs, 2×10^{13} W/cm² and the pump pulse is ≈ 800 nm, 40 fs, 3×10^{14} W/cm². Figure 5.1 shows the KER spectrum integrated over all delays from 1 to 198.95 ps after the pump-probe overlap. The energy calibration is in agreement with previous experiments^{65;160;169}. The high-energy O⁺ from the O₂ $\rightarrow$ O⁺+O⁺ channel (KER > 5 eV) does not show any quantum beats in the FFT spectrum, indicating that it originates from the interaction with the pump alone. This channel is not of interest here and will not be discussed further in this chapter. We focus our attention on two bands in the low-energy region — 0–250 meV and the 0.75–1.5 eV — where FFT spectra show bound wave packets. These regions are highlighted by colored vertical bands in the inset of Fig. 5.1.

5.3.2 The 0-250 meV band

The QB spectra of the 0-250 meV band are shown in Fig. 5.2, where panel (a) shows an FFT spectrum of the delay-dependent yield integrated over the range of KER from 0 to 130 meV. These spectra show that the delay dependence is dominated by $\nu = 4$ of the O₂⁺ $b^4\Sigma_g^-$ state, but weaker contributions from $\nu = 3$ can be identified as well. Importantly, there are no peaks that are not attributable to these two vibration states. This is in contrast with the assignment made by De *et al.*⁶⁵ in an experiment using 8-fs pump and probe pulses, where this energy range was assigned to vibrational levels of the O₂⁺ $a^4\Pi_u$ state. Please refer to Fig. 5.3 for a sketch of relevant potential energy curves.

Above-threshold (pre)dissociation of the *b* state

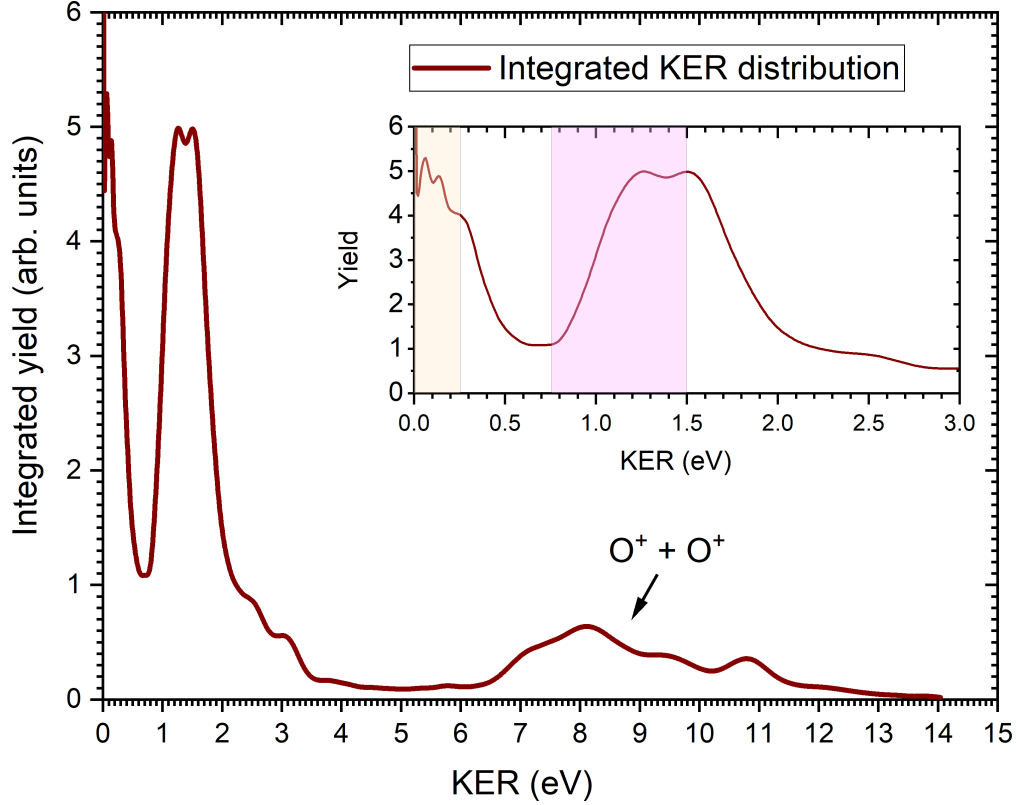


Figure 5.1: *KER spectrum integrated over all delays from 1 to 198.95 ps. The regions 0–250 meV and 0.75–1.5 eV, where FFT spectra show bound wave packets, are highlighted by colored vertical bands in the inset*

There are two states — $f^4\Pi_g$ and $d^4\Sigma_g^+$ — that predissociate the $b^4\Sigma_g^-$ state, where $\nu = 4, 5$ of b are predominantly predissociated by the d state, while $\nu = 6, 7$ are mixed, and $\nu \geq 8$ is predominantly predissociated via the f state¹⁶⁸. These states are not dipole-coupled to the b state. The predissociation is due mostly to the spin-orbit coupling between the states. The dissociation limit is just below $N = 9$ for $\nu = 4$ and $N = 31$ for $\nu = 3$ ¹⁶⁸ as marked in Fig. 5.2(a), respectively. Rotational levels $N \geq 9$ are expected to predissociate, with KERs determined by the energy molecules have in excess of the first dissociation limit which lies ≈ 2 meV below the $N = 9$. However, the observed KER-FFT spectrum cannot represent predissociation from these levels following their population by the pump pulse. To be seen in the FFT spectrum, the KER and/or angular distribution of the O^+ ions must be modulated by the probe pulse. Lines in the FFT spectrum show pump-excited coherences, while the KER distribution shows the energy after the probe.

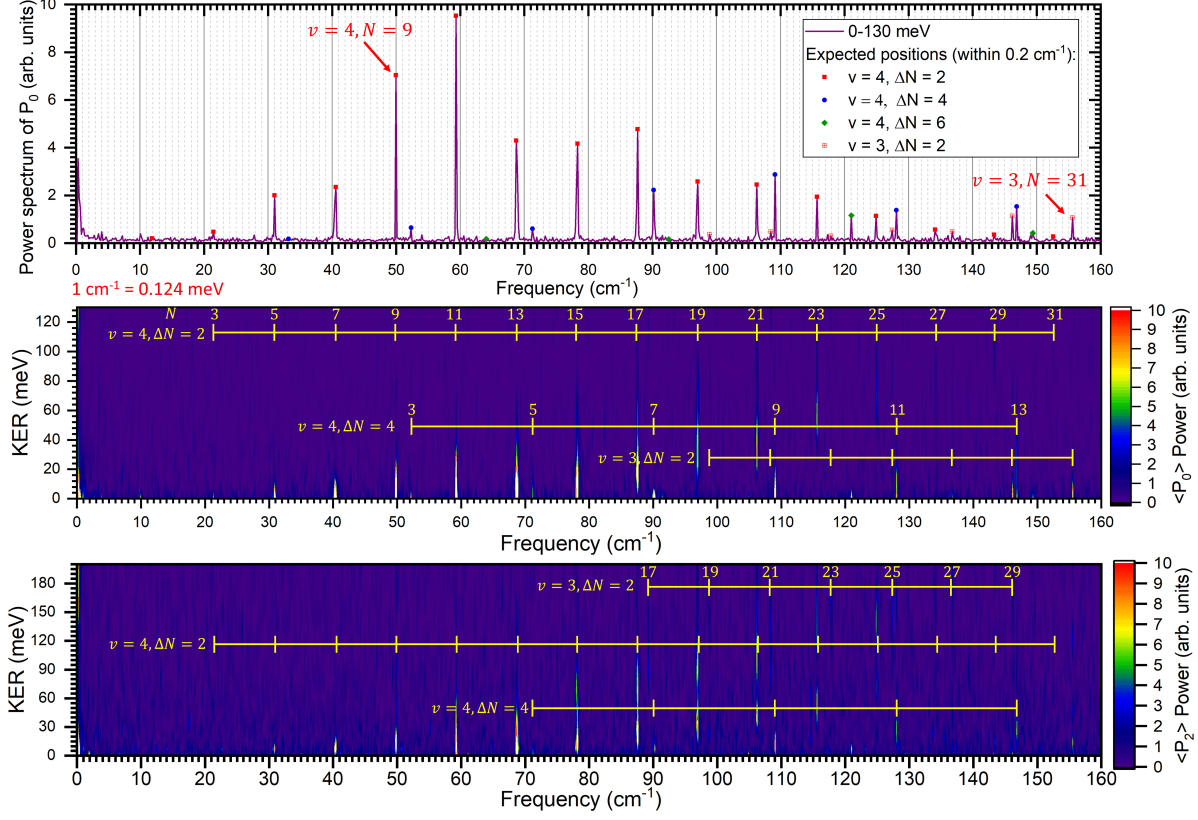


Figure 5.2: Quantum beat spectra of the 0-250 meV band. (a) Power spectrum of $\langle P_0 \rangle$ where the KER is integrated over the range of 0 to 130 meV. (b) Same as (a) but the KER is not integrated. (c) Same as (b) but for $\langle P_2 \rangle$. ν is the vibration quantum number, N is the rotational quantum number of the lower state, and ΔN indicates the transition of rotational states. The QB spectrum trends upwards in KER at higher N because the pump pulse excites molecules well past the threshold for predissociation (see Sec. 5.3.2 for more details and refer to Fig. 5.3 for a sketch of relevant potential energy curves).

The data shows a strong rotational excitation – a broad rotational wave packet up to $N = 31$ – by the pump pulse (note that the neutral ground state is predominantly $N = 1$ at $\approx 2 \text{ K}$ reported by Wangjam *et al.*³). Molecules in the $\text{O}_2^+ b^4\Sigma_g^-$ state absorb energy via multiple Raman cycles and ascend well past the threshold for predissociation at $\nu = 4, N = 9$ during the pump pulse. It is possible to observe this phenomenon in our experiments because predissociation of $\nu \leq 4$ is slow in this case. For example, the lifetime of $\nu = 4; N = 9$ is about 385-712 ps depending on the spin states¹⁷⁰.

The near zero KER in Fig. 5.2(b-c) suggests net-zero photon dissociation of the $\nu = 4$ state. The KER also increases with the initial N , showing the effect of rotational excita-

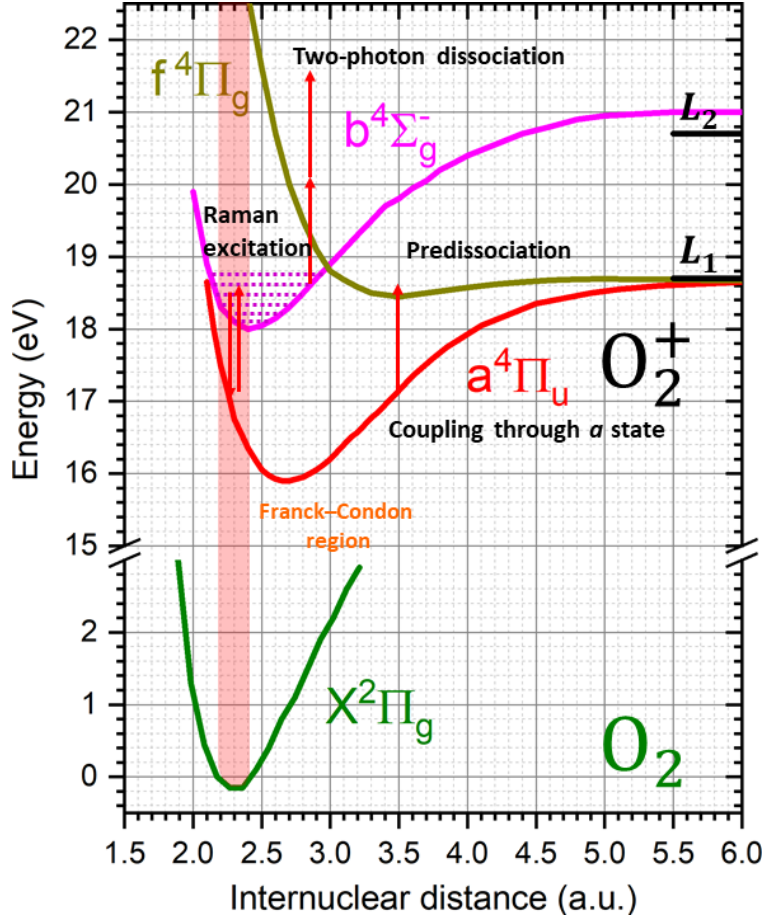


Figure 5.3: Sketch of relevant potential energy curves (adapted from Ref. ¹¹ and ⁴) for the dissociation of the $b^4\Sigma_g^-$ state. The pump excites a broad rotational wave packet in $O_2^+ b^4\Sigma_g^-$. This bound wave packet can then predissociate or dissociate by the probe via multiple pathways as discussed in Sec. 5.3.2.

tion on determining the final KER of the products. $\nu = 4$ lines extend to higher KER and show modulation. The long vertical tails suggest further rotational or rovibrational Raman excitation by the probe. This is because rovibrational Raman transitions to higher ν (by the probe) yield higher KER. These rovibrational Raman excitations are possible since vibrational spacings are ≈ 100 meV, comparable to the bandwidth of the laser of ≈ 120 meV.

The pump excites rotational coherences in $b^4\Sigma_g^-$ state for different ν levels, and the probe further “aligns” these molecules — exciting them to a higher N or v, N before the molecules predissociate into O^+ ions and neutral partners O. However we observed the $\nu = 3$ and $\nu = 4$ dominates the rotational lines in Fig. 5.2(b-c). This is because $b^4\Sigma_g^-$ state gets coupled to f

through a by two-photon Raman processes⁴. And when the two-photon coupling is resonant through the $a^4\Pi_u$ state there are enhancements for the specific vibrational levels ($\nu = 3$ and $\nu = 4$). The dissociation by two-photon coupling (one down, one up) will result in small KER values that increase with N observed in Fig. 5.2(b-c) as the QB spectrum ascends in KER with higher N . And the absence of $\nu = 5$ and above levels is because the pump starts to efficiently remove population from $b^4\Sigma_g^-$ $\nu \geq 5$ as there is no energy barrier to predissociate. With ≈ 60 ps lifetime even with pump efficiently removing population from $b^4\Sigma_g^-$ $\nu \geq 5$ it should have been visible in FFT, although the lines would be widened. Our 264 nm measurement shows that $\nu \geq 5$ does not survive after the pump in a state. In the experiment by De *et al.*⁶⁵ used 8 fs pulses for both pump and probe and the subsequent theoretical investigation of that experiment by Magrakvelidze *et al.*⁸⁷ also focused on ≤ 15 fs pulses, and included neither rotational motion nor predissociation of the $b^4\Sigma_g^-$.

Absence of the a state in the FFT spectrum

There is no clear signs of the $a^4\Pi_u$ state in our spectra. There can be two reasons why this is the case. The first possibility is that the pump already dissociates (or promotes to b) all a vibrational levels we can reach with our weak probe. The model by Xue *et al.*⁴ has already shown a significant population redistribution from the a state to the b state with a 15 fs pulse. Our pump pulse is longer (40 fs), and its intensity ($\approx 3 \times 10^{14}$ W/cm²) is also higher than the saturation intensity of the O⁺ component, estimated to be $\approx 2 \times 10^{14}$ W/cm² for a 100 fs pulse¹⁷¹. The second possibility is that the power spectrum of the a state is much more spread out. There are many more vibrational levels in $a^4\Pi_u$ that can contribute, and the rotational structure is more complex (Hund's case a).

Our data shows a weak but unidentified cluster of frequencies around 0.8 eV KER. Our result does not rule out the contribution of the a state, it may just not be detected in our measurement. We have evidence of $a^4\Pi_u$ state with the 264 nm probe and our data shows that $\nu \geq 5$ does not survive after the pump. That experiment will be discussed in the later section of this chapter.

Absence of other vibrational levels of the b state

With our ≈ 40 fs pulses, we expect less vibrational Raman excitation compared to the 8 fs

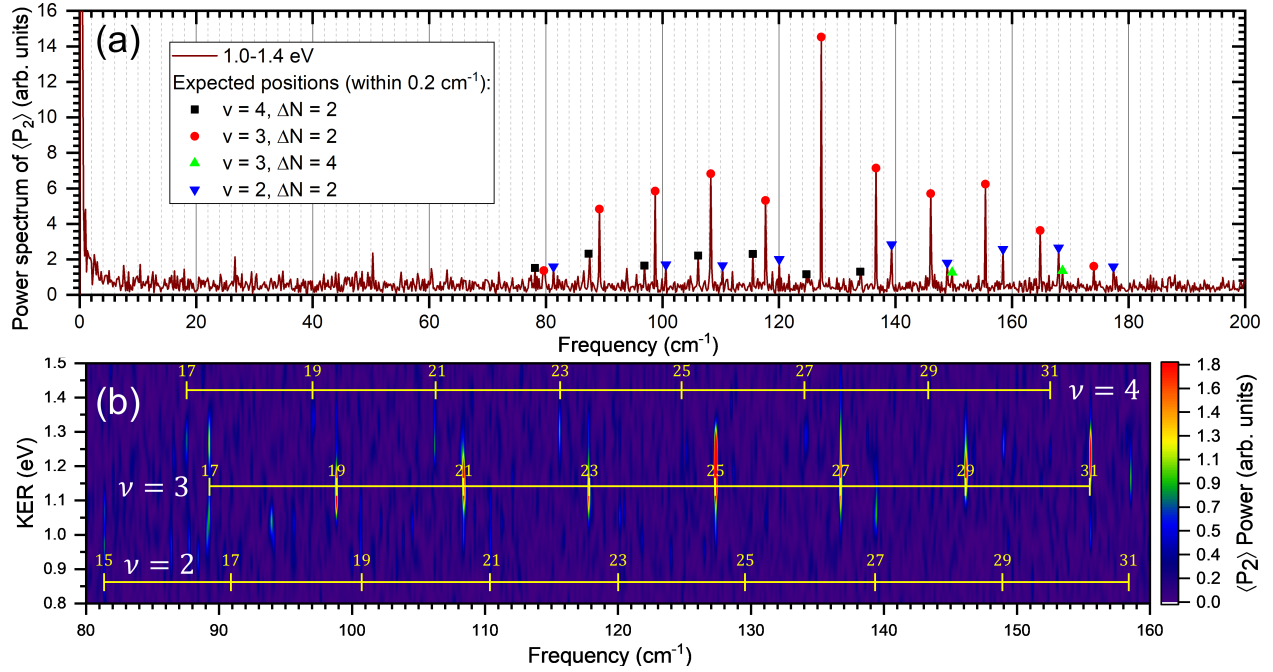


Figure 5.4: FFT spectra of the delay-dependent KER for $\langle P_2 \rangle$ of the high energy band (0.75-1.5 eV). In panel (a), the KER is integrated over the range of 1.0 to 1.4 eV. In panel (b), the KER is not integrated. The dominant channel is $\nu = 3$, channels $\nu = 4$ and $\nu = 2$ are weaker. In this case, the $b^4\Sigma_g^-$ state absorbs two photons and dissociate into the second dissociation limit.

pulses used by De *et al.*⁶⁵. Moreover, the predissociation lifetimes of high-lying vibrational levels of the b state ($\nu \geq 5$) are significantly shorter than $\nu = 4$ ¹⁶⁵. For example, the lifetime of $\nu = 5, N = 5$ is about 66 – 137 ps¹⁷⁰ and the lifetime of $\nu = 6, N = 5$ is about 5 times shorter compared to $\nu = 5, N = 5$ ¹⁶⁵. Molecules excited to $\nu > 4$ will predissociate rapidly and do not survive long enough to show up in our FFT spectra measured over 200 ps. On the other hand, $\nu < 3$ states do not predissociate. They also cannot dissociate by coupling to $f^4\Pi_g$ through $a^4\Pi_u$ with two 800-nm photons (one down, one up). They can absorb two photon and dissociate to the second dissociation limit as described in Fig. 5.3 and discussed in Sec. 5.3.3.

5.3.3 The 0.75-1.5 eV band

Fig. 5.4 shows FFT spectra of the delay-dependent KER for $\langle P_2 \rangle$ of the high energy band (0.75-1.5 eV). In panel (a), the KER is integrated over the range of 1.0 to 1.4 eV. In panel (b), the KER is not integrated. We can identify frequencies corresponding to $\nu = 2-4$ of the b state, where $\nu = 3$ has a dominant contribution, and $\nu = 4$ has higher KER at about 1.3 eV. As expected, the KER increases with ν while frequency decreases.

There is only one clearly identifiable peak (at 127.3 cm⁻¹) in the $\langle P_0 \rangle$ (yield) FFT. $\langle P_0 \rangle$ can be more sensitive to the experimental fluctuations, and the structure may be buried in noise since shot noise in the (dominant) probe-only signal appears as white noise in the FFT spectrum.

Potential pathway

X , a , d and f states all correlate to $O^+(^4S) + O(^3P)$, the lowest energy asymptote. The next asymptote is $O^+(^3S) + O(^1D)$, which is 1.97 eV higher¹⁷². There are five states (apart from b ; all quartet: $1^4\Sigma_u^-$, $2^4\Pi_g$, $1^4\Delta_g$, $2^4\Pi_u$, $1^4\Delta_u$)¹⁴ that correlate to the second asymptote. Three of them ($1^4\Sigma_u^-$, $2^4\Pi_u$, $1^4\Delta_u$) are ungerade and cannot be reached by two-photon transitions from b . $2^4\Pi_g$ is energetically ruled out. Only the $1^4\Delta_g$ remains as a candidate.

With 800 nm (1.55 eV photons), two-photon absorption from $v = 4$ followed by dissocia-

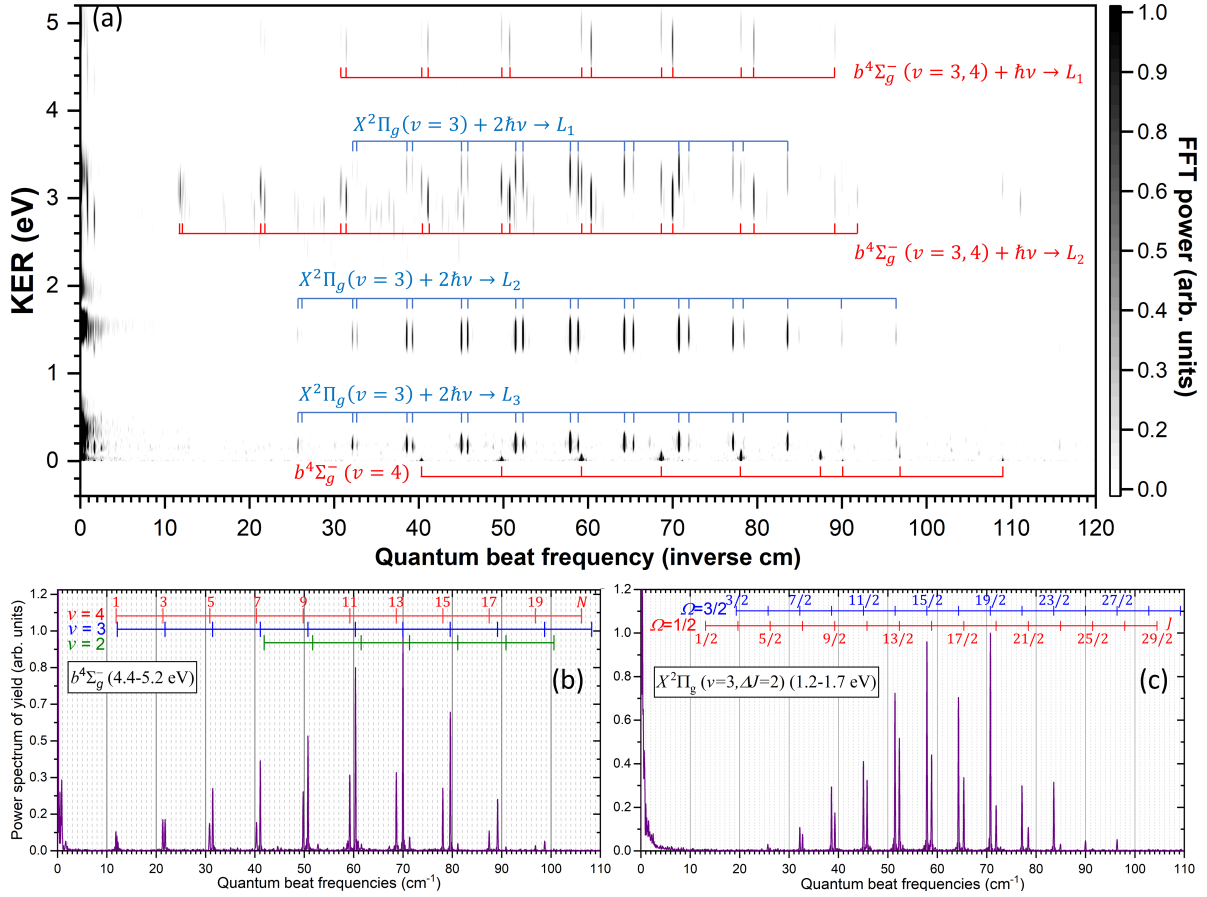


Figure 5.5: (a) FFT spectra of the delay-dependent KER for $\langle P_0 \rangle$ in the IR-UV pump-probe experiment. Panel (b) shows the FFT spectrum of the $b^4\Sigma_g^-$ state dissociated into the first dissociation limit (L_1) after absorbing one UV photon (the KER is integrated over the range of 4.8 to 5.4 eV). Panel (c) shows the FFT spectrum of the $X^2\Pi_g$ state dissociated into the first dissociation limit (L_1) after absorbing two UV photons. The KER is integrated over the range of 1.3 to 1.8 eV. The expected positions of Raman lines corresponding to $\Delta N = 2$ are shown above the spectra in (b) and (c). For $b^4\Sigma_g^-$, only odd N is allowed while for $X^2\Pi_g$, both odd and even N are allowed. See Sec. 5.4 for more details.

tion to this higher limit would result in slightly above 1.1 eV KER¹⁷². $\nu = 3$ and lower will have correspondingly lower KER. This can be the pathway producing the high energy band O^+ observed in our measurement.

5.4 Results and discussions: 264 nm probe

5.4.1 Multiple states can be observed in the KER-FFT spectrum with the third harmonic probe

In this section, the third harmonic of the fundamental (≈ 264 nm, 1.5 TW/cm², 120 fs), generated by using BBO crystals, is used as the probe pulse. The intensity of this UV probe is kept low such that no ionization of O_2 is observed with the probe alone. There is no resonant coupling between $a^4\Pi_u$ and $b^4\Sigma_g^-$ states with this probe pulse. The pump has similar intensity but a shorter duration compared to the previous section (≈ 800 nm, 3×10^{14} W/cm², ≈ 30 fs). The dissociation of $b^4\Sigma_g^-$ and $X^2\Pi_g$ states into multiple asymptotes can be observed in the KER-FFT spectrum in Fig. 5.5 and is discussed in detail below.

5.4.2 $b^4\Sigma_g^-(v = 3, 4)$ state

Using the third-harmonic probe, as seen in Fig. 5.5(a), the $b^4\Sigma_g^-$ state is ionized by one UV photon and dissociated into the first dissociation limit (L_1) (near 5 eV KER) and the second dissociation limit (L_2) (near 3.2 eV KER). The net-zero photon mechanisms via predissociation or coupling to f through a of the $b^4\Sigma_g^-(v = 3, 4)$ state are also observed (near zero KER). Fig. 5.5(b) shows the FFT spectrum of the yield for dissociation of $b^4\Sigma_g^-$ into L_1 since it is energetically separated from other channels. The frequencies are in excellent agreement with the expected Raman lines. $b^4\Sigma_g^- v = 3$ and $v = 4$ show up in measurements using both IR and third-harmonic probes, suggesting that they are efficiently populated by the pump and play important roles in the strong-field induced wave packet dynamics of O_2^+ . We also observe a weak signal from $\nu = 2$.

From potential energy curves calculated by Liu *et al.*¹⁴, only the $a^4\Pi_u$ state appears as a potential candidate for the dissociation pathway of $b^4\Sigma_g^-$ into L_1 [$O^+(^4S) + O(^3P)$, the lowest energy asymptote] following strict dipole selection rules. $c^4\Sigma_u^-$ and $2^4\Pi_u$ satisfy the selection rules to be potential candidates for dissociation of $b^4\Sigma_g^-$ into the second asymptote L_2 [$O^+(^4S) + O(^1D^0)$]. However, $c^4\Sigma_u^-$ is energetically unlikely, so $2^4\Pi_u$ would be the main candidate.

5.4.3 $X^2\Pi_g$ state

In Fig. 5.5(a), the bound wave packet in the ground state $X^2\Pi_g$ of O_2^+ can be observed via two-photon dissociation into the first three dissociation limits: L_1 (near 3.4 eV KER), L_2 (near 1.5 eV KER) and L_3 (near zero KER). The vibration level $v = 3$ dominates all channels. Why $X^2\Pi_g(v = 3)$ is dominant? According to the reference data provided by Krupenie¹¹ (page 472), there is a resonance between $X^2\Pi_g(v = 3)$ and $A^2\Pi_u(v = 4)$ of O_2^+ at 264.67 nm (as described in Fig. 5.6), and our probe spectrum is centered at 264 nm. Thus we see 1+1 resonance-enhanced multiphoton dissociation probe of the $X^2\Pi_g(v = 3)$ state of O_2^+ . Fig. 5.5(c) shows the FFT spectrum of the $X^2\Pi_g(v = 3) + 2h\nu \rightarrow L_2$ channel. Only frequencies corresponding to $\Delta N = 2$ are observed in the FFT spectrum of the yield suggests the absorption of the first UV photon may be the rate-determining step.

From potential energy curves calculated by Liu *et al.*¹⁴, only the $1^2\Sigma_g^+$ can be the candidate for dissociation of $X^2\Pi_g(v = 3)$ into L_1 . Similarly, $B^2\Sigma_g^-$ is the only candidate for dissociation of $X^2\Pi_g(v = 3)$ into L_3 [$O^+(^2D^0) + O(^3P)$]. No state has been identified as a potential pathway for dissociation into L_2 [$O^+(^4S) + O(^1D^0)$] following strict dipole selection rules since all states with this asymptote are quartet states.

We will take a closer look at $X^2\Pi_g(v = 3)$ dissociated into L_2 (near 1.5 eV KER) since it is separated in energy from other channels. The time-dependent yield of this channel as shown in Fig. 5.7 is complicated and nonperiodic without any regular revival structures. As discussed in chapter 4 section 4.4.5 the rotational wave packet on $X^2\Pi_g$ is perturbed by spin-orbit coupling. The frequencies are in good agreement with the expected positions of

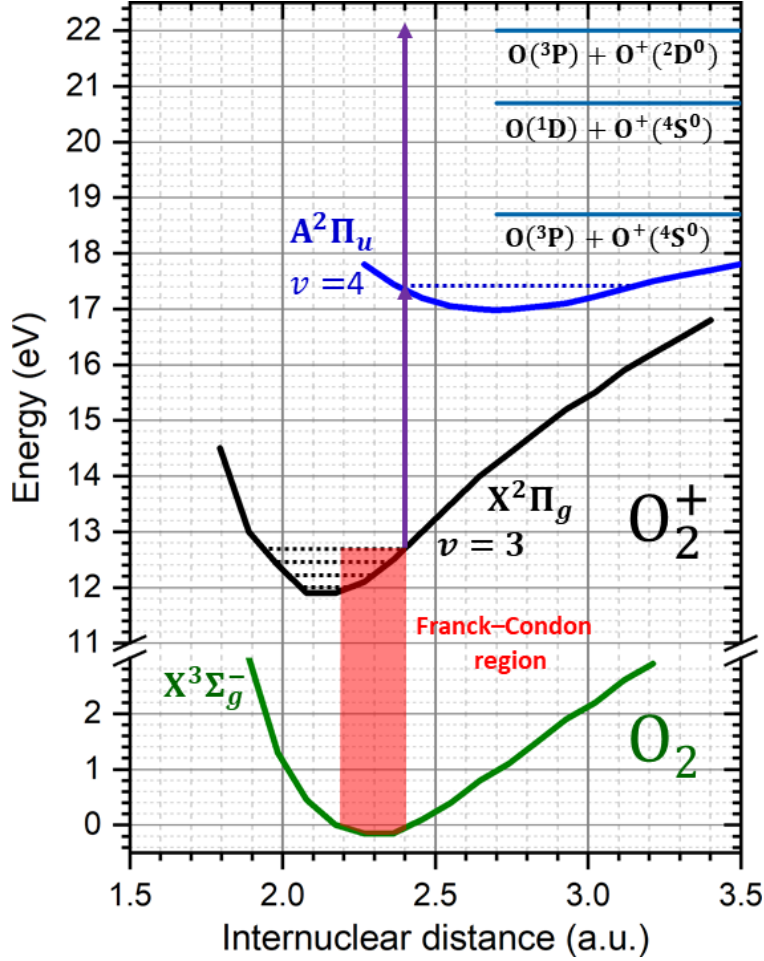


Figure 5.6: Sketch of relevant potential energy curves for the dissociation of the $X^2\Pi_g$ state. The potential curves are adapted from Ref.¹¹. The pump excites a rotational wave packet on $O_2^+ X^2\Pi_g$ state. This wave packet absorbs two UV probe photons and dissociates into different dissociation limits. The A-X transition is resonant with our probe wavelength at 264 nm. See Sec. 5.4.3 for more details.

Raman lines. We also do not observe any significant coherences between F_1 and F_2 states. Almost all transitions are purely rotational transitions.

Note that, in the case of $X^2\Pi_g$, frequencies corresponding to both odd and even N show up in the FFT spectra [see Fig. 5.5(c)]. Approximately, this can be interpreted as a consequence of the Λ -doubling effect¹⁷³ where the coupling between rotation with electronic angular momentum splits the $\Lambda \neq 0$ term into two nearby levels. However, for homonuclear diatomic molecules, only one of these two levels is allowed due to symmetry restriction. In our case of $^{16}O_2^+$, Bose-Einstein statistics requires the wave function of each level to be

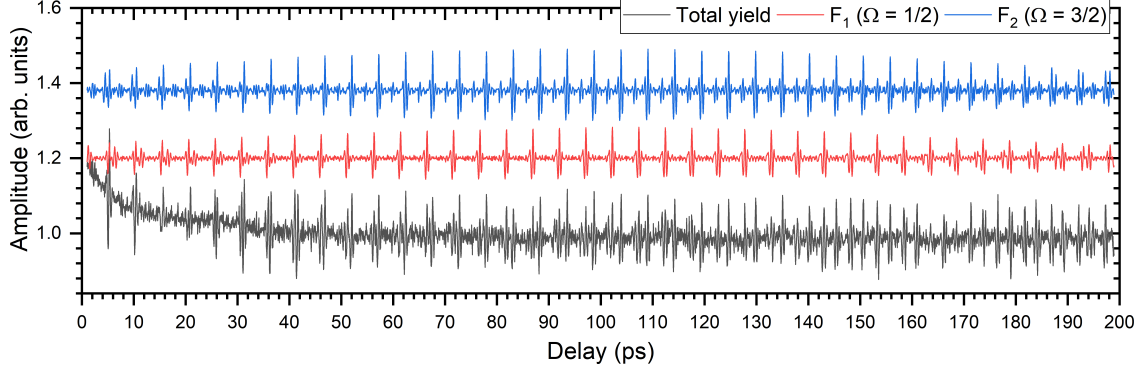


Figure 5.7: Due to the spin-orbit coupling, the time-dependent yield of $X^2\Pi_g(v = 3)$ dissociated into L_2 channel (integrating KER range from 1.3 eV to 1.8 eV) (black, bottom) is complicated and nonperiodic without any regular revival structures. Filtering in the frequency domain shows different time evolution of F_1 and F_2 series. The $\Omega = 3/2$ (blue, top) exhibits clear quarter revivals while it is not clear the $\Omega = 1/2$ (red, middle). The F_1 and F_2 curves are shifted up for clarity.

symmetric with respect to inversion through the center of the molecule since ^{16}O has a nuclear spin $I = 0$ ¹⁶⁶, hence, levels that are anti-symmetric with respect to inversion are absent. This Λ -doubling effect is not observed in the $b^4\Sigma_g^-$ state of O_2^+ and the ground state $^3\Sigma_g^-$ of O_2 ³ since $\Lambda = 0$ for these states.

The couplings between spin and other motions are typically not observed in the ground states of neutral molecules since the total spin is usually zero. Examples where these couplings were observed in gas phase diatomic molecules are the doublet ground state of NO ⁵⁴ and the triplet ground state of O_2 ³. However, these couplings are crucial in determining the dynamics of excited and ionic states of molecules with higher spin multiplicity¹⁷⁴.

5.4.4 $a^4\Pi_u$ to $f^4\Pi_g$ transition

In the following Fig. 5.8 (a) we have shown the logscale KER-FFT yield with KER range of 2-3.4 eV. Our 4000-point, 50-fs step-size scan provides sufficient resolution to identify coherences by vibrational and fine structure states. As mentioned above, the pump efficiently dissociates higher vibrational levels of the $a^4\Pi_u$ state and we can only discern up to $v = 4$ in the data. We also find that the FFT spectrum has significant contributions only from $\Omega = 1/2$ and $3/2$ with values of J that are an odd integer $\pm 1/2$ even though all half-integer

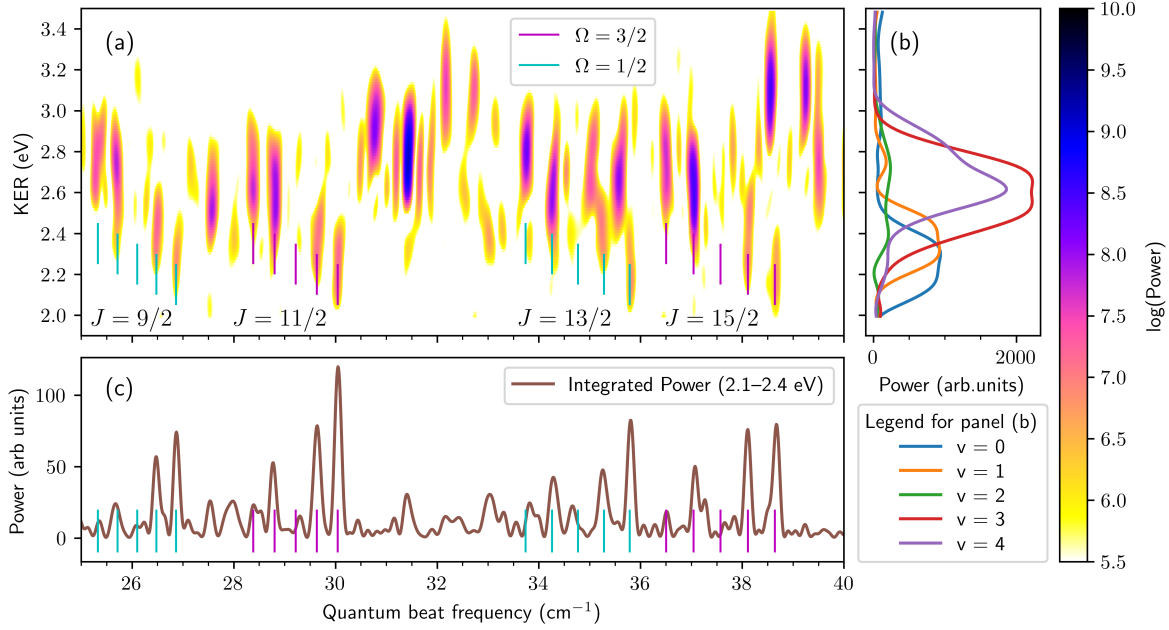


Figure 5.8: (a) A portion of the frequency-KER data selected to highlight the single-photon dissociation of the $a^4\Pi_u$ state of O_2^+ by 264-nm pulses. Stick spectra show the expected location of $v = 0-5$, $\Delta J = 2$, $\Delta\Omega = 0$ Raman lines in the $\Omega = 1/2$ and $\Omega = 3/2$ fine-structure levels. The signal visible between approximately 28 cm^{-1} and 31 cm^{-1} shows the typical dependence of KER on the vibrational level—internuclear distance increases with vibrational quantum number v due to the anharmonicity of the potential, which results in quantum beat frequencies decreasing with v . The absence of $v = 2$ is immediately evident. The same pattern of four vertical lines repeats for different values of J' and Ω , four of which are highlighted by the stick spectra. (b) KER spectra integrated over quantum beat frequency for $v = 0-4$ for the lines identified by $J' = 11/2$ (magenta, on the left) stick spectrum. In each case a width of 0.2 cm^{-1} was used, with the center located at the calculated frequency of the quantum beat. (c) QB spectrum integrated from 2.1 to 2.4 eV, with the range selected to highlight $v = 0$ and $v = 1$.

values are allowed by nuclear spin statistics¹⁶². The likely reason for the absent J values is that the $a^4\Pi_u$ state is populated by the removal of a π electron from the $X^3\Sigma_g^-$ ground state of the neutral, where only odd values of rotational angular momentum quantum number N are allowed (see, for instance,³). Furthermore, we do not observe any coherences between different fine structure states, which would be expected around 50 and 100 cm^{-1} for $\Delta\Omega = 1$ and $\Delta\Omega = 2$, respectively. For these reasons, what could have been a highly congested FFT spectrum is greatly simplified and regular and repeating patterns of four lines can easily be identified. We calculate the expected positions of quantum beats originating in the $a^4\Pi_u$

state, using spectroscopic data from¹⁶², for some of the stick spectrum shown in Fig. 5.8(b) to help identify the relevant peaks.

Only the vibrational Cooper minimum⁵ at $v = 2$ is apparent in the FFT data, but this minimum can be identified multiple locations since it is repeated both for different rotational coherences and for different fine-structure components. The widths of lines corresponding to $v = 0, 1, 3$ and 4 are narrow enough that there's essentially no overlap with expected locations of the $v = 2$ lines. Fig. 5.8(b) and (c) show projections along the frequency and KER axes (figure caption for details), respectively, highlighting the usefulness of FFT spectroscopy in separating contributions that overlap in KER.

5.5 Conclusion

Our experiment shows clear evidence of the residual ionic wave packet in the $b^4\Sigma_g^-$ state, predominantly in the $\nu = 3$ and $\nu = 4$ levels with both IR and UV probe pulses. The similarity in appearance of the $b^4\Sigma_g^-$ state quantum beat spectra with two different probes confirms the resonant coupling between $b^4\Sigma_g^-$ and $a^4\Pi_u$ induced by the 800-nm pump. On the other hand, the dominance of the $X^2\Pi_g(v = 3)$ state shows the importance of resonant coupling in the UV probe pulse. In almost all cases, we can identify unique potential pathways leading to dissociation. Our experiment also reveals the importance of rovibrational excitation and predissociation in determining the momentum spectrum of the O^+ fragments. This provides valuable insights into the laser-induced dissociation of O_2^+ ^{65;87;91;94;160;169;175–178} and strongly supports the three-state model by Xue *et al.*⁴.

We observe a very broad rotational wave packet in the $b^4\Sigma_g^-$ state. It can be owing to a strong population redistribution into the $b^4\Sigma_g^-$ state. We do see weak evidence of wave packet in the $a^4\Pi_u$ state but can be seen only in the log-scale and we found in the rotational spectrum of the $a^4\Pi_u$ there are different vibrational level from $v = 0$ up to $v = 4$ present with the absence of $v = 2$ and the vanishing $v = 2$ is due to the presence of vibrational cooper minimum⁵, hence confirming the presence of the photo-dissociation from $a^4\Pi_u$ to $f^4\Pi_g$ in 264 nm.

The rotational spectra that we observe are strikingly clean and simple, even for a diatomic molecule. The long-scan FFT spectroscopy with a “weak” probe pulse does not expose to short-lived states (e.g., all vibrational levels of the B state that have predissociation lifetimes of ≈ 1 ps) and deeply-bound long-lived states (e.g., the ground state is too deeply bound for IR probe). It can expose to long-lived states within a photon (or two) of a dissociation limit (selection rules permitting). As the anharmonicity of the potential energy curves (or surfaces) increases, the spectra will be more complicated, making it more difficult to identify states. However, at least for diatomic molecules, we believe that high-resolution Fourier spectra obtained from this type of measurement (can be with different pump-probe wavelengths) will allow unambiguous identification of the electronic, vibrational and rotational states, providing valuable insights into the laser-induced dynamics of the molecular cations.

Chapter 6

Work in Progress : Probing Light-Induced Potential in D_2^+

We study the bound wave packet launched by an ionizing 30 fs, 800 nm pulse in the ground state of D_2^+ by using a lower intensity pulse to dissociate the ion. The momentum distribution of D^+ ions is measured using a velocity map imaging spectrometer. A long delay scan provides enough resolution in the rotational quantum beat spectrum that we can unambiguously separate contributions from vibrational levels between $v=4$ to $v=10$. By filtering the momentum spectra in the Fourier domain, we reconstruct momentum distributions from either a single vibrational state or even from a single rotational coherence. These spectra provide us the opportunity to investigate the passage of coherently-prepared D_2^+ ions through light-induced conical intersections between light-dressed $1s\sigma_g$ and $2p\sigma_u$ states.

6.1 Introduction

In the Born-Oppenheimer Approximation (BOA) regime, nuclear motion is assumed to be slow compared to the electronic motion, which allows electronic states to be written separately. Each of the potential energy curves (PECS) generated with BOA is the solution of the electronic part of the Schrödinger's equation with a fixed nuclear position. This is

always not the case : when two or more PECS are very close or have similar energies then, the BOA is not a good approximation anymore and it breaks down completely when the energies are the same. At this point where the energies are similar, there is non-adiabatic coupling leading to radiationless transitions from one electronic state to another. However, in a diatomic molecule if the electronic states are of the same symmetry it forms avoided crossing because of the no-crossing rule. In polyatomic molecules (molecules with three or more atoms), this site is also known as a conical intersection¹⁷⁹.

Conical intersections¹⁷⁹ are very common occurrences in state dynamics of polyatomic molecules¹⁸⁰. The significance of conical intersections emerges in the interaction between an electronically excited state and the ground state within a molecule, particularly in processes involving radiationless deexcitation. A noteworthy example is the stability of DNA under UV radiation^{35,36}, wherein the swift transfer of population from excited states to the ground state occurs efficiently through conical intersections. Also, studies have shown evidence of conical intersection dynamics playing a role in photo-isomerization, which is an important event in the preliminary process of vision³⁷.

In this chapter, we will be using a deuterium molecular ion which is the most elementary molecular system with two atoms and an electron. Due to the simplicity of the deuterium molecule, this investigation can be carried out considering only two potential curves $1s\sigma_g$ and $2p\sigma_u$ states in Fig. 6.1(b) in the absence laser field as other potential curves are far away. Now in the presence of an intense field, the coupling between the electronic states and the light becomes significant leading to the formation of light-induced potential and it is denoted by n in $|g, n\rangle$, where $n - 1$ expressed as absorption of a photon of light. When the dressed electronic states of two same symmetry overlap potential curves, for example, the $|g, n\rangle$ and the $|u, n - 1\rangle$ there is avoided crossing giving us the picture shown in Fig. 6.1(b). However, if we consider the rotational degree of freedom for a diatomic in the presence of light, suddenly we have two degrees of freedom R : the inter-nuclear axis and θ : the angle between the Laser polarization and the inter-nuclear axis. Now this creates a site called light-induced conical intersection (LICI) at $\theta = \pm\frac{\pi}{2}$ in the potential surface whereas $\theta = 0$ is where the adiabatic dynamics prevail (see Fig. 6.1(a)).

Theoretical studies done by G. J Halász *et al.*¹⁸¹ have predicted that the photo-dissociation process of D_2^+ provides a direct signature of LICI which can be found in the angular distribution of the photo-fragments. According to the study, if the population transfer takes place via the LICI, photo-dissociation of D_2^+ around $\theta = \pm\frac{\pi}{2}$ there will be 0. Another study was done by A. Natan *et al.*¹² has shown experimentally and also simulated this signature effect in the angular distribution of the photo-fragments around LICI of H_2^+ . Both studies only explain the phenomena using only one initial rotational state ($J = 0$) however, we know that this is not the case in most experiments. Here we will explore this feature experimentally by preparing a coherent rotational wavepacket as our initial states.

Our goal is to investigate the strong-field-induced rotational wavepackets around the region where BOA breakdown occurs and look for anomalous behavior in the time-dependent momentum distribution for a single rotational coherence. In regions of the potential characterized by these features, slight alterations in nuclear geometry can lead to notable shifts in the electronic wave function's character. From a time-domain standpoint, this implies that electronic dynamics progress on a timescale close to nuclear dynamics when the energies of electronic states converge in the crossing region of potential energy surfaces. In the following sections, we will show that we have successfully prepared coherent rotational wavepackets around the LICI region of the potential energy curves and show the momentum distribution reconstructed from a single rotational coherence which should contain characteristics of LICI.

6.2 Methodology

The strong-field induced coherent rotational wavepackets on the ground state $1s\sigma_g$ of D_2^+ are prepared using 30 fs, 800 nm with 500 TW/cm² pump after ionizing the cold D_2 (~ 10 K) from Even-Lavie valve delivered using 300 psi pure bottle and a relatively weak probe with 10 TW/cm² dissociates D_2 to D^+ and D neutral. Similar to the previous experiments shown in chapter 4 and 5, we used the same experimental setup and data acquisition machinery for this experiment. We maintained ~ 10 counts per shot of D^+ as detected by the camera

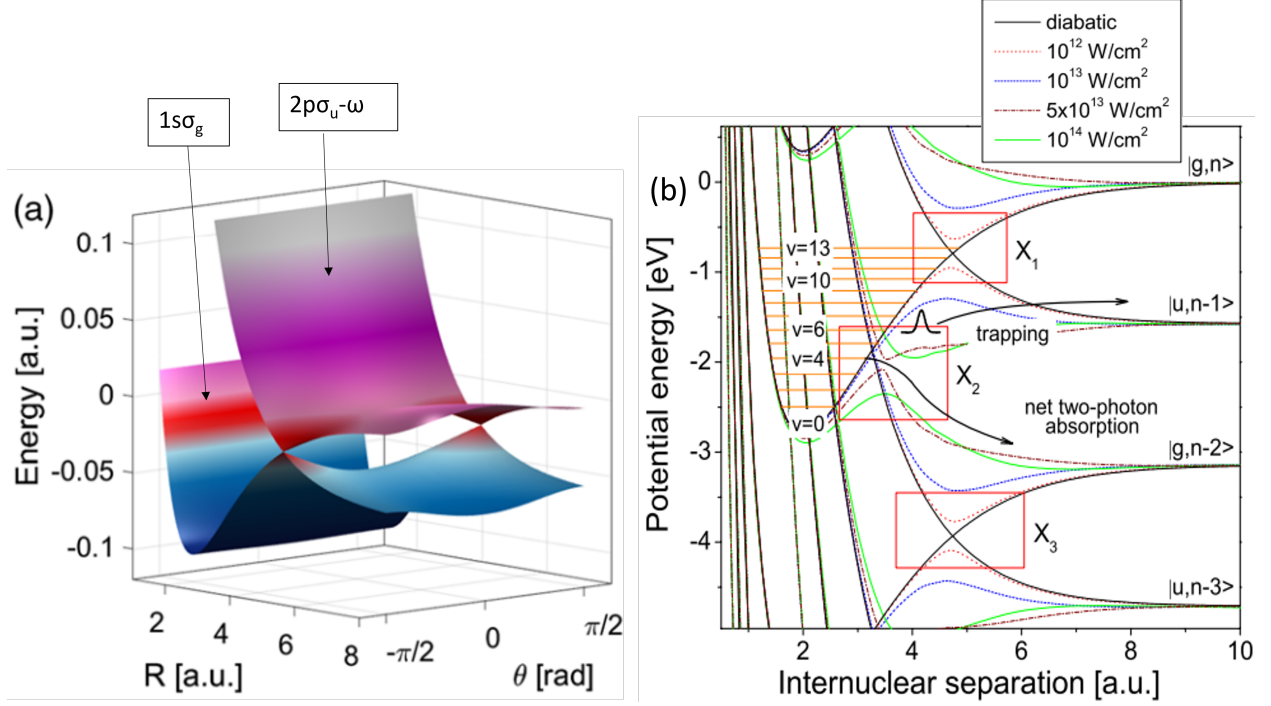


Figure 6.1: (a) 2D surface potential of H_2^+ adopted from work done by A. Natan et al.¹² (b) Relevant light-induced potential energy of D_2^+ adopted from thesis of D. Pavičić's thesis¹³. In panel (a), the potential is generated using the light-induced adiabatic coupling term which contains both the angle θ which is the angle between the polarization axis and the inter-nuclear distance and the coupling strength which is determined by the electric field strength and the dipole value at the inter-nuclear distance. In panel (b), the generated plots are for different electric field strengths as shown in the legend and the dipole value at the inter-nuclear distance only but the angle is fixed with $\theta = 0$.

and it is determined by the intensity of the pump laser. With these statistics, we acquired 50 scans for about 2 days each with a delay step size of 20 fs and each scan was set up for 2000 points/scan.

The data acquired is analyzed with the same procedure of normalization as shown in chapter 4 and 5 for every delay and perform inverse Abel transformation using pBasex to convert 2D projections to 3D distributions as both the pulses are linearly polarized parallel to the plane of the detector. Fig. 6.2(a) shows the image of the delay-integrated yield of D^+ which shows a faint outer channel which is coming from the coulomb explosion creating $D^+ + D^+$ and the Fig. 6.2(b) highlights the region of interest for this experiment with a 1D KER plot which is obtained by angle and delay integration of the analyzed images. In

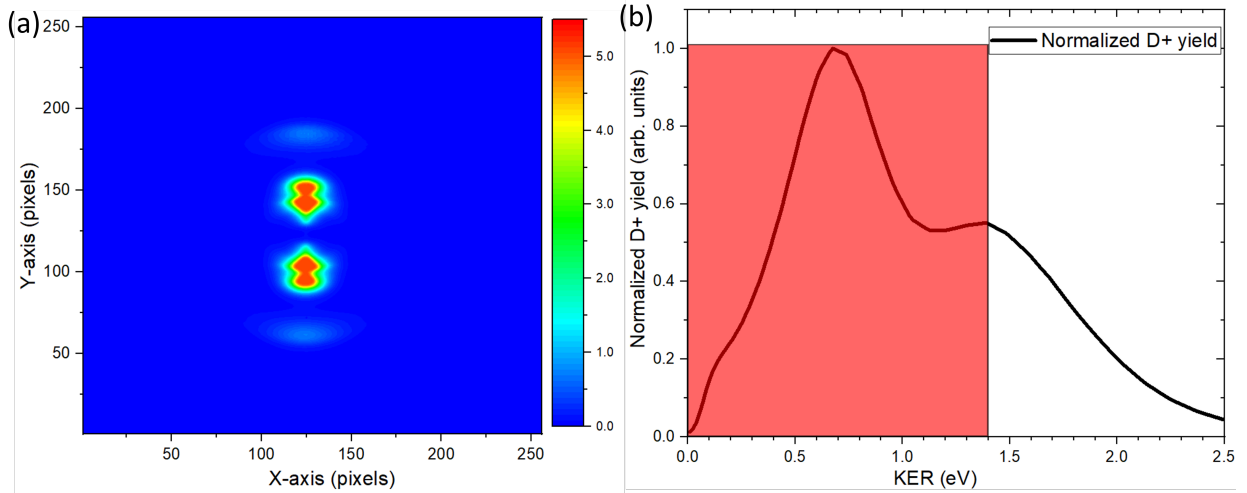


Figure 6.2: (a) Delay-integrated VMI image of D^+ photo-fragments (b) Angle and delay-integrated KER distribution of D^+ photo-fragments

the next section, we will find out that the high energy part in Fig. 6.2(b) doesn't have any rotational coherence as it only comes from the pump-only and probe-only signal is suppressed hence it appears at zero frequency. For this chapter, we want to reconstruct the momentum distribution D^+ acquired by filtering a particular rotational coherence in the frequency domain and inverse FFT it into the time domain to look at the effects of rotational coherence going through LICl. We restrict the basis function expansion up to $L = 8$ in Abel inverse transform as the delay-dependent data becomes noisy for anything coefficient after $L = 8$. Except for the reconstruction, all the steps leading up to frequency filtering and applying inverse FFT remain the same. Similarly, we will use the information encapsulated by the rotational coherence to figure out which vibrational level (v) of the $1s\sigma_g$ state it is coming from by comparing the power spectrum of the coefficients $L = 0$ (see Fig. 6.3) and the rotational quantum beats acquired from Hunter *et al.*¹⁸². The data observed from the 2D KER-FFT plot of $L = 0$ Fig. 6.3 has dense spectrum spread over the KER we are interested in so to identify which range of KER contains which vibrational levels we divide KER into 0.2 eV range and look into the rotational Raman spectrum¹⁸² and compare it with the QB at the data, each coherence peak is detected using a peak finding routine with a threshold with normalized intensity to the maximum peak for each

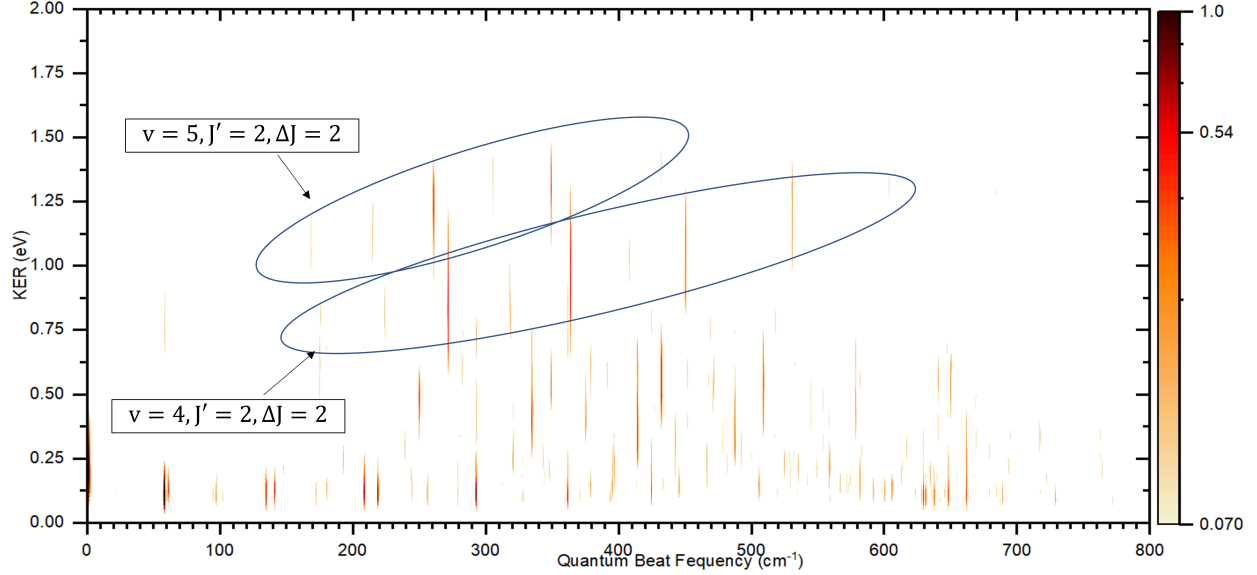


Figure 6.3: 2D KER-FFT plot of $L = 0$ coefficients from the VMI images of D^+ photo-fragments showing QB frequencies in different vibrational levels of Duetrium molecular ion. In this yield KER-FFT plot, we can already identify the different vibrational levels of $1\sigma_g$.

KER range. This procedure is carried out for each range and we identified each vibrational levels μ using the $\Delta J = 2$ peaks with experimental peak. Once the identification is done to generate Fig. ?? we binned the number of rotational coherence occurred in each KER range, any bin frequency less than 4 is not considered as the rotational coherence is less reliable.

Furthermore, we have attempted to propagate the error estimates using the error estimates acquired from the pBasex coefficients. We will generate many momentum distributions by doing a Monte Carlo sampling assuming a standard Gaussian distribution and using the mean and standard deviation acquired from the pBasex coefficients in the previous step described in [152](#). We will estimate the standard deviation for each pixel and plot the signal-to-noise ratio as a test for the reliability of the reconstructed distributions.

6.3 Summary

In conclusion, the rotational coherences induced by the pump can isolate specific vibrational states using a long delay scan, which provides sufficient frequency resolution to uniquely

identify them. This enables the observation of the one-photon and net-two photo-dissociation processes, which happen in a light-induced potential, particularly near $v=4, 5$ and $8, 9, 10$. Additionally, the momentum distribution of the two-state rotational coherence is observed, and we see the quantum beat of the $\Delta J = 2$ coherence. However the quality of experimental data is needs to be improved for this work as the delay dependent data was noisy and to reach our goal of studying light induced potential we will need a cleaner dataset.

Chapter 7

Summary and outlook

In this dissertation, we aimed to investigate various processes induced by a strong field and ask if we can understand, and explore new physics using the tools at our hand. Overall we have modified, developed, and taken advantage of the already existing tools to probe ultrafast molecular motion both in time, frequency, and energy spectroscopy. We have used orientation-resolved rotational coherent spectroscopy (ORRCS) and updated our new version of it which works with spin-coupled rotational wavepackets. In our case, the tools that provided insights into both frequency and kinetic energy released were the combination of velocity-mapped imaging (VMI) spectroscopy with coherently excited rotational wavepackets.

Starting with the investigation of strong-field ionization of ground-state molecular Oxygen where we observed anomalous behavior in the molecular alignment. Eventually, after analyzing both the time-domain and frequency-domain measurement we found the reason is that oxygen has a triplet ground state, its nuclear rotational angular momentum is coupled to its electronic spin angular momentum, and the spins of the two unpaired electrons are also coupled. Due to these couplings, the alignment pulse excites both rotation and spin dynamics in oxygen molecules. The rotational wave packet is no longer purely rotational, and the delay-dependent ionization yield is non-periodic.

We have already demonstrated that these measurements provide not only spectroscopic

insights into the states coherently populated by the pump pulse but also contribute to characterizing the interaction between the molecule and the probe pulse. Following this idea, we also wanted to look at the spin-rotational wavepackets in ionic states of N_2^+ , O_2^+ and D_2^+ with different goals in mind. The motivation behind initially conducting measurements on the spin-rotational ionic wavepackets of O_2^+ stemmed from the potential to gain substantial insights into the intricate chemical pathways described by Xue *et al.* We confirm the resonant coupling between b $^4\Sigma_g^-$ and a $^4\Pi_u$ states induced by the 800 nm pump and also point out the significance of resonant transition during the probe step in a photodissociation process.

For N_2^+ , initially we wanted to probe the low-lying ionic states (X $^2\Sigma_g^+$, A $^2\Pi_u$ and B $^2\Sigma_u^+$) involved in the strong-field induced air-lasing process to gain insight into the process and chemical pathways involved. Our observation indicates that the intermediate resonant transition significantly shapes the type of transition observed, acting as a rate-limiting step. Similarly, the pivotal significance of the resonant transition during the probe step in a photodissociation process is highlighted again for the N_2^+ . Overall we found evidence of an intriguing dissociative pathway triggered by strong-field ionization (SFI) and a resonant probe, leading to stimulated emission and photodissociation for the low-lying ionic states of N_2^+ .

Finally, we have investigated the light-induced conical intersection between light-dressed $1s\sigma_g$ and $2p\sigma_u$ states of D_2^+ using this technique. Our aim for this experiment was to look for the direct signature of LICI predicted by G. J Halász *et al.*¹⁸¹ and measured by A. Natan *et al.*¹². We expect to observe new physics in this experiment as both the previous studies were done with the ground rotational states as the only initial rotational state leaving the rotational wavepackets involved purely thermal. However, in our experiment, we have a coherently prepared rotational wavepacket as the initial rotational wavepacket which is driven by the strong field of the intense laser. Our analysis was able to produce the momentum distribution of the D^+ for a specific rotational coherence, hence measuring the momentum distribution coming from a two-state rotational state which was impulsively prepared by the laser.

From our demonstration, we have realized that it would be an interesting measurement to

look at the photoelectron phase from a spin-rotation excited wavepacket using Reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) as it can provide useful insights into the effect of nuclear coupling during a photoionization process.

This technique has allowed us to point out electronic states which are overlapped in energy with minimal theoretical support, and eventually deduce the chemical pathways involved in the low-lying ionic states. Therefore, we believe this technique to impulsively excite rotational wavepackets in combination with a kinetic energy release can be useful in isolating molecular motion in large molecules. This can be done by doing three pulse experiments where a UV pump excites the molecule to a specific potential surface preferably with a single photon and then uses a second IR pump to align it in the electronic state then finally probing it with another UV pulse which would preferably be a single photon probe to photodissociate into the photoproducts. This type of measurement should provide us with a very specific signal corresponding to the electronic states coming from the rotational states hence making the analysis easier with more information from the experimental side, especially for big molecules that can have multiple electronic states.

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Appendix A

Calculation of rotational energy levels

Spectroscopic constants for Dunham equations are provided in work done by Dunham¹⁵⁴. We calculate the rotational Raman lines as the following,

$$\begin{aligned}\Delta E_{N,M} &= B_v[N(N+1) - M(M+1)] \\ &\quad - D_v[(N(N+1))^2 - (M(M+1))^2],\end{aligned}\tag{A.1}$$

the rotational constant is defined as $B_v = B_e - \alpha_e(v + \frac{1}{2})$ and the centrifugal distortion constant as $D_v = D_e + \beta_e(v + \frac{1}{2})$. The subscript e means it is measured at the equilibrium position of the cation, and the α_e and β_e are the first-order corrections in the Dunham equation. Here, N and M represent the rotational energy levels for the calculated Raman lines, and v represents the vibrational energy level. However, the energy equations from which the A $^2\Pi_u$ (see 4.4.2) and $X^2\Pi_g$ (see 5.4.3) state Raman lines are calculated as the following⁸¹,

$$\begin{aligned}E_{\Pi_{1/2}}(J) &= B \left[\left(J + \frac{1}{2}\right)^2 - 1 + \frac{1}{2}X(J) \right] - D \left(J + \frac{1}{2}\right)^2 \\ &\quad \left[\left(J + \frac{1}{2}\right)^2 + 1 + \frac{4(J + \frac{1}{2})}{X(J)} \cdot \left(\left(J + \frac{1}{2}\right) - \frac{Y(J)}{2(J + \frac{1}{2})} \right) \right],\end{aligned}\tag{A.2}$$

$$E_{\Pi_{3/2}}(J) = B \left[\left(J + \frac{1}{2}\right)^2 - 1 - \frac{1}{2}X(J) \right] - D \left(J + \frac{1}{2}\right)^2 \left[\left(J + \frac{1}{2}\right)^2 + 1 - \frac{4(J + \frac{1}{2})}{X(J)} \cdot \left(\left(J + \frac{1}{2}\right) - \frac{Y(J)}{2(J + \frac{1}{2})} \right) \right], \quad (\text{A.3})$$

$$Y(J) = \frac{(A + A_D(J + \frac{1}{2})^2)}{B} \quad (\text{A.4a})$$

$$X(J) = 4 \left(J + \frac{1}{2}\right)^2 + ((Y(J))^2 - 4) \quad (\text{A.4b})$$

The $A \ ^2\Pi_u$ state needs a particular treatment as the spin-orbit coupling comes into play; further discussion will be in the section 4.4.2. The rotational, centrifugal, spin-orbit, and centrifugal distortion spin-orbit constants (B , D , A , and A_D respectively) are taken from Klynning *et al.*¹⁸³. Unlike the Dunham equation constants, these constants are for a particular vibrational level.

For the case of $b^4\Sigma_g^-$ state, the quartet nature of the $b^4\Sigma_g^-$ state can be ignored for our experimental resolution ($< 0.169 \text{ cm}^{-1}$) since the spin-spin and spin-rotation constants are small ($\leq 0.14 \text{ cm}^{-1}$)¹⁶². These constants for $b^4\Sigma_g^-$ have been measured^{11;162–164;167}. Higher order corrections have been ignored, see section 5.4.2.

For the $X^2\Pi_g$ state, beside the rotational constant B_ν and the centrifugal distortion D_ν , the spin-orbit coupling constant A_ν is included. The spin-rotation coupling constant and the Λ -doubling constants (p_ν and q_ν) are small and not included. However, we still observe the consequence of the spin-rotation coupling as discussed in Sec. 5.4.3. The mentioned constants are provided by the table IV in the work done by Coxon and Haley¹⁶⁶. The rotation energy levels of the $X^2\Pi_g$ state are then determined by

$$E_{vJ}^\mp = B_\nu(J_p^2 - 1 \pm 0.5X_\nu) - D_\nu J_p^2(J_p^2 + 1 \pm (4J_p/X_\nu)(J_p - Y_\nu/2J_p)), \quad (\text{A.5})$$

where $Y_\nu = A_\nu/B_\nu$, $X_\nu = \sqrt{4J_p^2 + Y_\nu(Y_\nu - 4)}$ and A_ν is the spin-orbit coupling constant.

Appendix B

List of calculated and experimentally observed rotational lines

The rotational lines used in identifying the experimental lines observed and the lines detected by the used of peak finding algorithm in the experimental data is compared in the following tables. The frequencies are in cm^{-1} .

B $^2\Sigma_u^+$								
–	$\nu = 4$		$\nu = 4$		$\nu = 5$		$\nu = 6$	
–	$\Delta J = 2$		$\Delta J = 4$		$\Delta J = 2$		$\Delta J = 2$	
J	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
0	11.83	11.80	39.43	–	11.63	–	11.41	11.42
1	19.71	19.65	55.20	–	19.39	19.06	19.02	19.03
2	27.60	27.59	70.97	–	27.14	–	26.63	26.63
3	35.49	35.48	86.75	86.74	34.90	34.51	34.23	34.24
4	43.37	43.40	102.52	102.50	42.65	–	41.84	41.86
5	51.26	51.24	118.29	118.22	50.41	50.25	49.45	49.46
6	59.15	59.14	134.06	134.62	58.16	58.07	57.06	57.07
7	67.03	67.02	149.84	149.72	65.92	65.86	64.67	64.65
8	74.92	74.95	165.61	–	73.67	73.65	72.27	72.25
9	82.80	82.71	181.38	–	81.43	81.45	79.88	79.82
10	90.69	90.67	108.22	–	89.18	89.22	87.49	87.41
11	98.58	98.48	117.72	–	96.93	96.98	95.10	95.00
12	106.46	106.39	127.19	–	104.69	104.72	102.71	102.55
13	114.35	–	136.63	–	112.44	112.42	110.31	110.11
14	122.23	122.53	146.03	–	120.20	119.89	117.92	–
15	130.12	–	155.40	–	127.95	127.64	125.53	–
16	138.01	–	164.72	–	135.71	135.37	133.14	–
17	145.89	–	174.00	–	143.46	143.07	140.75	–

Table B.1: Calculated and measured rotational quantum beats for the $B^2\Sigma_u^+$ state (KER is integrated over the range of 200 to 270 meV for $\nu = 4$, 600 to 700 meV for $\nu = 5$ and 850 to 1000 meV for $\nu = 6$). This data is discussed in Sec. 4.4.1.

$X^2\Sigma_g^+$		
–	$\nu = 1$	
–	$\Delta J = 2$	
J	Calc.	Expt.
0	11.4204	11.4163
1	19.0336	19.0258
2	26.646	26.6332
3	34.2575	34.2451
4	41.8676	41.8576
5	49.4762	49.4578
6	57.0829	57.0689
7	64.6875	64.654
8	72.2896	72.2525
9	79.889	79.8249
10	87.4854	87.4124
11	95.0785	95.0015
12	102.668	102.553
13	110.254	110.117
14	110.254	–
15	125.412	–
16	132.985	–
17	132.985	–

Table B.2: *Calculated and measured rotational quantum beats for the $X^2\Sigma_g^+$ state (KER is integrated over the range of 850 to 1000 meV for $\nu = 1$). This data is discussed in Sec. [4.4.3](#).*

$A^2\Pi_u, \nu = 4$						
–	$\Omega = 1/2, \Delta N = 2$			$\Omega = 3/2, \Delta N = 2$		
J	N	Calc.	Expt.	N	Calc.	Expt.
1/2	1	13.56	13.59	2	19.49	19.49
1 1/2	1	20.33	20.35	3	25.99	25.99
2 1/2	2	27.10	27.10	4	32.49	32.48
3 1/2	3	33.87	33.94	5	38.99	38.98
4 1/2	4	40.64	40.68	6	45.50	45.50
5 1/2	5	47.39	47.40	7	52.01	52.01
6 1/2	6	54.14	54.14	8	58.52	58.51
7 1/2	7	60.89	60.91	9	65.03	65.03
8 1/2	8	67.62	67.63	10	71.54	71.54
9 1/2	9	74.35	74.34	11	78.06	78.06
10 1/2	10	81.07	81.09	12	84.58	84.57
11 1/2	11	87.78	87.76	13	91.10	91.09
12 1/2	12	94.49	94.49	14	97.62	97.62
13 1/2	13	101.18	101.16	15	104.15	104.14
14 1/2	14	107.86	107.87	16	110.67	110.66
15 1/2	15	114.54	–	17	117.19	117.17
16 1/2	16	121.20	–	18	123.72	123.69

Table B.3: *Calculated and measured rotational quantum beats for the $A^2\Pi_u(\nu = 4)$ state. The KER is integrated over the range of 1.8 to 2.2 eV. This data is discussed in Sec. [4.4.2](#).*

$b^4\Sigma_g^-$						
–	$\nu = 4$					
N	$\Delta N = 2$	Expt.	$\Delta N = 4$	Expt.	$\Delta N = 6$	Expt.
1	11.87	–	33.23	–	64.08	–
3	21.36	21.30	52.21	52.17	92.53	–
5	30.85	30.81	71.17	71.16	120.97	120.90
7	40.33	10.33	90.12	90.10	149.37	149.28
9	49.79	49.77	109.04	108.98	177.73	177.65
11	59.25	59.22	127.93	127.88	206.04	–
13	68.69	68.65	146.79	–	–	–
15	78.11	78.06	165.61	–	–	–
17	87.51	87.46	184.39	–	–	–
19	96.88	96.83	203.11	–	$\nu = 3, \Delta N = 2$	
21	106.23	106.18	221.79	–	108.22	108.24
23	115.55	115.50	240.40	–	117.72	117.77
25	124.84	124.79	258.95	–	127.19	127.25
27	134.10	134.01	277.43	–	136.63	136.70
29	152.51	143.25	295.83	–	146.03	146.05
31				–	155.40	155.46
33				–	164.72	164.80

Table B.4: Calculated and measured rotational quantum beats for the $b^4\Sigma_g^-$ state (KER is integrated over the range of 0 to 130 meV). This data is discussed in Sec. 5.3.2.

$b^4\Sigma_g^-$								
–	$\nu = 2$		$\nu = 3$		$\nu = 3$		$\nu = 4$	
–	$\Delta N = 2$		$\Delta N = 2$		$\Delta N = 4$		$\Delta N = 2$	
N	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
1	12.32	–	12.09	–	33.85	–	11.87	–
3	22.17	–	21.76	–	53.18	–	21.36	–
5	32.02	–	31.42	–	72.49	–	30.85	–
7	41.86	–	41.07	–	91.79	–	40.33	–
9	51.69	–	50.72	–	111.07	–	49.79	–
11	61.50	–	60.35	–	130.31	–	59.25	–
13	71.30	–	69.96	–	149.53	149.72	68.69	–
15	81.09	81.32	79.56	79.64	168.70	168.67	78.11	78.13
17	90.85	90.84	89.14	89.20	187.83	–	87.51	87.35
19	100.59	100.60	98.69	98.75	206.91	–	96.88	96.91
21	110.31	110.32	108.22	108.31	225.94	–	106.23	106.13
23	120.00	120.04	117.72	117.70	244.91	–	115.55	115.52
25	129.66	–	127.19	127.25		–	124.84	124.74
27	139.28	139.33	136.63	136.64		–	134.10	133.96
29	148.88	148.88	146.03	146.03		–	143.32	–
31	158.43	158.44	155.40	155.42		–	152.51	–
33	167.95	168.00	164.72	164.81		–	161.65	–
35	177.43	177.38	174.00	174.03		–	170.75	–

Table B.5: Calculated and measured rotational quantum beats for the $b^4\Sigma_g^-$ state dissociated into the first dissociation limit (L_1). The KER is integrated over the range of 4.8 to 5.4 eV. This data is discussed in Sec. 5.3.3.

$b^4\Sigma_g^-, \Delta N = 2$								
–	$\nu = 2$		$\nu = 3$		$\nu = 4$		$\nu = 5$	
N	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
1	12.32	–	12.09	12.04	11.87	11.81	11.63	11.59
3	22.17	–	21.76	21.78	21.36	21.33	20.93	20.93
5	32.02	–	31.42	31.43	30.85	30.79	30.22	30.17
7	41.86	–	41.07	41.09	40.33	40.31	39.51	39.50
9	51.69	–	50.72	50.73	49.79	49.77	48.78	48.68
11	61.50	61.59	60.35	60.37	59.25	59.21	58.05	57.98
13	71.30	71.34	69.96	69.99	68.69	68.64	67.29	67.25
15	81.09	81.12	79.56	79.58	78.11	78.06	76.52	–
17	90.85	90.82	89.14	89.17	87.51	87.45	85.72	–
19	100.59	–	98.69	98.73	96.88	96.86	94.91	–

Table B.6: Calculated and measured rotational quantum beats for the $b^4\Sigma_g^-$ state dissociated into the first dissociation limit (L_1). The KER is integrated over the range of 4.8 to 5.4 eV. This data is discussed in Sec. 5.4.2.

$X^2\Pi_g, \nu = 3$						
–	$\Omega = 1/2, \Delta N = 2$			$\Omega = 3/2, \Delta N = 2$		
J	N	Calc.	Expt.	N	Calc.	Expt.
1/2	1	13.08	–	2	19.30	–
1 1/2	1	19.62	–	3	25.73	25.70
2 1/2	2	26.16	26.14	4	32.16	32.16
3 1/2	3	32.70	32.71	5	38.59	38.57
4 1/2	4	39.24	39.25	6	45.02	45.04
5 1/2	5	45.77	45.78	7	51.45	51.42
6 1/2	6	52.30	52.31	8	57.87	57.88
7 1/2	7	58.83	58.84	9	64.30	64.29
8 1/2	8	65.36	65.35	10	70.72	70.73
9 1/2	9	71.88	71.90	11	77.14	77.13
10 1/2	10	78.40	78.84	12	83.56	83.56
11 1/2	11	84.92	84.94	13	89.97	89.99
12 1/2	12	91.43	91.48	14	96.38	96.38
13 1/2	13	97.94	97.89	15	102.79	102.83

Table B.7: Calculated and measured rotational quantum beats for the $X^2\Pi_g(\nu = 1)$ state dissociating into L_2 . The KER is integrated over the range of 1.3 to 1.8 eV. This data is discussed in Sec. 5.4.3.

Appendix C

List of dissociation limits for N_2^+ and O_2^+

Lowest dissociation limits relevant to our measurements for N_2^+ dissociating to N^+ and N .

<i>Limits</i>	state of fragments	Dissociation energy (eV)
L1	$^3P(\text{N}^+) + ^4S_0(\text{N})$	24.293
L2	$^1D(\text{N}^+) + ^4S_0(\text{N})$	26.192
L3	$^3P(\text{N}^+) + ^2D_0(\text{N})$	26.676
L4	$^3P(\text{N}^+) + ^2p_0(\text{N})$	27.869
L5	$^1S(\text{N}^+) + ^4S_0(\text{N})$	28.345
L6	$^1D(\text{N}^+) + ^2D_0(\text{N})$	28.575
L7	$^1D(\text{N}^+) + ^2p_0(\text{N})$	29.768
L8	$^1S(\text{N}^+) + ^2D_0(\text{N})$	30.728
L9	$^1S(\text{N}^+) + ^2p_0(\text{N})$	31.921

Table C.1: *Dissociation energies for the lowest ten dissociation limits of N_2^+ . All energies are measured with respect to $X^1\Sigma_g^+ v = 0$ state (N_2 ground state). This table is adapted from Aoto et al.⁹*

Lowest dissociation limits relevant to our measurements for O_2^+ dissociating to O^+ and O .

<i>Limits</i>	state of fragments	Dissociation energy (eV)
L1	$^4S_u(O^+) + ^3P_g(O)$	0
L2	$^4S_u(O^+) + ^1D_g(O)$	1.96736
L3	$^2D_u(O^+) + ^3P_g(O)$	3.32408

Table C.2: *Dissociation energies for the lowest three dissociation limits of O_2^+ . All energies are measured with respect to lowest dissociation limit L1 of O_2^+ . This table is adapted from Liu et al.*¹⁴