

NORTHWESTERN UNIVERSITY

Applications of Quantum Control of Diatomic Molecular Ions

A DISSERTATION

SUBMITTED TO THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

for the degree

DOCTOR OF PHILOSOPHY

Applied Physics

By

Sruthi Venkataramanababu

EVANSTON, ILLINOIS

June 2022

© Copyright by Sruthi Venkataramanababu 2022

All Rights Reserved

ABSTRACT

The last two decades have seen tremendous growth in the development of techniques for molecular state control. The goal of achieving complete control over the quantum states of a molecule is motivated by a plethora of applications ranging from many-body physics to precise tests of fundamental physics. The level of control required for such applications involves state-preparation of molecules not just in their ground rotational states but also in any quantum state of choice. Also important is to be able to sustain them for a duration long enough to probe them, and to re-prepare the molecules quickly.

This thesis presents a glimpse into the applications of molecular ion quantum control and for this purpose, our molecule of choice is SiO^+ (Silicon monoxide cation). I start off with the description of a technique to pump SiO^+ to a narrow distribution of rotational states ($\Delta N=2$) around a target state of choice.

Following that, I discuss the spectroscopy of SiO^+ at and beyond equilibrium bond lengths as the first application of molecular quantum control. To measure the constants of molecular Hamiltonian at energies far from equilibrium bond-lengths, the molecules were pumped to and sustained at high rotational energies. State detection was carried out via the $C^2\Pi$ state, which was discovered and characterized simultaneously.

Another interesting application of molecular quantum control is to study and control chemical reactions at the quantum level. With the ability to sustain molecular control over a long period of time, we were able to study the reaction of SiO^+ with H_2 as a function of the rotational states of SiO^+ . We discovered that rotation of the SiO^+ molecules increases the rate of its reaction with H_2 . These results were supported by calculations from Prof. Hua Guo and Prof. Anyang Li.

In the remainder of the thesis, I talk about the progress towards non-destructive state detection of SiO^+ . For this purpose, we performed double resonance spectroscopy and determined the line positions of $R(0)$ and $P(1)$ transitions on $|X, v = 0\rangle \rightarrow |B, v = 0\rangle$ with an accuracy of $\sim 50\text{MHz}$. Attempts to detect fluorescence were, however, not successful. Nevertheless, the determination of line positions sets the path for using fluorescence as state detection and Doppler cooling of SiO^+ in the future.

I conclude the thesis with a quick discussion of another prospective application of molecular quantum control in the form of blackbody thermometry and the potential of SiO^+ for such a measurement.

ACKNOWLEDGEMENTS

My experience in the lab and at Northwestern University has been very rewarding both academically and personally.

I am grateful to Brian for taking me on as a PhD student. I have received valuable suggestions from him on all aspects of my work and he has always put his best efforts to ensure we had all the resources we could ever need in the lab. Above all, I have only ever seen him with a bright smile and optimism - even during difficult times.

Apart from Brian, my scientific development in graduate school has largely come from interactions with Ivan and Pat. They had a wealth of scientific experience between them that it even seemed scary many-a-times to think about how much they knew. Their complementary areas of expertise covered several aspects of the experiment. They kept me on my toes and constantly learning and I am glad to have worked with them during my PhD.

I would also like to thank other members of the Odom lab whom I have overlapped with over the years - James, Skye, Panpan, Jiafeng, Qiming, Greg, Carissa, and Joseph. In particular, I am grateful to James for taking care of the laser farm, and data servers in addition to his own graduate research; he also deserves a big shout-out for his determination to keep the tradition of “Burrito-Thursdays” going despite the fact that we are the only ones in the lab now.

I am also thankful to all the staff in the applied physics and physics business offices - in particular Clarence and Laura. They have in so many ways, small and big, supported us in what we do.

I must thank my parents, K Venkataramanababu and Latha Babu. They sacrificed several personal and material comforts to provide me with good education and access to

opportunities, believed in me, prayed for my well-being, and are my strongest pillars of support.

I met Nitin in the first few weeks of coming to Northwestern. In these 5 years, we have gone from being mere acquaintances to being married. A PhD student himself, and often the wiser one among the two of us, he has stood firmly by me during difficult times. He also had the insight of bringing our dog Nishu into our lives (despite my reluctance) and I am so glad he did, because our lives have become richer with her presence.

I am grateful to Kannan Ramaswamy - professor and mentor during my undergrad. He guided me on every step of my way to Northwestern. I continue to rely on him for advice from career choices to personal relationships. Souri Banerjee, also a professor during undergrad, has sincerely cared for my academic progress and personal growth since the day I met him and he has always pushed me to do well in my chosen path. I cannot thank them enough for everything they have done for me.

Anirudh and I have known each other since the first year of our undergrad and he is someone in whom I have confided my fears while also equally sharing my happiness and success. I am glad he chose to come to Northwestern University for his PhD and I hope that our lives will cross paths once again. I will cherish the times when Jovan and I just dropped into each other's offices to chat, grabbed lunch together or went to get a hot-chocolate. His cheerfulness and optimism can lift anyone's spirits. I enjoyed working with Ali in the applied physics graduate student council, admired her leadership skills, and learned a lot from her.

I was fortunate to have experienced a good social life during grad school and it had a significant and positive impact on my academic progress. I had a lot of fun hanging out with Shweta, Nikhil, Namratha, Hari, Rajita, Krithika, and Phalguni. A warm hug to you all for the amazing memories.

ABBREVIATIONS

A list of abbreviations used in the thesis is collected here for quick reference.

AMO - Atomic, Molecular and Optical

AOM - Acousto-Optic Modulator

BBO - Beta Barium Borate

BBR - Blackbody Radiation

CW - Continuous Wave

DCS - Differential Cross Section

DPSS - Diode Pumped Solid State Laser

ECDL - External Cavity Diode Laser

FCF - Franck Condon Factor

LBO - Lithium triborate

LCFMS - Laser Cooled Fluorescence Mass Spectrometry

LIF - Laser Induced Fluorescence

OPO - Optical Parametric Oscillator

PES - Potential Energy Surface

PMT - Photomultiplier Tube

QLS - Quantum Logic Spectroscopy

RF - Radio Frequency

SiO⁺ - Silicon Monoxide cation

SNR - Signal to Noise Ratio

SVD - Singular Value Decomposition

SVP - Sudden Vector Projection

TDC - Time to Digital Converter

UHV - Ultra High Vacuum

UV - Ultra-violet

YAG - Yttrium Aluminum Garnett

Dedicated to Jayanth anna who was the first person to tell me, when I was in 8th grade,
that I must do a Ph.D in physical sciences.

TABLE OF CONTENTS

Acknowledgments	4
Abbreviations	7
List of Figures	15
List of Tables	22
Chapter 1: Introduction to Quantum State-Control in Diatomic Molecules .	23
1.1 Quantum control of diatomic molecules	23
1.2 Techniques for molecular quantum control	24
1.3 Requirements for optical pumping of molecular ions	25
1.3.1 Born-Oppenheimer approximation	25
1.3.1.1 Franck Condon factor	25
1.3.1.2 Rotational fine-structure	27
1.3.1.3 Presence and role of low-lying states	30
1.3.1.4 Miscellaneous and nice-to-have properties	31
1.4 Background review of studies on SiO^+	33

	11
1.4.1 Experimental and Theoretical studies on SiO^+	34
1.5 Organization of the thesis	35
Chapter 2: Experimental Methods	36
2.1 Introduction	36
2.2 Loading ions into the trap	36
2.2.1 Loading lasers	38
2.2.2 Doppler cooling and sympathetic cooling	38
2.2.2.1 Doppler cooling of Ba^+	38
2.2.2.2 Sympathetic cooling of SiO^+	41
2.3 Detection	41
2.4 Rotational state control	43
2.4.1 Setup for rotational control	44
2.4.1.1 Optical pumping to ground rotational state	45
2.4.1.2 Optical pumping to a target rotational state	49
2.4.1.3 Pumping to extremely high rotational states	50
2.5 Probing	52
2.5.1 Lasers used	52
2.5.1.1 Survey spectroscopy:	52
2.5.1.2 Rotational line resolution:	52
2.5.1.3 High-resolution spectroscopy	54

	12
2.6 Timing Control	56
Chapter 3: Dissociation Spectroscopy - at and beyond equilibrium bond lengths	57
3.1 Introduction	57
3.2 Dissociation spectroscopy on the X-C transition	59
3.2.1 Single frequency LCFMS for dissociation	61
3.3 Low - resolution vibrational spectroscopy	62
3.4 Resolution of rotational lines and Pumping to ground rotational state	64
3.4.1 Population in a target-state	65
3.4.2 Pumping to high-energy super-rotor states	69
3.5 High-resolution spectroscopy with narrow linewidth CW laser	71
3.5.1 Setup and timing controls	72
3.5.2 Determination of linewidth and vibrational state lifetimes	73
3.6 Conclusion	76
Chapter 4: Towards fluorescence as state detection	77
4.1 Introduction	77
4.2 Limits on the existing information on SiO^+	78
4.3 Additions and modifications to the experimental setup	78
4.3.1 Determination of detection efficiency	79
4.3.2 Alignment of the M-Squared laser into the trap	80

	13
4.3.3 Locking the M-Squared Laser	81
4.4 Search for fluorescence	82
4.4.1 Method 1: M-Squared laser parked at a fixed wavelength	82
4.4.2 Method 2: Scanning the M-Squared	84
4.5 Double resonance spectroscopy - finding R(0) and P(1) lines	85
4.6 Summary and Further Work	88
Chapter 5: Reaction Kinetics of SiO^+ in an ion trap	90
5.1 Introduction	90
5.2 Setup and Data analysis	93
5.2.1 Gaussian Global Fit method	94
5.2.2 Singular Value Decomposition	95
5.3 Experimental Results	97
5.3.1 Rate constant measurement using a sample of rotationally uncontrolled SiO^+	97
5.3.2 Reaction rate of super-rotor SiO^+	99
5.4 Simulations and theoretical understanding - adapted from the summary of the work done by Prof. Anyang Li and Hua Guo	101
5.5 Conclusions and Future Work	104
Chapter 6: Future work	105
6.1 Blackbody thermometry	105

6.2 Summary and Conclusion	107
References	121
Vita	122

LIST OF FIGURES

1.1	Potential energy curve showing the $X^2\Sigma^+$, $B^2\Sigma^+$, $A^2\Pi$ and the $C^2\Pi$ states. These curves were calculated by Antonio G. S. de Oliveira-Filho and A. P. de Lima Batista.	27
1.2	Fortrat diagram representing the P and R type transitions for $X(v = 0) \rightarrow B(v = 0)$ in SiO^+ . The R branch turns around at $N = 85$ implying well-matched rotational constants for the X and B states. At room temperature only about 25 rotational states are expected to be populated. The R branch turnaround is therefore, at a much higher N than what is populated at room temperature. Inset: Zoomed in figure showing the separation between the P and R branches near the band origin.	28
2.1	Schematic of the lasers in a typical experimental set up. The Doppler cooling lasers, the rotational cooling laser, and the ablation laser are fixed wavelengths, while the remaining pulsed lasers (OPOs and dye laser) and the M-Squared SolsTis frequently change wavelength from UV to VIS wavelengths and serve multiple purposes (e.g. photo-ionization and dissociation, and fluorescence). To accommodate the flexibility required for the dynamic lasers, multiple flip mirrors and dichroic mirrors are installed. The counter-propagating Doppler beams are useful for easy alignment of the multipurpose lasers. Band-pass filters on the fixed wavelengths prevent damage to components downstream of the counter-propagating pulsed lasers along the path of the CW lasers. A single pass AOM is used for fast switching and controlled timing of the Doppler cooling lasers, the rotational cooling laser and the M-Squared laser. This figure has been modified from Ref. [60] to show the updated experimental setup. The doubling and quadrupling beams from the SolsTis suffer from a drop in the power over an extended period of time. To compensate for that, we have a layman version of a power lock. This setup is shown as an inset on the bottom left.	37

- 2.2 Simplified energy level diagram of Ba^+ . All of the dipole allowed transitions from the 6S, 6P $1/2$, and 5D states with transition wavelengths longer than 210 nm are listed. 39
- 2.3 Figure showing the path towards cooling SiO^+ to the ground rotational state. SiO^+ ions are pumped repeatedly on the P -type $|X, v = 0\rangle \rightarrow |B, v = 0\rangle$ transition from arbitrarily high starting rotational states. 44
- 2.4 A stick-spectrum of the $X(v = 0) \rightarrow B(v = 0)$ transition overlapped with the spectrally filtered light from the pulse-shaping setup, where the R branch transitions have been blocked, leaving light only on the P type transitions. This pumps SiO^+ to $N = 0$ 45
- 2.5 Cartoon illustration of the most likely mechanism for the parity flip process to cool into $|X, v = 0, N = 0\rangle$. The potential energy curve (not to scale) of the lowest three electronic states, X , A and B with representative vibrational and rotational fine structure. The bold lines represents the diagonal $v \rightarrow v$ transitions with the black one specifically indicating $v = 0 \rightarrow v = 0$ and the grey lines indicating higher $v \rightarrow v$ transitions. The dotted lines (grey) represent off-diagonal decay into either a different vibrational or electronic state. 47
- 2.6 Figure showing the path towards cooling SiO^+ to an arbitrary rotational state. SiO^+ ions, having a spread of about 25-30 rotational states, are pumped repeatedly on the P -type and R -type $|X, v = 0\rangle \rightarrow |B, v = 0\rangle$ transitions to any arbitrary rotational state of choice. The straight lines represent absorption and the squiggly lines represent spontaneous emission. 48
- 2.7 A stick-spectrum of the $X(v = 0) \rightarrow B(v = 0)$ transition overlapped with the spectrally filtered light with P branch transitions below $N = 9$ cut-off using a metal ribbon and R branch transitions above $N = 9$ cut-off using a blade. This pumps SiO^+ to a distribution with $\Delta N = 2$ centered around $N = 10$ 50
- 2.8 A fortrat (rotational number Vs frequency) of the $X(v = 0) \rightarrow B(v = 0)$ transition overlapped with the **Step 1:** spectrally filtered light with R branch transitions below $N = 160$ exposed and P -type transitions completely cut-off (bright orange) and **Step2:** Additional portion of the R - branch exposed to pump to even higher rotational states (light orange). 51

- 2.9 The linewidth was determined using two different Ba^+ transitions, the first one at 224.639 nm, $5\text{D}_{3/2} \rightarrow 7\text{P}_{1/2}$ and the second at 455 nm, $6\text{S}_{1/2} \rightarrow 6\text{P}_{3/2}$. This gives the linewidth of the fundamental light from the laser, the frequency doubled light has a linewidth that is roughly double that of the fundamental. 55
- 3.1 **a:** RF chirp was applied over a range of 200-550KHz for 200ms with an amplitude of 1V. **b:** 50 sweeps of the in-situ mass spectra averaged over 10 seconds recorded before and after a photo-dissociation laser pulse. **b:** A broadband waveform consisting of 8 frequencies separated by 2.5 kHz and centered at the SiO^+ secular frequency near 230 kHz **d:** Exponential decay of SiO^+ depletion with time when photo-dissociation occurs, the waveform depicted in **c** is used. 59
- 3.2 Spectrum of the $X^2\Sigma^+ \rightarrow C^2\Pi$ transition taken using a broad 0.5 cm^{-1} linewidth OPO. Transitions originating from $X^2\Sigma^+(v=0)$ to $C^2\Pi_{\Omega=1/2}(v=0, 1, 2, 3)$ and $C^2\Pi_{\Omega=3/2}(v=0, 1, 2, 3)$ are seen (Black and Blue spectrum). Blue lines represent the spectrum obtained without rotational cooling, whereas the black lines represent the spectrum after pumping to $|X, v=0, N=0\rangle$. Red lines represent the spectrum obtained by pumping SiO^+ to $|X, v=1\rangle$, figure adapted from the thesis of Patrick Stollenwerk 60
- 3.3 Spectrum for $X^2\Sigma^+(v=0) \rightarrow C^2\Pi_{\Omega=1/2}(v=0)$ taken using a narrow 0.3 cm^{-1} linewidth dye laser with a hope to resolve rotational transitions. 62
- 3.4 Spectrum taken after pumping SiO^+ molecules to the ground rotational state, a small fraction is in the first excited rotational state of $X^2\Sigma^+(v=0)$. The transitions are to $C^2\Pi_{\Omega=1/2,3/2}(v=0, 1)$. The spectrum was obtained using Scanmate dye laser. 63
- 3.5 Spectrum taken after pumping SiO^+ molecules to a distribution with $\Delta N = \pm 2$ around $N = 10, 25, 40, 55$ and 65 in $X^2\Sigma^+(v=0)$. The transitions are to $C^2\Pi_{\Omega=1/2,3/2}(v=0)$. The spectrum was obtained using Scanmate dye laser. . 66
- 3.6 **(a)** The $X^2\Sigma^+ \rightarrow C^2\Pi_{3/2}(0, 1)$ dissociation spectrum of SiO^+ optically pumped by the pulse-shaped spectrum to the ground rotational state. **(b)** The $X^2\Sigma^+ \rightarrow C^2\Pi_{3/2}(0, 1)$ dissociation spectrum of SiO^+ optically pumped to $N = 8 - 11$. **(c)** The relative rotational state populations inferred by fitting the dissociation spectrum in (a) and (b) using PGOPHER's contour fit feature are shown and compared to the thermal ($T = 293 \text{ K}$) distribution in red. 67

3.7	The rate of dissociation of super-rotors, the onset of dissociation is $\sim N = 196$. The X and B state Hamiltonian constants are not accurately determined for these energies and thus the rotational state is an estimate using available rotational lines data up to $N = 100$ and fitting them using additional higher order parameters. This matches well ($\Delta N \sim 2$) with the prediction from LEVEL calculations	70
3.8	Spectrum obtained for the $X, v=0$ to $C(v=0, 1, \text{ and } 2)$ using the M-Squared SolsTiS laser which is frequency quadrupled to the desired wavelength range. Also shown is the contour fit obtained using PGOPHER to extract the line position and linewidth.	73
4.1	Number of photons collected as a function of Ba^+ ions in the trap. The total number of measurements were 1,000,000. The fit gives the detection efficiency of the system as 0.0623%. It should be noted that there is a 50-50 beam splitter that splits the light collected using the imaging optics to the camera and the PMT. The Hamamatsu PMT has a quantum efficiency of $\sim 25\%$ at 385 nm and $\sim 19\%$ at 493 nm. Inset shows the fit parameters and the figures at the bottom are images of 1, 2, 3, and 10 Ba^+ loaded in the trap.	79
4.2	Timing diagram for fluorescence detection. M-Squared is parked at a particular wavelength and fired at an interval of 10 ms using an AOM. During the time M-Squared is on, the Mai-tai is shut off to prevent it from overwhelming the detector photon counts. The TDC is triggered before the M-Squared is turned on and provides a time-resolved measurement of the photons.	81
4.3	Data taken at a fixed wavelength using Method 1 for fluorescence detection. The TDC starts counting just before the Mai-Tai turns off. The photon counts registered by the TDC when the M-Squared laser is on is summed up and plotted as a function of wavelength.	82
4.4	The sum of the photon counts when the M-Squared is on is plotted after background subtraction. Background is obtained in the absence of SiO^+ and accounts for the scattered photons from the M-Squared laser. The plot also shows the fluctuations in the background photons.	83

- 4.5 Timing diagram for fluorescence detection. M-Squared is parked at a particular wavelength and fired at an interval of 10 ms using an AOM. During the time M-Squared is on, the Mai-tai is shut off to prevent it from overwhelming the detector photon counts. The TDC is triggered before the M-Squared is turned on and provides a time-resolved measurement of the photons. 84
- 4.6 Timing diagram for the detection of $R(0)$ and $P(1)$ lines using a double resonance method - wherein, the dye laser is used to dissociate out of a state different from the initial state provided the excitation on the $R(0)$ or $P(1)$ transition using the M-Squared laser is successful. 85
- 4.7 The M-Squared beam is used to excite the SiO^+ atoms either on the $R(0)$ or the $P(1)$ transition. The M-Squared is locked to an accuracy of ± 2 MHz using the wavelength locking system in the laser-farm. Since the M-squared as well as the dye-laser are required for the double resonance spectroscopy, and we propagate both the lasers axially, we use a D-mirror on the path of the dye-laser to ensure that we can also get the M-Squared laser go through the trap. To keep the power from the M-Squared beam stable, we have a layman version of a power-lock. The zeroth order beam from the AOM is continuously read and the first order power is calculated using a pre-determined factor. This is then fed into a LabView code that determines the on-duration for the AOM so that the product of power and on-duration remains a constant. This setup is shown as an inset on the bottom left. 86
- 4.8 The line positions obtained for $R(0)$ using double resonance spectroscopy. The spectrum obtained using $50\mu\text{W}$ for $10\mu\text{s}$ shows a splitting in the peak. We do not understand the origin of this peak and cannot point it to any particular fine structure that we expect. One possibility is that the AOM could be causing it, however, we have not verified it. 87
- 4.9 The line positions obtained for $P(1)$ using double resonance spectroscopy. The spectrum shows a splitting in the peak. We do not understand the origin of this peak and cannot point it to any particular fine structure that we expect. The inset shows the Pgopher simulation for the $X \rightarrow B$ transition and the expected lines originating from $N = 1$. We only expect to see two lines, however, there is an unexplained doubling of the lines similar to our observation in the $R(0)$ spectrum. 88

5.1	The shift in excitation frequency of the Ba^+ fluorescence dip indicates a shift in the mass over time due to H_2 reaction with SiO^+ . Each horizontal time slice is modeled by the sum of two Gaussians, one at the mass of SiO^+ ($m = 44 \mu$) and one at SiOH^+ ($m = 45 \mu$)	91
5.2	Each measurement of the secular frequency spectrum contains reacted and unreacted SiO^+ that is modeled by the sum of two Gaussians.	93
5.3	a: The data set obtained from the experiment. b: Components of the Singular value matrix that depict the overall spectrum and the change in the spectrum as a function of time.	94
5.4	Stern-Volmer plot depicting the reaction rate as a function of H_2 number density; slope obtained from the linear fit gives us the bi-molecular rate constant for the reaction.	96
5.5	Reaction rates for SiO^+ pumped to super-rotor states compared to an uncontrolled rotational distribution of SiO^+ . A higher exponential decay constant indicates that the reaction rate is faster.	98
5.6	Scatter plot showing the reaction rate outcomes from repeated measurements for uncontrolled and super-rotor SiO^+ . The dotted lines indicate the average of all the measurements.	100
5.7	a: Energetics of the ground state reaction pathways for the $\text{SiO}^+ + \text{H}_2$ reaction in potential energy surface(PES), the relative energies are in eV. b: Contours of the PES in reactant Jacobi coordinates along R and θ_1 with fixed $r_{HH} = 0.74$ at H_2 equilibrium distances and optimized r_{SiO} , θ_2 and ϕ . The attractive potential is isotropic until $R = 4 \text{ \AA}$	101
5.8	a: The evolution of the O-H1, O-H2 and H1-H2 distances with time from an exemplary reactive trajectory. b: Differential cross sections at three $J = 0, 100$ and 140	102
5.9	The calculated rate constants as a function of J (rotational quantum number of SiO^+), experimental data is indicated in red	103

6.1	a: Comparison of time-scales for blackbody redistribution as a function of the rotational state occupied by SiO^+ . b: BBR spectrum at 300K overlapped with regions where the rotational blackbody transitions are accessible and where BBR via A state is accessible.	106
-----	---	-----

LIST OF TABLES

1.1	The molecular constants for the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states calculated by Cameron <i>et.al</i> and Rosner <i>et.al</i> . These constants are from the de-perturbed fit and therefore to estimate correctly the transition energies, one would have to diagonalize the Hamiltonian (see Cameron <i>et.al</i> (1995) [54]). For our case, we were primarily interested in obtaining a reasonable model to predict transitions for $X^2\Sigma^+$ ($v = 0$) $\rightarrow$ $X^2\Sigma^+$ ($v = 0$). The easiest way to do that is to take all experimentally known energies of the transition and fit them to the Hamiltonian constants to obtain a specific band-to-band set of molecular constants. Since the $A^2\Pi$ state is far away enough, it doesn't perturb the low-lying rotational states in $X^2\Sigma^+$ $v = 0$	34
3.1	Molecular constants for the $C^2\Pi$ state	68
3.2	Molecular constants of the $C^2\Pi$ state (cont.)	69
3.3	Line positions obtained via high-resolution spectroscopy	74
3.4	Calculated values of vibrational state lifetimes from Antonio G. S. de Oliveira-Filho and A. P. de Lima Batista and experimentally determined lifetimes.	75
5.1	SVP values for rotational and vibrational modes of SiO^+ and H_2 projected onto the reaction coordinates at different transition states	104

CHAPTER 1

INTRODUCTION TO QUANTUM STATE-CONTROL IN DIATOMIC MOLECULES

1.1 Quantum control of diatomic molecules

The field of Atomic, Molecular and Optical (AMO) physics, and quantum state preparation and control in particular, has historically been dominated by advancements in the atomic and optical domain [1, 2]. Even the simplest of molecules, a diatomic molecule, is already one atom too many and the fear of tackling multiple degrees of freedom had kept scientists away for several decades from attempting to tame it [3]. Nevertheless, the rich internal structure of molecules and its potential applications have become way too attractive to stay away from it any longer. The past two decades have seen a tremendous growth in the development of quantum control techniques exclusive to molecules. The overarching goal in attempting to achieve quantum control of molecules is to have a tool-kit for molecules in the same way as we have for atoms - one that could then be used for a variety of applications such as quantum information [4, 5], many-body physics [6–8], tests of fundamental physics such as standard model and beyond-standard-model theories [9–16], ultra-cold chemistry [17–24], and spectroscopy at and beyond equilibrium bond lengths [25, 26] and many more. Diatomic molecules are also the first step in tackling increasingly complex systems, they can be accurately modeled using advanced theories and several methods for production, and spectroscopy have already been identified and performed for several well-known diatomic

molecules [27].

1.2 Techniques for molecular quantum control

Sympathetic cooling [28], supersonic expansion of molecular beams [29], buffer gas cooling [30], optical centrifuges [31] and photo-association [32] are some of the widely used techniques for molecular quantum control. While each of these techniques have their merits and demerits, they have all, with the exception of optical centrifuges and photo-association, largely been intended for cooling to the ground state. Ideally, controlling a molecular ion would not just involve ground-state cooling but also preparing them in an arbitrary rotational and vibrational state of choice. Photo-association overcomes this problem of achieving arbitrary state control, however, it suffers from the inability to quickly re-prepare a state. Optical centrifuges have been used to pump molecules to extremely high rotational energies with the caveat that the spread in the distribution remains the same before and after going through the optical centrifuge.

Optical pumping [33–36] is one technique where there is a possibility to pump the molecules to states of choice, and being a dissipative technique, there is also a possibility of achieving a reduction in the spread of the final distribution compared to the initial distribution. While this has been attempted before in supersonic beams of Cs_2 [37–39], the control was for a very limited time. In this work, and work that has been done in the Odom group previously [35, 40], we use optical pumping in conjunction with pulse shaping to prepare molecules in an ion-trap in specific target states. The long storage times of ion-traps are great for the purpose of sustained control. Throughout this thesis, I will focus on a particular molecule - SiO^+ and demonstrate three applications of achieving quantum control of SiO^+ molecules.

1.3 Requirements for optical pumping of molecular ions

The additional degrees of freedom in a molecule, compared to atoms, increases the complexity in the level structure. Atomic species that have been successfully cooled have a simple electronic structure where the numbers of lasers required to cycle molecules repeatedly on a particular transition is limited to mostly just two [41]. Transferring this idea naively to a molecule would mean looking for molecules with a simple structure. That effectively means a limited number of electronic states that the molecule can decay into from an excited state. However, for molecular transitions, rotational and vibrational sub-structure also need to be considered in addition to the electronic structure and that causes the number of available states grow exponentially with the degrees of freedom of a molecule. In this section, I will describe why SiO^+ is a good candidate for molecular optical pumping [42, 43].

1.3.1 Born-Oppenheimer approximation

Often, it is useful in the study of diatomic molecules to work under the Born-Oppenheimer approximation [27]. The basis of this approximation is, the mass of the nuclei and electrons being very different implies that the timescales of their motions are also very different with the nuclei moving a lot more slowly than the electrons. This leads to the wave-function of the molecules (ψ_{total}) being expressed as a product of the nuclear and electronic wavefunctions. ($\psi_e \cdot \psi_\nu \cdot \psi_s$).

1.3.1.1 Franck Condon factor

$$\mu_{e'\nu',e''\nu''} = \langle \psi_{e'} \psi_{\nu'} \psi_{s'} | \mu_e + \mu_n | \psi_{e''} \psi_{\nu''} \psi_{s''} \rangle \quad (1.1)$$

where, $\mu_{e'\nu',e''\nu''}$ is the transition moment from one state to another and $\mu_e + \mu_n$ are

the electronic and nuclear dipole moments for the transition. Using the Born-Oppenheimer approximation and the orthogonality of electronic states,

$$\mu_{e'v',e''v''} = (\psi_{v'}|\psi_{v''})(\langle \psi_{e'}\psi_{s'}|\mu_e|\psi_{e''}\psi_{s''} \rangle) \quad (1.2)$$

We may define, $\langle \psi_{v'}|\psi_{v''} \rangle$ as the Franck-Condon Factor which is essentially a scaling term for the intensity of a particular transition. The overall intensity of the transition is high when the overlap integral is close to 1 ((provided that the electronic transition moment is non-zero)) and low if the overlap is poor. In other words, electronic transitions are relatively instantaneous compared with the time scale of nuclear motions, therefore if the molecule is going to a new vibrational level during the electronic transition, this new vibrational level must be instantaneously compatible with the nuclear positions and momenta of the vibrational level of the molecule in the originating electronic state.

Furthermore, if we assume that vibrational energies are well described by the harmonic potential energy function, then the magnitude of the FCF depends on the difference in the equilibrium inter-nuclear separations in the two states. For a highly diagonal molecule, the equilibrium bond-lengths are equal to within one part in a thousand or even less [44].

In SiO^+ , the diagonal pair of states are the $X^2\Sigma^+$ and the $B^2\Sigma^+$ states. The minima in their potentials are well matched and the $B \rightarrow X$ transition is ideal for optical pumping without having to worry about vibrational state changes during spontaneous decay process [43, 45–47]. The wavelength for the $B \rightarrow X$ is also conveniently centered at 385 nm making it accessible by frequency doubling near-IR lasers.

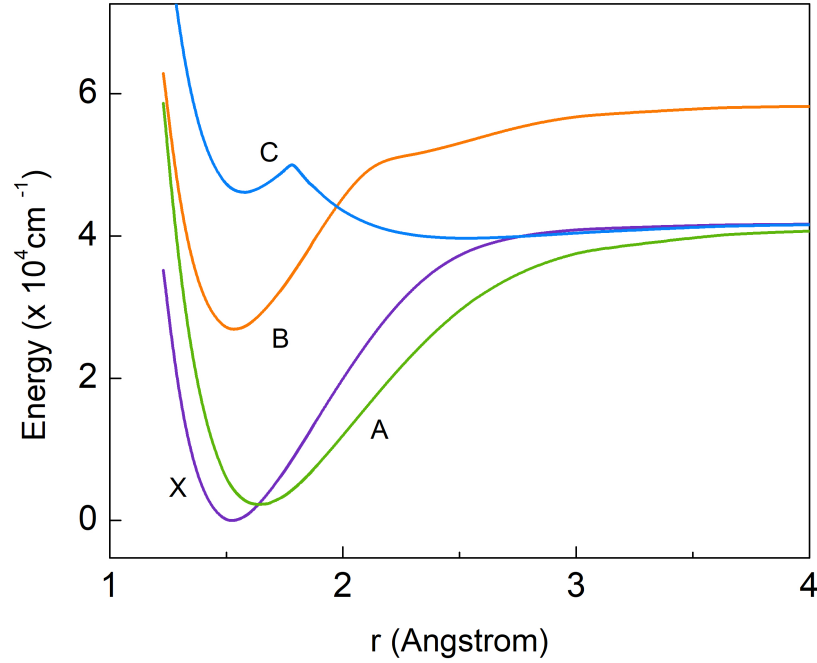


Figure 1.1: Potential energy curve showing the $X^2\Sigma^+$, $B^2\Sigma^+$, $A^2\Pi$ and the $C^2\Pi$ states. These curves were calculated by Antonio G. S. de Oliveira-Filho and A. P. de Lima Batista.

1.3.1.2 Rotational fine-structure

For molecules with diagonal FCFs, the rotational fine structure can be considered independent of vibrations [27]. In a rigid rotor model, where the bond length does not change due to rotations, the rotational constant can be written as

$$B_v = \frac{\hbar^2}{2I} \quad (1.3)$$

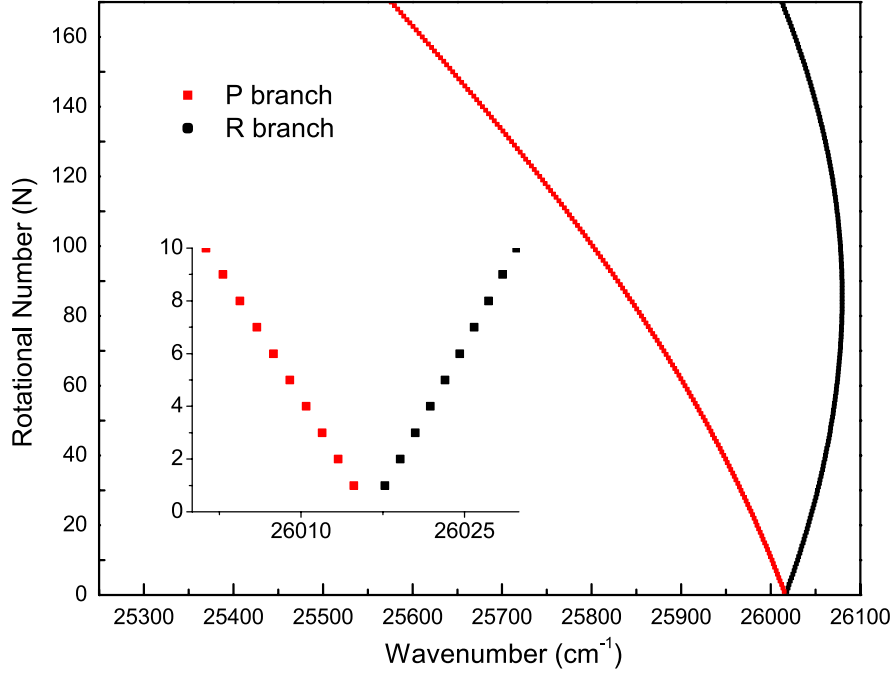


Figure 1.2: Fortrat diagram representing the P and R type transitions for $X(v = 0) \rightarrow B(v = 0)$ in SiO^+ . The R branch turns around at $N = 85$ implying well-matched rotational constants for the X and B states. At room temperature only about 25 rotational states are expected to be populated. The R branch turnaround is therefore, at a much higher N than what is populated at room temperature. **Inset:** Zoomed in figure showing the separation between the P and R branches near the band origin.

where $I = 2\mu r_e^2$ is the moment of inertia of the molecule with a reduced mass μ and an equilibrium bond length r_e . The rotational energy of a rigid rotor is

$$E = B_v N(N + 1) \quad (1.4)$$

where, N is the rotational quantum number.

Selection rules for rotational transitions are defined by

$$\Delta J = 0, \pm 1 \quad (1.5)$$

The X and B states in SiO^+ belong to the Hund's case B in the classification of molecules according to the dominant contributions in the rotational Hamiltonian. In this case, the spin-orbit coupling is weak/non-existent and both the total angular momentum (J) and the total angular momentum excluding the electron spin (N) are good quantum numbers. The total energy can be expressed either in terms of J or N [27]. The transitions are then classified as P , Q and R type to refer to $\Delta J = -1, 0$ and $+1$ respectively. The P and R branch transitions can be combined into one single expression given by

$$E_{P,R} = (B'_v + B''_v)m + (B'_v - B''_v)m^2 \quad (1.6)$$

where, B'_v and B''_v represent the rotational constants of the lower and upper electronic states, $m = -N$ for the P branch and $m = N + 1$ for the R branch.

The lowest R branch transition is $R(0)$ corresponding to a transition from $N = 0$ in the lower vibronic state to $N = 1$ in the upper vibronic state. The lowest P branch is $P(1)$ corresponding to $N = 1$ in the lower vibronic state to $N = 0$ in the upper vibronic state. For low N , it is clear that there is a separation between two branches $\approx 2B'_v$ and with increasing value of N , the P and R type transitions grow in opposite directions. When B'_v (B''_v) is greater, the $P(R)$ branch transitions grow apart in energy whereas the $R(P)$ branch transitions come closer to each other in energy. The branch that comes close together in energy ultimately has a “turnaround” at high enough N when the quadratic term starts to dominate. In the case of SiO^+ , the rotational constants B'_v and B''_v for the X and B states

respectively are matched well enough, with B_v'' being slightly smaller, that the R branch turn-around occurs at $N = 85$.

There is no Q branch in the $B \rightarrow X$ transitions. Each transition in the main branch has a satellite transition next to it, corresponding to $\Delta J = 0$. For the P branch, the satellite branch is PQ where $\Delta N = -1$ and $\Delta J = 0$; similarly, for the R branch, the satellite branch is RQ where $\Delta N = +1$ and $\Delta J = 0$. The satellite branches flip the spin and thus are weaker than the main. The main and the satellite transitions are resolved due to the spin-rotational interaction $\gamma \mathbf{L} \cdot \mathbf{S}$ where $\mathbf{L}$ and $\mathbf{S}$ are the pure rotation angular momentum, and spin angular momentum respectively, and γ is the spin-rotation coupling constant.

1.3.1.3 Presence and role of low-lying states

The first three low-lying electronic levels in SiO^+ are the $X^2\Sigma^+$, $A^2\Pi$, and the $B^2\Sigma^+$ [48–51]. In addition to the diagonal pair of $X^2\Sigma^+$ and $B^2\Sigma^+$ states, SiO^+ also has an intervening low-lying $A^2\Pi$ state around 2000 cm^{-1} above the $X^2\Sigma^+$ state. The A -state potential is not aligned with the X and B states and therefore the transitions $B \rightarrow A$ and the $A \rightarrow X$ transitions are not diagonal. Despite $B \rightarrow A$ transitions being fully allowed, the transition moments are weaker compared to $B \rightarrow X$, and therefore, the predominant channel for spontaneous decay from $B^2\Sigma^+$ is via the $B \rightarrow X$ channel where vibrational state is preserved due to diagonality of the states. Furthermore, the $A \rightarrow X$ transitions have reasonably large transition moments. The general implication is if there is an off-chance that SiO^+ decays on the $B \rightarrow A$ channel, then the $A \rightarrow X$ decay is fast enough that the overall build-up in the $A^2\Pi$ state is very low.

Due to the directly proportional dependence of the Einstein A coefficient on ω^3 , the highest rate of decay from the lowest occupied v of the A state is to $v = 0$ in X state. A

state plays a very important role in parity exchange process (Sec.3.4.1) as well as in diffusion out of targeted rotational states when optical pumping is turned-off. This is despite the fact that the branching ratio for the $B \rightarrow A$ transition is very small.

1.3.1.4 *Miscellaneous and nice-to-have properties*

In addition to diagonal FCFs, there are several other properties that are nice to have in a molecule before attempting to control it. Some of these are:

(a) Convenient wavelengths: Optically pumping molecules requires the use of lasers and despite several advancements in laser technology over the years, wavelengths in the deep UV are not accessible by lasers. In fact, that was one of the important reasons for the development of quantum logic spectroscopy in the Al^+ clock. The rotational transitions in SiO^+ can be covered using a frequency doubled femto-second laser centered at 385 nm. The rotational spacing between the ground and the first excited rotational state in $X^2\Sigma^+$ is 46 GHz which is easily accessible using microwaves.

(b) Isotopes: It is important that the molecule has one dominant isotopologue. Presence of several isotopes with abundances that are significant and comparable can cause systematics due to isotope shifts in the transitions [52]. The most abundant isotopologue is $^{28}\text{Si}^{16}\text{O}$ with a natural abundance of 92%. The other naturally occurring isotopologues are primarily due to the other isotopes of Si which are ^{29}Si (4.7%) and ^{30}Si (3.1%). The shift due to the $^{29}\text{Si}^{16}\text{O}$ and $^{30}\text{Si}^{16}\text{O}$ isotopes is significant and noticeable in the $|X^2\Sigma^+\rangle \rightarrow |C^2\Pi\rangle$ transition and is expected to be 0.51 cm^{-1} and 0.99 cm^{-1} respectively. The low abundance of these isotopes is important when loading these ions into the trap (see Sec.2.2) as well as when

mapping the spectrum; the purity is sufficient enough that we primarily only load the abundant $^{28}\text{Si}^{16}\text{O}^+$ into the trap and the abundance of the other isotopologues are low enough that they can often be safely ignored as spectral peaks from the low abundance species are unlikely to be significant compared to the abundant one. During measurements to determine the cooling time-scales and steady-state ground rotational state preparation statistics, the probability of dissociation for the isotopes of lower abundance is reduced according to the detuning and the Lorentzian profile of the laser and needs to be accounted for when estimating the systematic corrections to the measurements. Thus, the probability of dissociation for the isotopes of lower abundance is reduced according to the detuning and the Lorentzian profile of the laser. For instance, when measuring the time-scales for rotational cooling by dissociation spectroscopy, transitions originating from $|X^2\Sigma^+, v = 0, N = 1, J = 0.5\rangle$ and $|X^2\Sigma^+, v = 0, N = 1, J = 1.5\rangle$ are roughly one laser linewidth away from the probing transition at 44044.5 cm^{-1} and therefore also contribute to the dissociated fraction.

(c) Hyperfine structure: Many applications require the ability to prepare a well-defined quantum state, including the nuclear degrees of freedom. Non-zero nuclear spin of an element in the molecule couples with the rotational degree of freedom as well as any non-zero nuclear spin of any other element, making high-fidelity optical pumping challenging [45, 53]. In contrast, diatomic molecules with two $I = 0$ species, such as those involving $^{28}\text{Si}^{16}\text{O}$ (99.8% natural abundance), have no complicating hyperfine structure making state preparation an easier task.

(d) Existing spectroscopic data: Any previously existing study of the molecule is very valuable - theory or experiment. In particular, if experimental studies have already

been performed on the molecule and the transitions of interest, it makes life easier as the precise wavelengths and molecular constants are already known and can directly be used in spectroscopy and cooling. Theoretical studies can be used to map out possible transitions that can be used for probing the molecule [50, 51, 54].

1.4 Background review of studies on SiO^+

In attempting to control SiO^+ molecules, we are fortunate in that there is already a substantial amount of theory as well as experimental data available on the molecule.

Transitions between $B \rightarrow A$ and $B \rightarrow X$ have been extensively studied and modeled to extract the molecular constant listed in the Table.1.1.

The energy of a $^2\Sigma$ state, when it is not significantly disturbed by near-by $^2\Pi$ states is given by,

$$E = T_e + \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + B_e(J)(J + 1) - D_e[(J)(J + 1)]^2 - \frac{1}{2}\gamma_v J \quad (1.7)$$

When the energy difference between two electronic states is not large compared to the interaction strength that causes mixing of wavefunctions, then the energy relation in Eq.1.7 cannot be simply used. The close by $A^2\Pi$ state perturbs the $X^2\Sigma^+$ quite extensively. The mixing of $X^2\Sigma^+$ and $A^2\Pi$ is caused by a spin-orbit interaction and the $\mathbf{L.S}$ coupling interaction. This can be overcome by obtaining the molecular constants of the Hamiltonian on a band-by-band basis and by excluding the regions of heavy perturbation. However, it becomes difficult to attribute meaning to the molecular constants in that case. To resolve this issue the authors adopted a de-perturbative analysis approach where they consider the entire set of experimental data.

State	T_e (cm $^{-1}$)	R_e (nm)	ω_e (cm $^{-1}$)	$\omega_e x_e$ (cm $^{-1}$)	B_e (cm $^{-1}$)
$X^2\Sigma^+$	0	0.15162	1162.18	6.9698	0.72062
$A^2\Pi$	2242.25	0.16365	946.28	7.005	0.61859
$B^2\Sigma^+$	26029.01	0.15243	1136.58	6.9215	0.71303

Table 1.1: The molecular constants for the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states calculated by Cameron *et.al* and Rosner *et.al*. These constants are from the de-perturbed fit and therefore to estimate correctly the transition energies, one would have to diagonalize the Hamiltonian (see Cameron *et.al* (1995) [54]). For our case, we were primarily interested in obtaining a reasonable model to predict transitions for $X^2\Sigma^+ (v=0) \rightarrow X^2\Sigma^+ (v=0)$. The easiest way to do that is to take all experimentally known energies of the transition and fit them to the Hamiltonian constants to obtain a specific band-to-band set of molecular constants. Since the $A^2\Pi$ state is far away enough, it doesn't perturb the low-lying rotational states in $X^2\Sigma^+ v=0$.

1.4.1 Experimental and Theoretical studies on SiO^+

One of the earliest observations of SiO^+ was by Pankhurst in 1940. However, at the time, the spectrum was mistakenly attributed to SiO_2 and was corrected by Woods later on in 1943. More spectroscopy experiments on SiO^+ include Lagerqvist and Renhorn [55]; Colbourn et al. [56]; Ghosh et al. [57] as well as the fast-ion-beam spectroscopy efforts from Rosner and Cameron [50, 54] mentioned above. Several theoretical studies have been carried out to map state electronic states and energies.

In 1999 Cai and Francois predicted avoided-crossings of low-lying $^2\Pi$ states that result in quasi-bound states. They calculated the quasi-bound $3^2\Pi$ state to have an energy $T_e=49760\text{cm}^{-1}$ and therefore inaccessible with our current lasers except with a two-photon transition. Poor vibrational wave-function overlap was also expected to be an issue as the potential minimum is shifted outward by $\sim 0.3 \text{ \AA}$ leading to low intensities of the transition moment. On the other hand the $2^2\Pi$ state was calculated to be in a range of $T_e = 44000 - 45000 \text{ cm}^{-1}$ and therefore accessible with lasers that were available in the lab. These calcu-

lations led us to try using the $2^2\Pi$ (later re-named $C^2\Pi$) state for dissociation spectroscopy. Theoretical studies have also been published by Chattopadhyaya *et. al* and Li *et. al* [58] more recently. Most recent calculations were by Antonio G. S. de Oliveira-Filho and A. P. de Lima Batista [25], where the $C^2\Pi$ state was modeled with much better accuracy. In their calculations of the electronic structure, performed using MOLPRO [59], the spin-orbit coupling was accounted for using the spin-orbit matrix elements calculated via the Breit-Pauli operator at the CASSCF/aug-cc-pwCV5Z level of theory and couplings of the $C^2\Pi$ electronic state with $1^4\Pi$, $2^2\Delta$, and $2^2\Sigma^-$ were considered.

1.5 Organization of the thesis

The remainder of this thesis is organized as follows: in Chapter 2, I discuss the experimental setup used in the thesis including the lasers, detection systems and hardware-software integration using LabView. I also elaborate on the techniques for rotational state control. After that, I proceed to describe the applications of rotational state control of molecular ions. In Chapter 3, I describe the setup and experimental results that demonstrate the use of rotational state control to perform spectroscopy on molecules at and beyond equilibrium bond lengths. In Chapter 4, I talk about our progress towards a technique for non-destructive state detection using fluorescence as a second example of rotational state control. And as the final example, in Chapter 5 I discuss the reaction chemistry of $\text{SiO}^+ + \text{H}_2$ in our ion trap and the dependence of the reactions on the rotational state of SiO^+ . In the final Chapter ??, I present some concluding thoughts, and future applications.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Introduction

The set up required for molecular and atomic ion control is vast and involves a combination of several lasers, detectors, passive and active optical elements. At the time of my joining in 2017, we had 4 lasers aligned into the trap; over the last 4.5 years, this number has grown to 10. The operation of each of these is critical to the experiment and the functionality of these lasers are unique and non-interchangeable with other lasers for the most part; something I have learned in most painful ways when we had to pause the experiment for long periods due to the failure of one laser. In this chapter, I will describe the setup used for different aspects of the experiment -loading, trapping and detection, state control, and spectroscopy. I will also go over the experimental and timing sequences where ever applicable. To the best possible extent, I have tried to refer to already existing details in the thesis of other students from the lab, thereby avoiding repetition. However, for the sake of logical continuity, some repetition has become unavoidable.

2.2 Loading ions into the trap

We load our atomic and molecular ions into the trap via ablation followed by photo-ionization. We ablate a pellet containing the species we would like to load. In our trap, there is one pellet each of Ba and SiO. Ablation typically generates a plume that predominantly con-

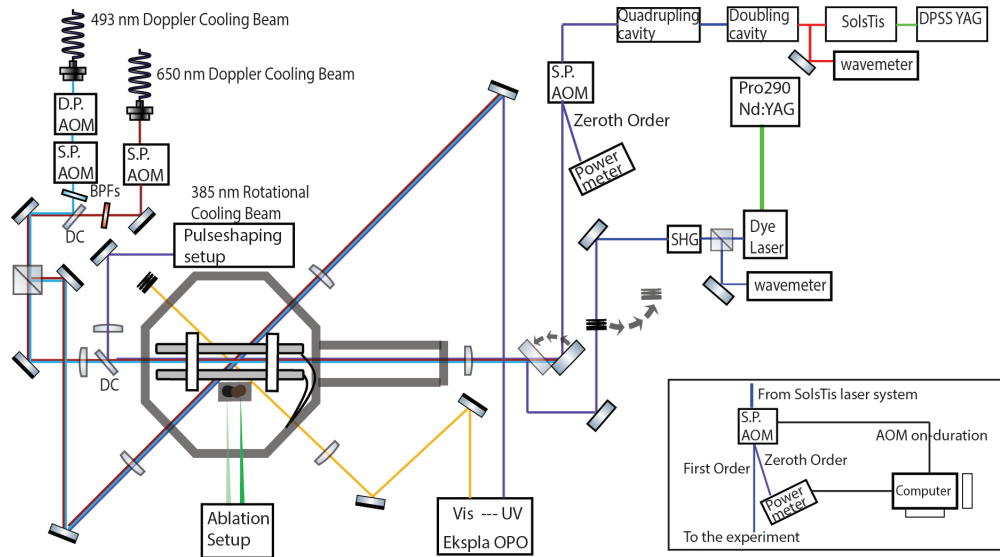


Figure 2.1: Schematic of the lasers in a typical experimental set up. The Doppler cooling lasers, the rotational cooling laser, and the ablation laser are fixed wavelengths, while the remaining pulsed lasers (OPOs and dye laser) and the M-Squared SolsTis frequently change wavelength from UV to VIS wavelengths and serve multiple purposes (e.g. photo-ionization and dissociation, and fluorescence). To accommodate the flexibility required for the dynamic lasers, multiple flip mirrors and dichroic mirrors are installed. The counter-propagating Doppler beams are useful for easy alignment of the multipurpose lasers. Band-pass filters on the fixed wavelengths prevent damage to components downstream of the counter-propagating pulsed lasers along the path of the CW lasers. A single pass AOM is used for fast switching and controlled timing of the Doppler cooling lasers, the rotational cooling laser and the M-Squared laser. This figure has been modified from Ref. [60] to show the updated experimental setup. The doubling and quadrupling beams from the SolsTis suffer from a drop in the power over an extended period of time. To compensate for that, we have a layman version of a power lock. This setup is shown as an inset on the bottom left.

tains neutral atoms and molecules comprising of the elements in the pellet and in different stoichiometric compositions. By photo-ionizing the neutral atom/molecule at a specific wavelength, we load an ion into the trap. Photo-ionization ensures specie selectivity and that we load stoichiometrically-pure ions of our choice into the trap. One thing to note is that the photo-ionization laser has a bandwidth of about 5 cm^{-1} , and isotope purity is not possible. However, the general abundance of ^{138}Ba is $\sim 71 \%$ and the $^{28}\text{Si}^{16}\text{O}$ is $\sim 94\%$ and these are

sufficient for our purposes. There are experiments where we have had to take into account systematic effects due to isotope shifts of SiO^+ .

2.2.1 Loading lasers

We carry out ablation with the *Continuum Mini-Lite low power pulsed Nd:YAG*. This laser outputs pulses at a repetition rate of 10 Hz and each pulse is a few nanoseconds long. We split the 532 nm 2^{nd} harmonic of the YAG into two beams each of which is then sent via a half-wave plate followed by a polarizing beam splitter to control the amount of ablating power. The half-wave plate is mounted on a servo-motor allowing us to adjust the ablating power as needed. A focusing lens then focuses the beams onto the pellet.

Photo-ionization is achieved with the help of a *Ekspla NT342/1/UVE OPO* which has a repetition rate of 10 Hz. For Ba, we perform a non-resonant photo-ionization. In practice, any wavelength below 303 nm is sufficient for this purpose. To load SiO^+ , we use the (5,0) band of the 1+1 REMPI via the $A^1\pi \rightarrow X^1\Sigma$ transition. The details of this scheme are described in detail in a journal article [61] and the thesis of Patrick Stollenwerk [citestollenwerk-thesis](#).

2.2.2 Doppler cooling and sympathetic cooling

2.2.2.1 Doppler cooling of Ba^+

Ba^+ is continuously Doppler-cooled on the 493 nm $6S_{1/2} \rightarrow 6P_{1/2}$ transition and re-pumped on the 650 nm $5D_{3/2} \rightarrow 6P_{1/2}$ transition to avoid Ba^+ accumulating on the long-lived $5D_{3/2}$ state. We load around 500-1000 Ba^+ atoms and they form a Doppler cooled Coulomb crystal in the trap [62] Both these are addressed using CW lasers. The 493 nm is obtained by frequency doubling a Toptica ECDL at 986 nm, and amplified using a Toptica BoostA

Figure 2.2: Simplified energy level diagram of Ba^+ . All of the dipole allowed transitions from the 6S, 6P1/2, and 5D states with transition wavelengths longer than 210 nm are listed.

The ground state of Ba^+ is $6\text{S}_{1/2}$ and with the $6\text{P}_{1/2}$ and the $5\text{D}_{3/2}$ state it forms a closed cycling system. That is, a single pump (493 nm) and repump (650 nm) laser is capable of indefinitely sustaining a continuous cycle of excitation and spontaneous emission resulting in a rapid rate of scattered photons ($> 10^7 \text{ s}^{-1}$) capable of removing translational energy

via Doppler cooling. Coherent population trapping is avoided by applying a magnetic field perpendicular to the z-axis of the trap with a field strength of ~ 10 Gauss. The three states described in the closed cycling system are often referred to as a Λ -type system in the literature. Decay from D-state to the S-state is dipole forbidden, thus it can be ignored in the three-level system. Decay into the $5D_{5/2}$ state from $6P_{1/2}$ is also dipole forbidden. Given the distribution of states, Ba^+ has a number of transitions beginning in the Λ system states that span UV through the visible range of the spectrum. The level structure of Ba^+ has been well-studied these transitions can be used to calibrate a broad range of wavelengths. Similarly, it can be used to characterize the line-widths of the various pulsed lasers and is useful as a way to ensure proper alignment of lasers in the ion trap.

Another advantage of the Λ system is deterministic pumping. By temporarily turning off exactly one of the lasers (either the pump or the repump), the ion can be pumped into either the S or the D state. We used this to make an absolute measurement of the quantum detection efficiency of the imaging system (Sec. 4.3.1). Deterministic pumping can also be used to intentionally avoid populating particular states of Ba^+ in the presence of another laser. For example, a pulsed laser scanning the dissociation spectrum of a co-trapped species may encounter a line in Ba^+ that either doubly ionizes Ba^+ or causes the ion crystal to go dark. In this case, the unwanted effect can be avoided by pumping Ba^+ into a state not involved in the transition (Fig. 3.2). An exactly opposite case arises when searching for lines to calibrate laser wavelengths - the state involved in the desired transition can be intentionally populated to enhance the signal (Sec. 2.5.1.2).

2.2.2.2 *Sympathetic cooling of SiO^+*

When we co-load SiO^+ along with Ba^+ , the Doppler-cooled Ba^+ sympathetically cools the translational motion of SiO^+ via Coulomb interactions. The coupling is important not just for sympathetically cooling SiO^+ but also for in-situ spectrometry techniques discussed below in Sec. 2.3. Since SiO^+ molecules do not fluoresce, they are visible as dark ions in the center of a bright Ba^+ cloud under properly compensated and optimized trapping conditions (RF voltage and end-cap voltage). Coupled mode frequencies of Ba^+ and SiO^+ are typically in the 10^6 Hz range whereas internal energy of a molecule such as rotational and vibrational frequencies are on the order of 10^{12} - 10^{13} Hz. Therefore, coulomb interactions between SiO^+ and Ba^+ are not sufficiently strong to affect the internal degrees of freedom of SiO^+ ions. The photo-ionization loading scheme for SiO^+ puts it in the ground vibrational state and majorly rotational states 12-20 are populated. In the absence of any other external factors, the rotational distribution of SiO^+ will equilibrate to a thermal distribution on the time-scale of minutes.

2.3 Detection

We need a tool to non-destructively confirm loading of SiO^+ ions. In addition, we also need a way to roughly estimate how much SiO^+ is too much to hold in the trap (loading too many SiO^+ de-stabilizes the Ba^+ Coulomb crystal). For this purpose, we adapted a technique called Laser cooled fluorescence mass spectrometry (LCFMS) developed first by Baba and Waki [64, 65] and later extensively used Schiller and co-workers [23]. This technique relies on the detection of a non-fluorescing ion in the trap by coupling it to the fluorescence of the bright ions. All species of ions have their own unique frequencies of motion in an ion trap

which is inversely proportional to their mass, also known as the secular frequency. Secular frequency is given by

$$\omega_i = (i + \frac{\beta}{2})\Omega_{RF}, \quad 0 \leq \beta \leq 1, \quad i = \pm 1 \pm 2 \pm 3 \dots \quad (2.1)$$

where β is obtained from the Mathieu's equation and is dependent on trap parameters and inversely on the mass to charge ratio (m/z) of the ion.

We applied a low-voltage (0.5 - 1 V) excitation chirp sweeping through frequencies from 150 kHz to 500 kHz to one of the rods in the RF trap. As the chirp hit the secular frequency of a particular species of ions in the trap, their motion was resonantly enhanced and coupled weakly to the motion of Ba^+ . The coupling to Ba^+ is determined by the extent to which the Ba^+ pump laser (493 nm) is de-tuned from resonance. We red de-tuned the 493 nm Ba^+ pump laser by 6-10 MHz. As the frequency of the chirp hit the secular frequency of SiO^+ , it increases the motion of SiO^+ . This in turn increases the motion of Ba^+ ions and as a result, they spend less time on resonance which reflects as a drop in the fluorescence counts from Ba^+ . The reduction in fluorescence is proportional to the number of SiO^+ ions. A photo-multiplier tube (PMT) was used to detect the fluorescent photons of Ba^+ cloud. A digital counter that was binned into 1 ms intervals counted the number of PMT events in each bin. As a result, each timestamp corresponded to a particular frequency over the course of one sweep. By detecting the frequency at which the Ba^+ fluorescence goes down, we can tell the mass of the ion in the trap.

The signal is better when the Ba^+ is de-tuned further from resonance, however, this also makes the crystal unstable as it heats up to a point of no-recovery. This is when coulomb crystal of Ba^+ goes into a gas-phase and leads to a loss of SiO^+ ions as the Ba^+ ions them-

selves are not cold enough to keep the SiO^+ translationally cold. The trap parameters are not optimized for SiO^+ mass and therefore they don't stick around in the trap in the absence of cold Ba^+ . So, there is a fine balance increasing the de-tuning to maximize contrast and not going too far that it de-stabilizes the crystal. Loading of too many SiO^+ into the Ba^+ cloud can also lead to de-stabilization of the crystal, as can sudden spikes/fluctuations of more than 5-6 MHz in the frequency of Doppler-cooling lasers. Trap instabilities due to uncompensated patch potentials and non-optimal trap voltages can also kick the ions out of the trap. A common joke in our group is that the determination the combination of correct trap parameters, chirp amplitude and de-tuning frequency is more art than science and varies on a day-to-day basis. It has taken over 4 years and several hundreds of data-sets to perfect this art! The effect of this is minimal when we use it only to qualitatively detect the loading of SiO^+ . However, as I will describe in a future chapter on reaction kinetics of SiO^+ (Ch. 5), it is a hindrance for clean, and quantitative measurements.

Under "optimized" conditions, we load SiO^+ ions until we see a dip in the fluorescence by about 10-13 %. We estimate this to be caused by about 20-100 SiO^+ molecules by looking at the size of the dark-core. Molecular dynamics simulations can give a more accurate number prediction. One day, if we achieve fluorescence measurements of SiO^+ , we may know this number accurately.

2.4 Rotational state control

To pump the SiO^+ molecules into targeted rotational states, we use the technique of broad-band rotational optical pumping, where the main aim is to address populations of SiO^+ in several rotational states simultaneously. This is especially useful because at room tempera-

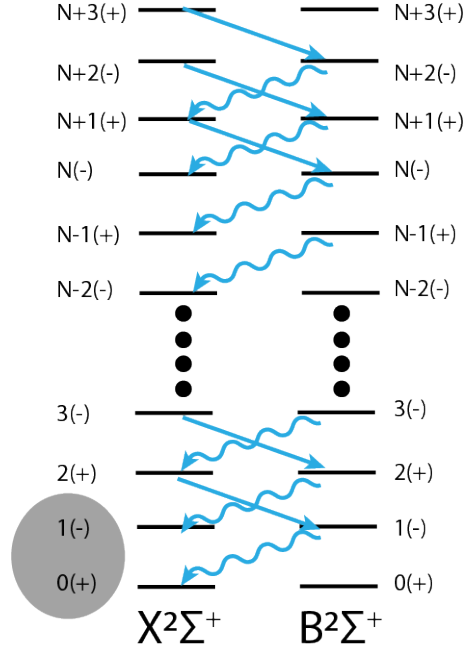


Figure 2.3: Figure showing the path towards cooling SiO^+ to the ground rotational state. SiO^+ ions are pumped repeatedly on the P -type $|X, v=0\rangle \rightarrow |B, v=0\rangle$ transition from arbitrarily high starting rotational states.

ture around Boltzmann statistics allows for 25-30 rotational states of SiO^+ to have significant population.

2.4.1 Setup for rotational control

A broadband Ti:Saph femtosecond laser (*Spectra-Physics Mai-Tai HP*) that can produce up to 2.8 W of power at 769 nm with a rep rate of 80 MHz was used. The output from the laser was passed through an AOM for switching control and was doubled using an LBO crystal before being sent to the spectral pulse-shaping setup.

The pulse shaping setup was used to spectrally filter out unwanted frequency components. This was done by dispersing the doubled beam using a grating to spatially separate the frequency components. The dispersed beam was then focused onto a mask (razor blade) to

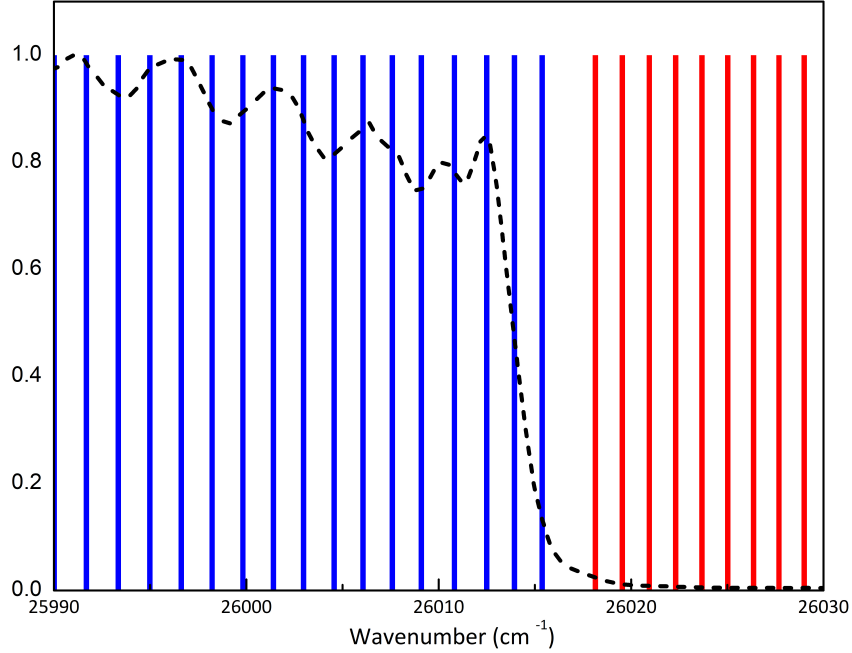


Figure 2.4: A stick-spectrum of the $X(v=0) \rightarrow B(v=0)$ transition overlapped with the spectrally filtered light from the pulse-shaping setup, where the R branch transitions have been blocked, leaving light only on the P type transitions. This pumps SiO^+ to $N=0$.

spatially block unwanted frequency components. The spectrally filtered light was reflected from a mirror, recombined onto the same grating and sent into the ion trap. Details of the spectral filtering setup, in particular, optical components, and characterization of the mask and filtered spectrum can be found in the thesis of Yen-Wei Lin [42] and certain modifications to the setup are available in Pat Stollenwerk's thesis [60].

2.4.1.1 Optical pumping to ground rotational state

At room temperature (300 K), about 25-30 rotational states in the ground vibronic state of SiO^+ are populated. Achieving rotational cooling to the ground state implies each of

these rotational states needs to be addressed with a laser tuned to the P -type transition originating from that state. Say, a laser is tuned to $P(14)$ of $X(v = 0) \rightarrow B(v = 0)$ transition in SiO^+ , it pumps the electron from $N = 14$ in the $X(v = 0)$ state to $N = 13$ in $B(v = 0)$. It can then decay back to $N = 14$ on the R -branch or $N = 12$ on the P -branch while still being in $v = 0$ as a result of the good Franck-Condon overlap in the vibrational wavefunctions. When it decays via the $P(R)$ branch, it has lost two (zero) quanta of angular momenta during one cycle involving pumping followed by spontaneous relaxation. Thus, with a certain probability that depends on the line strengths of the P and R branches, the molecule loses two quanta of angular momentum and ends up in a lower rotational state (see Fig. 2.6). It is important to note here that each cycle involves two dipole-allowed transitions, therefore parity is exchanged twice in one cycle and thus the electron returns to the original parity-state at the end of one cycle. This process can be repeated again with another laser tuned to the $P(13)$ transition and so on until the electron is pumped into the lowest parity eigenstates. Since parity is conserved for every cycle of this process, parity-states cannot be cooled using this pumping scheme. However, the feasibility of this scheme is questionable as pumping using this scheme implies that at least 25-30 lasers tuned to different transitions are required.

The problem of using many lasers can be avoided if the scheme can be modified to make use of the spectral features of the optical pumping transitions. For diagonal transitions like the $X^2\Sigma^+ (v = 0) \rightarrow B^2\Sigma^+ (v = 0)$ in SiO^+ , the separation of the P and R type transitions and their branching out in opposite directions is ideal as it allows addressing a whole bunch of rotational transitions simultaneously with a broadband laser instead of addressing each of it individually. The transfer of population between the lowest parity states (*i.e*) from $N = 1$ to $N = 0$ will need either a microwave source to directly transfer population between the

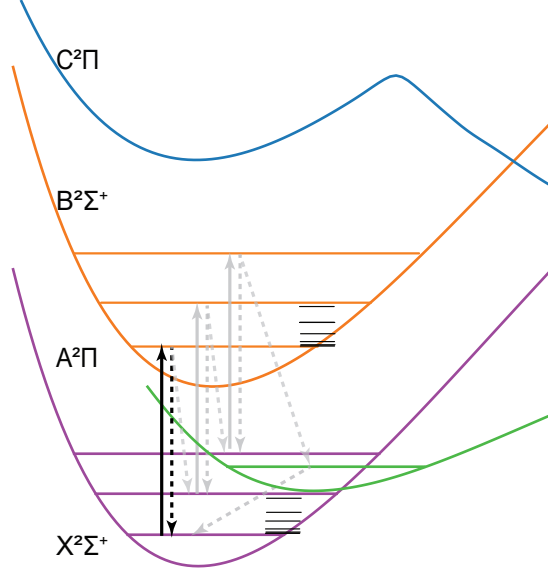


Figure 2.5: Cartoon illustration of the most likely mechanism for the parity flip process to cool into $|X, v = 0, N = 0\rangle$. The potential energy curve (not to scale) of the lowest three electronic states, X , A and B with representative vibrational and rotational fine structure. The bold lines represents the diagonal $v \rightarrow v$ transitions with the black one specifically indicating $v = 0 \rightarrow v = 0$ and the grey lines indicating higher $v \rightarrow v$ transitions. The dotted lines (grey) represent off-diagonal decay into either a different vibrational or electronic state.

rotational levels of different parity, say $N = 1$ to $N = 2$ within $X(v = 0)$ state, or make use of a rare off diagonal decay to an intermediate state (either a different electronic state or a vibrational state) and eventually relax to $|X(v = 0, N = 0)\rangle$. The off-diagonal decay method involves a total of 3 dipole allowed transitions and thus results in a parity flip. The scheme that most likely results in the parity flip is demonstrated in Fig. 2.5.

The process involves SiO^+ being cooled to the lowest negative parity state ($N = 1$) after being continuously driven on the quasi-cycling $P(1)$ transition, until it leaks elsewhere. The required odd number of electric-dipole transitions to go from $N = 1$ to $N = 0$ either

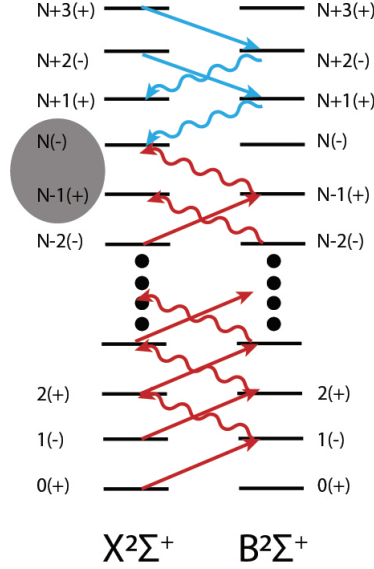


Figure 2.6: Figure showing the path towards cooling SiO^+ to an arbitrary rotational state. SiO^+ ions, having a spread of about 25-30 rotational states, are pumped repeatedly on the P -type and R -type $|X, v=0\rangle \rightarrow |B, v=0\rangle$ transitions to any arbitrary rotational state of choice. The straight lines represent absorption and the squiggly lines represent spontaneous emission.

occur in decay channels passing through intermediate $|X, v > 0\rangle$ or $|A\rangle$ states. Off-diagonal decay from $|B, v=0\rangle \rightarrow |X, v > 0\rangle$ occurs faster than the observed parity-flip timescale, but subsequent $|X, v > 0\rangle$ vibrational relaxation is much slower than the observed timescale. Likewise, although the predicted lifetime of $|A\rangle$ is itself short enough, decay from $|B, v=0\rangle \rightarrow |A\rangle$ is predicted to have too small a branching ratio. However, a hybrid mechanism seems plausible, shown in Fig. 2.5. In this sequence, population in $|X, v=2\rangle$ is be driven to $|B, v=2\rangle$ by the cooling laser and eventually undergoes a decay $|B, v=2\rangle \rightarrow |A, v=0\rangle$, as discussed above. Relaxation from $|A, v=0\rangle \rightarrow |X\rangle$ is expected to occur on the order of a few milliseconds.

In all of the work carried out in this thesis, we use the parity flip technique to cool to the ground rotational state. When the razor blade cut-off is set perfectly, around 94% of

the population can be pumped to the ground rotational state. This number can change by quite a bit if the mask is not optimized. The mask needs to be set such that there is enough light on the $P(1)$ line that the SiO^+ can repeatedly be pumped to $|B, v = 0, N = 0\rangle$ and eventually undergoes a rare off-diagonal decay and ultimately ends up in $|X, v = 0, N = 0\rangle$. The time scale for this to happen is on the order of 100 ms. It is however, possible to decrease the time for ground rotational state preparation to even fast time-scales by using a microwave of frequency ~ 86 GHz to pump the SiO^+ molecules from $|X, v = 0, N = 1\rangle$ to $|X, v = 0, N = 2\rangle$. This brings all of the SiO^+ to even parity and from there it is gets pumped down to $N = 0$ via the stimulated absorption on $P(2)$ transition followed by spontaneous emission to $N = 0$.

2.4.1.2 Optical pumping to a target rotational state

This scheme can be extended to pump the SiO^+ population to not just the ground rotational state but to any arbitrary rotational state by using an additional component in the mask such as a thin metal ribbon along with the razor blade. The principle behind pumping to any arbitrary state is the following : all the SiO^+ population below the target state need to be pumped using R branch transitions so as to increase their angular momentum up to the target state and SiO^+ population that start out in states higher than the target state need to be pumped using the P branch transitions in order to decrease their angular momentum. This effectively means blocking a certain region in the P branch corresponding to transitions below the target state and moving the razor blade on the R branch so as to expose the R -type transitions up to the target state. The filtered spectrum used to pump to $N = 10$ is shown in Fig. 2.7. Note that we cannot pump to target states between $N = 80$ and $N = 160$ due to the R -branch turnaround.

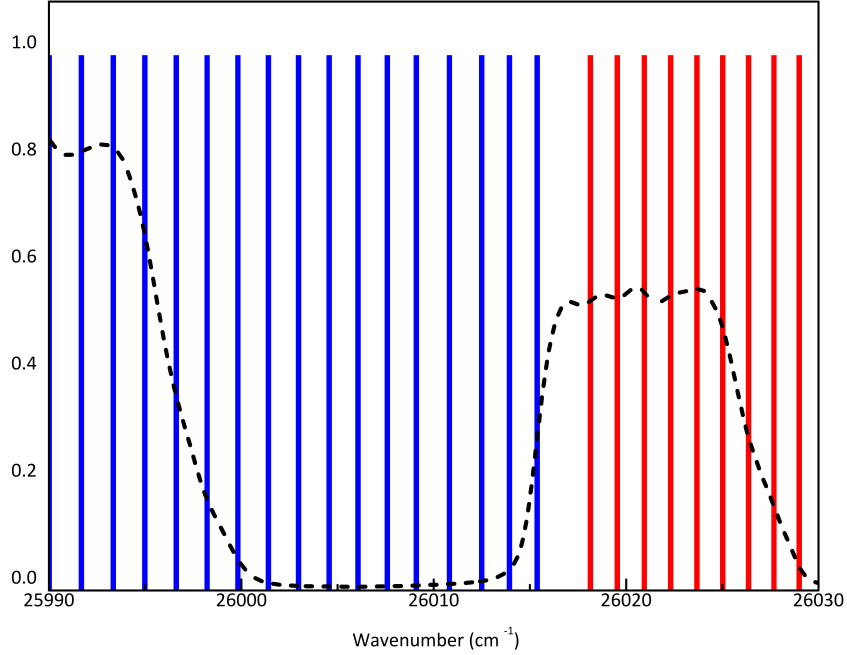


Figure 2.7: A stick-spectrum of the $X(v = 0) \rightarrow B(v = 0)$ transition overlapped with the spectrally filtered light with P branch transitions below $N = 9$ cut-off using a metal ribbon and R branch transitions above $N = 9$ cut-off using a blade. This pumps SiO^+ to a distribution with $\Delta N = 2$ centered around $N = 10$.

2.4.1.3 Pumping to extremely high rotational states

We can take the optical pumping scheme one step further to pump SiO^+ to extremely high rotational states known as super-rotors [66]. This is a two step process. In the first step, SiO^+ is exposed to R -type transitions all the way up to $\sim N = 160$ and the P -branch is completely cut-off. $N = 160$ is chosen as the cut-off for the first step as this is roughly where the P -branch starts to overlap the R -branch (*i.e* for a given wavenumber, there is one P -type transition and one R -type transition). In the first-step we don't want to expose the SiO^+ to any P -type transition so that they are pumped up to $N = 160$ without any

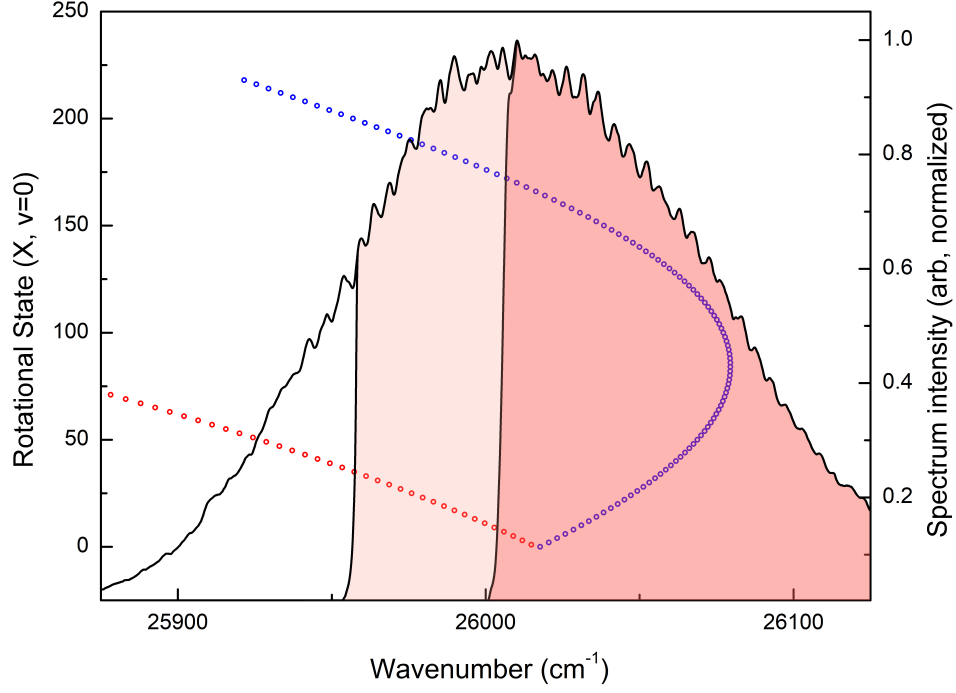


Figure 2.8: A fortrat (rotational number Vs frequency) of the $X(v = 0) \rightarrow B(v = 0)$ transition overlapped with the **Step 1**: spectrally filtered light with R branch transitions below $N = 160$ exposed and P -type transitions completely cut-off (bright orange) and **Step2**: Additional portion of the R - branch exposed to pump to even higher rotational states (light orange).

conflicts. We wait for up to 30 seconds on this step to ensure that all the SiO^+ population is pumped up to $N = 160$. In the second step, we expose some more of the R -branch beyond $N = 160$, up to say, $N = 170, 200, 220$ and so on. In the second step, the conflicting P and R -type transitions are not a problem because there is no SiO^+ population in the lower rotational states that may get pumped on the P -type transition, they have all been pumped to $N = 160$ in the first step.

2.5 Probing

For the experiments described in Chapter 3 and 4, we used different types of probe lasers. Each laser served its own purpose as outlined in detail in the following chapter, but they were all tuned to a region near ~ 225 nm for dissociation spectroscopy and ~ 385 nm for fluorescence detection attempts.

The reason for the use of several probe lasers is as follows: the $C^2\Pi$ state of SiO^+ was theoretically predicted around the 225 nm region but was yet to be experimentally discovered. Once we knew that we could prepare SiO^+ in a target state of choice, we needed a system to verify. The experimental detection of the rotational fine structure from $X^2\Sigma \rightarrow C^2\Pi$ served the dual purpose of rotationally resolved state-detection as well as spectroscopy that led to the determination of the spectroscopic constants of the Hamiltonian for the $C^2\Pi$ state.

2.5.1 Lasers used

2.5.1.1 Survey spectroscopy:

Being a broad linewidth OPO, the *Ekspla NT342/1/UVE OPO* that we used for photo-ionization also doubled up as the probe laser for surveying the dissociation spectrum of the $X^2\Sigma \rightarrow C^2\Pi$. For the purposes of the spectroscopy, the laser was used in the 213 - 225 nm region with a step-size of around $5\text{-}10\text{ cm}^{-1}$.

2.5.1.2 Rotational line resolution:

The rotational fine structure could not be resolved with the *Ekspla NT342/UVE OPO*. For this purpose, we used a dye laser *Lambda Physik Scanmate* with a resolution according to specifications of 0.15 cm^{-1} (0.3 cm^{-1} after frequency doubling to ~ 225 nm). For all ex-

periments mentioned in this thesis, we used Coumarin 450 dye with 0.15 g/L in Methanol solvent for the oscillator and 0.05 g/L in Methanol for the amplifier. We also used 0.01 M DABCO to prevent fast dye degradation [67]. It is pumped by the 355 nm, third harmonic from *Spectra Physics Quanta-Ray Pro 290*. The dye-laser was re-hauled with equivalent new motors available online, home-built control electronics for grating movement and wavelength selection, and software interfacing via LabView. We also took the doubling stage completely apart and replaced it with a combination of similar parts from another Lambda Physik laser and integrated with home-built electronics and software. New BBO crystals now occupy the doubling stage with the frequency range of the crystal centered at 225 nm. As a result of this, the laser can now tune itself on command to the desired wavelength and rotate the doubling crystal to the correct angle to produce the wavelength desired. We also realized that the stepper motor controlling the grating skips a step or two every so often, this can throw off the stored calibration of the wavelength as a function of position of the grating and result in error of 1-3 cm^{-1} . To overcome this, we pick-off a small portion of the fundamental beam before it goes into the doubling stage and sent it to a Bristol wavemeter. After reading off the wavelength from the wavemeter, we enter small adjustments to the grating position to bring it to the desired wavelength. The Bristol wavemeter is internally calibrated using a He-Ne source and is accurate to 35 MHz. Since the linewidth of the laser is more than the accuracy of the wavemeter, the wavelength reading from the wavemeter was sensitive to the alignment of the beam into the wavemeter; readings often jumped to adjacent modes. The correct mode was determined by matching with a known Ba^+ line at 224.639 nm, $5\text{D}_{3/2} \rightarrow 7\text{P}_{1/2}$ transition. Despite having most of its components replaced, this laser continues to be a work-horse in the lab.

The linewidth of the *LambdaPhysikScanmate* dye-laser was calibrated by measuring flu-

orescence depletion of Ba^+ on several transitions within the range of the dye-laser. It is small enough to resolve rotational lines, however, the calculated vibrational-states lifetime of $|C^2\Pi, (v=0)\rangle$ is on the same order of magnitude. As a result, it was uncertain whether the linewidth of the rotational lines obtained with the dye-laser was limited by the linewidth of the laser or if we were power broadening the transition. The linewidth of the laser was determined using two different Ba^+ transitions, the first one at 224.639 nm, $5D_{3/2} \rightarrow 7P_{1/2}$ and the second at 455 nm, $6S_{1/2} \rightarrow 6P_{3/2}$ (Fig. 2.9). When the Scanmate is tuned to these transitions, they remove Ba^+ from the Doppler cooling cycling transitions and therefore cause the Ba^+ cloud to go dark. When the intensity of the scanmate laser tuned close to the transition is small enough, the depletion in the fluorescing Ba^+ is slow enough to be captured by the single frequency technique detailed in Sec. 3.2.1. By plotting the decay rate of the Ba^+ fluorescence as a function of wavelength and fitting it to a Lorentzian line function, we were able to determined the linewidth of the scanmate laser's fundamental beam. The overall linewidth of the frequency doubled beam is $\sim 0.4 \text{ cm}^{-1}$.

2.5.1.3 High-resolution spectroscopy

The *MSquared SolsTis* is continuous-wave Ti:Sapph laser. It is compact, ultra-narrow linewidth, fully automated, low noise and widely tunable. It is pumped by a DPSS (diode pumped solid state laser) and can be used with up to 2 doubling cavities in series to reach deep UV wavelength range. There are pick-offs available at each stage of the laser (pump, SolsTis, doubling cavity, quadrupling cavity). The UV power at 225 nm can go up to 70-100 mW. Although, we used a nominal power of 5-10 mW for our measurements.

This laser was used both as a CW and was adapted as a 10 Hz pulsed laser with pulse widths of 500 ns - 10 μ s using a fast AOM outside the laser. The light from the quadrupling

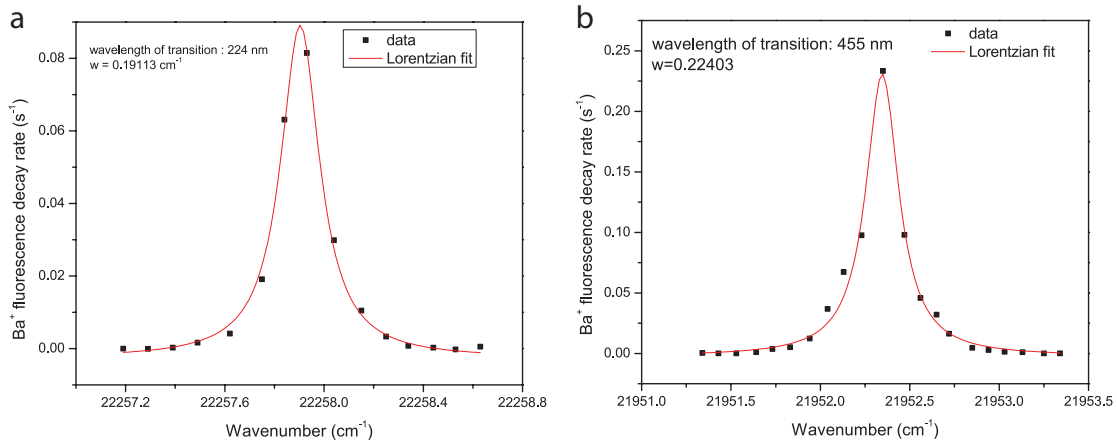


Figure 2.9: The linewidth was determined using two different Ba⁺ transitions, the first one at 224.639 nm, $5D_{3/2} \rightarrow 7P_{1/2}$ and the second at 455 nm, $6S_{1/2} \rightarrow 6P_{3/2}$. This gives the linewidth of the fundamental light from the laser, the frequency doubled light has a linewidth that is roughly double that of the fundamental.

cavity was used for dissociation measurements whereas the light from the doubling cavity was used for fluorescence spectroscopy.

The laser system has a wavemeter with a resolution of ~ 600 MHz for wavelength control. To get to an accuracy of 2 MHz, we pick off from the output of the SolsTis and fiber it to the wavemeter in the laser farm which is in a different room. We use a PID loop in combination with constant feedback in the form of an analog signal (0 - 10 V) to the ICE-BLOC of the laser to keep the wavelength to within ± 2 MHz of the set point. The 2 MHz accuracy is only required for fluorescence measurements as the expected natural linewidth of the transition is ~ 2.5 MHz. For the X-C dissociation measurements in the 225 nm region, the accuracy of the wavemeter that was bought with the laser is sufficient.

2.6 Timing Control

Many of the experiments described in this thesis require nanosecond timing of events. The bulk of the timing is done using two 5 V, 8-Channel counter/timer devices (National Instruments PCI-6602) controlled through LabView. As most of the experiments are structured around 10 Hz pulsed lasers, the timing of the experimental sequence is controlled using a 10 Hz ‘master clock’. The firing of the flash lamps and Q-switches of the three 10 Hz pulsed lasers, and the single pass AOMs of the Doppler cooling lasers, femtosecond molecular control lasers and high-resolution spectroscopy CW laser are all run on a repeated 10 Hz timing sequence with delays in reference to the 10 Hz ‘master clock’. The pulsed lasers need to run continuously to ensure stable operation, however, we don’t need the pulsed lasers to go into the trap all the time. To block the pulsed-laser beams we make use of shutters controlled with servo motors and beam blocks mounted on stepper motors to control the firing of pulsed-laser pulses into the trap.

CHAPTER 3

DISSOCIATION SPECTROSCOPY - AT AND BEYOND EQUILIBRIUM BOND LENGTHS

3.1 Introduction

Ion traps offer long storage time periods in isolation from unwanted environmental interactions. This allows for long-probing times which are often only limited by chemical reactions. As the diatomic molecule rotates, it also stretches. This results in a coupling between the rotational and vibrational degrees of freedom and the effect becomes pronounced as the molecule rotates faster. Diatomic potentials are often determined by a measurement of vibrational energies, however, it is difficult to get the molecules to states very close to dissociation and at bond-lengths far from the equilibrium. Moreover, several potential functions can give the same vibrational levels and therefore, it is necessary to account for the vibration-rotation coupling to determine how good a potential function is. The Kratzer relationship allows the estimation of centrifugal distortion constant based on the equilibrium bond distance and the force constant. The relationship is exact for a Morse potential and deviates for other realistic diatomic potentials. Determination of spectroscopic constants such as centrifugal distortion from the spectra of highly excited rotational states is an alternative way to map the potential in regions far away from equilibrium bond-lengths and by matching the estimated value from Kratzer relationship to the measured value, one can conclude about the harmonicity of the potential as well.

To measure the spectroscopic constants of a molecular Hamiltonian, it is required that there are sufficient numbers of molecules in the highly excited states so that a decent signal-to-noise ratio may be obtained through spectroscopy. About 25 rotational states of SiO^+ have appreciable population at room temperature. To populate rotational states such that the Boltzmann peak is somewhere around rotational states 60-80, the equivalent temperature is about 50000 K, which is far beyond any achievable temperatures in a laboratory experiment. One way of overcoming this is to create and sustain highly non-equilibrium distributions for long enough that spectroscopy can be performed.

Optical pumping of molecular ions offers several advantages in terms of preparing and sustaining the molecular ions in a target state of choice. Being a driven and a dissipative approach, it overcomes the disadvantages of dissipation-only techniques such as buffer gas cooling or supersonic expansion which can only populate ground states with a good efficiency. Techniques that only rely on driving the molecules to a target states such as using methods of coherent manipulation are limited by the initial spread of the distribution (*i.e*) there is no way to narrow the spread in states. Using the pulse shaping technique described in Sec. 2.4.1, we can put the SiO^+ molecules in a target-rotational state with a narrow distribution and keep them there for long enough to perform spectroscopy on the molecules. One big advantage of this method of preparing the molecules in target states is that close to 100% of the molecules are in the target state distribution (within $\Delta N \pm 2$ of the target state). So with roughly about 100 molecules in the trap, it is possible to have numbers in the range of 40-60 molecules in the target state. Coupled with the spectroscopy technique described in Sec. 3.2.1, spectroscopy with a good SNR can be performed for the molecules in high energy rotational states.

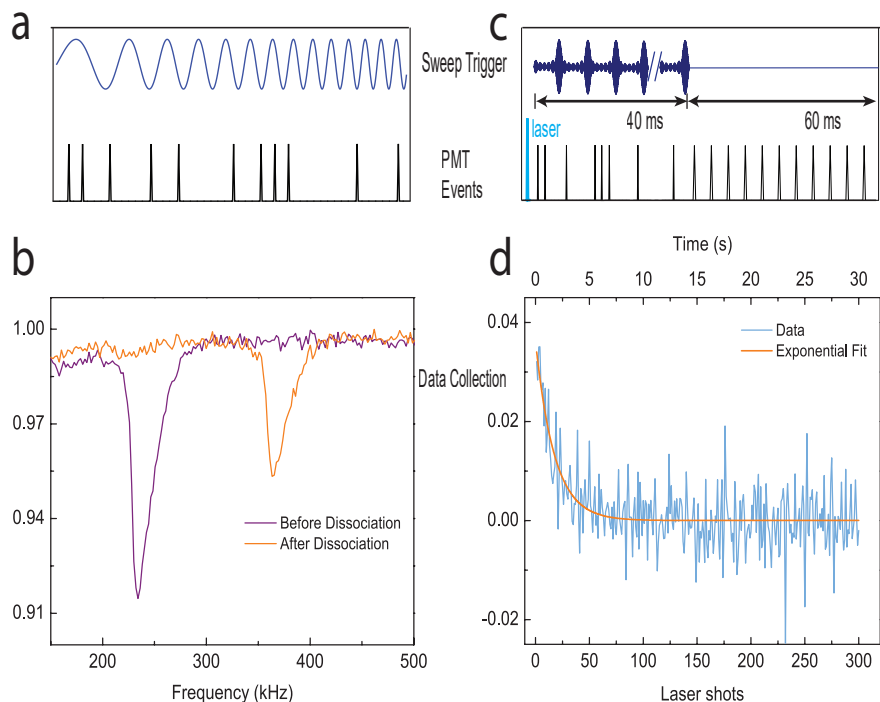


Figure 3.1: **a:** RF chirp was applied over a range of 200-550KHz for 200ms with an amplitude of 1V. **b:** 50 sweeps of the in-situ mass spectra averaged over 10 seconds recorded before and after a photo-dissociation laser pulse. **c:** A broadband waveform consisting of 8 frequencies separated by 2.5 kHz and centered at the SiO⁺ secular frequency near 230 kHz. **d:** Exponential decay of SiO⁺ depletion with time when photo-dissociation occurs, the waveform depicted in **c** is used.

3.2 Dissociation spectroscopy on the X-C transition

Once the molecules were pumped into a target rotational state, single photon spectroscopy was performed with on the $X^2\Sigma^+ \rightarrow C^2\Pi$ transition. Resonantly enhanced photodissociation is an efficient technique that has been used for state detection of molecular ions [68–70]. The $C^2\Pi$ state which was previously only predicted theoretically as $2^2\Pi$ state was detected and confirmed to exist prior to performing spectroscopy. The $C^2\Pi$ state has a double-well potential; the outer well is extremely shallow whereas the inner well is deep-enough for the

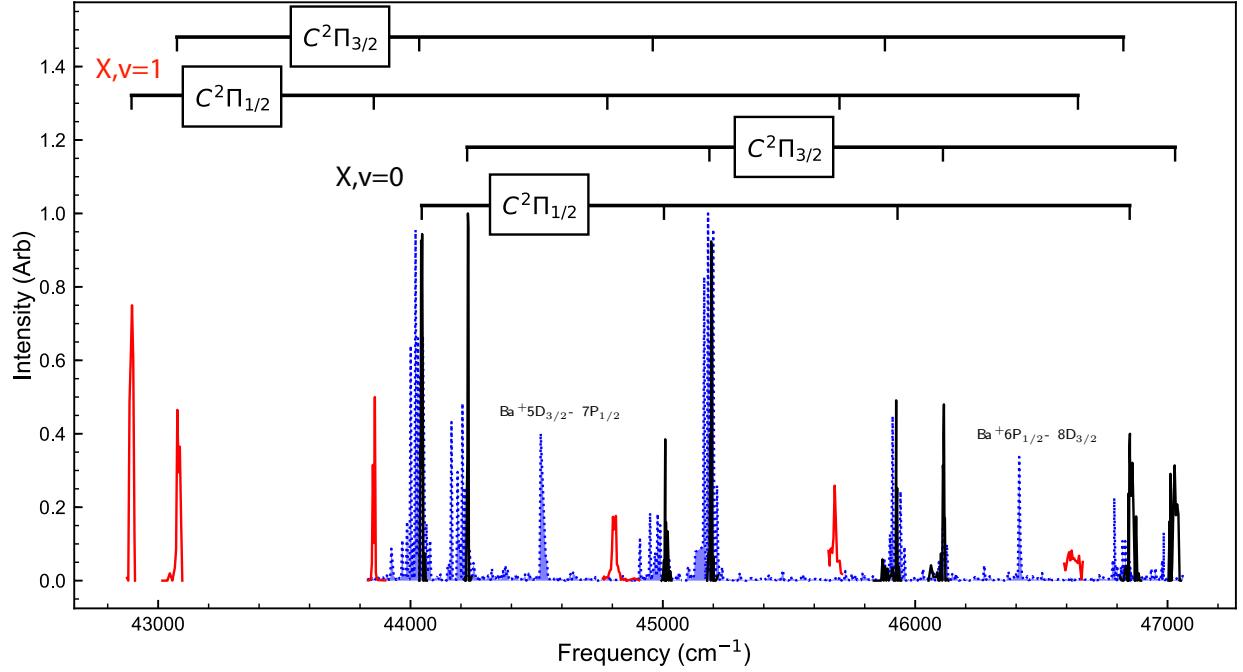


Figure 3.2: Spectrum of the $X^2\Sigma^+ \rightarrow C^2\Pi$ transition taken using a broad 0.5 cm^{-1} linewidth OPO. Transitions originating from $X^2\Sigma^+(v=0)$ to $C^2\Pi_{\Omega=1/2}(v=0, 1, 2, 3)$ and $C^2\Pi_{\Omega=3/2}(v=0, 1, 2, 3)$ are seen (Black and Blue spectrum). Blue lines represent the spectrum obtained without rotational cooling, whereas the black lines represent the spectrum after pumping to $|X, v=0, N=0\rangle$. Red lines represent the spectrum obtained by pumping SiO^+ to $|X, v=1\rangle$, figure adapted from the thesis of Patrick Stollenwerk

ground vibrational state hold about 100-120 rotational states. A single photon transition takes the SiO^+ from the $X^2\Sigma^+$ state to the inner-well of the $C^2\Pi$ state. It then undergoes pre-dissociation to form Si^+ . The pre-dissociation lifetimes are long enough to obtain rotational line resolution for the excitation from $X^2\Sigma^+$ to the inner-well of the $C^2\Pi$.

3.2.1 Single frequency LCFMS for dissociation

As pointed earlier in Sec.2.3, LCFMS is useful in detecting the presence of non-fluorescing ions in the trap. We modified the LCFMS technique to monitor the signal only around the secular frequency corresponding to SiO^+ . The applied excitation, instead of being a sinusoidal wave centered at just one frequency, was a combination of 8 different sinusoids separated by 5 KHz and centered at 235 kHz which were combined together to generate a single ‘excitation’ waveform. And hence the name, “single frequency” method. The reason for using 8 different frequencies centered around 235 kHz was that we saw the fluorescence mass spectrum shift a little as ions were dissociated and there was an addition of Si^+ ions into the Ba^+ cloud in addition to SiO^+ . We presumed that this caused some spurious couplings between the ions leading to a shift in the peak of the fluorescence mass spectrum as SiO^+ was being continuously dissociated. To overcome that, we used a combination of sinusoids of 8 different frequencies separated by 5 KHz. Also, the phase of the sinusoidal functions were appropriately set so that the resultant waveform does not have its maximum amplitude as soon as it starts. Such a sudden kick to the SiO^+ molecules heats them enough to melt the Ba^+ cloud. The phase was set so that the burst started at a low amplitude and then hit its peak.

The waveform generator was set to alternate between excitation frequency of SiO^+ (235 kHz for SiO^+) and silence (no excitation) with a duty cycle of 40% and 60% at a rate of 10 Hz. In other words, every 100 ms, there is excitation for 40 ms and silence for 60 ms. This is repeated for 300 such cycles. A probe laser (Sec.2.5.1) fires at the same repetition rate of 10 Hz. During the probing, *MaiTai* is kept on for rotational state preparation. The fraction of SiO^+ that is dissociated per pulse (depletion signal) is measured as a relative change in the fluorescence between the excitation and silence period. The entire experiment is run in

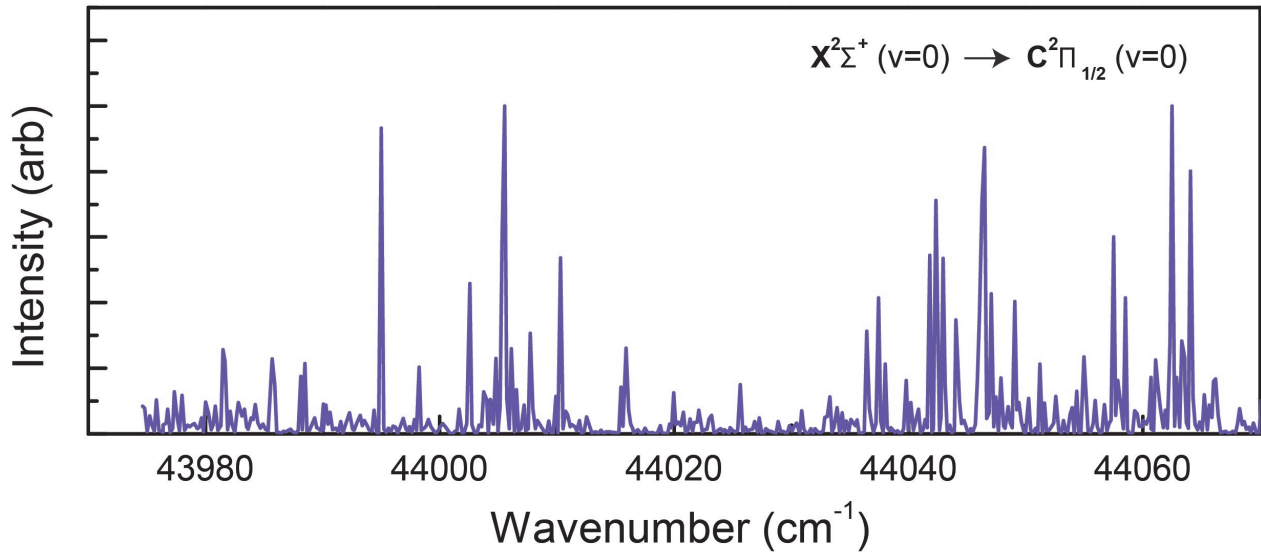


Figure 3.3: Spectrum for $X^2\Sigma^+(v=0) \rightarrow C^2\Pi_{\Omega=1/2}(v=0)$ taken using a narrow 0.3 cm^{-1} linewidth dye laser with a hope to resolve rotational transitions.

a steady-state regime where the rotational state preparation happens on a time-scale much faster than the rate of dissociation. By operating in this regime, we can guarantee that the SiO^+ that remains after one single shot of the probe laser quickly reaches the steady-state rotational distribution before the next dissociation pulse. To achieve this, the dissociation rate needs to be slow enough so that not all the molecules are destroyed in one pulse rather only a small fraction is and the rest of the molecules can once again reach steady-state in the time interval between two dissociation pulses; more on that in Sec.3.4.1.

3.3 Low - resolution vibrational spectroscopy

A survey spectrum was obtained without any optical pumping using the Ekspla OPO (ref Sec.2.5.1) as shown in Fig. 3.2. The vibrational progression of $\Omega = 1/2$ and $\Omega = 3/2$ was the first confirmation of the existence of the $C^2\Pi$ state. The uncontrolled SiO^+ population

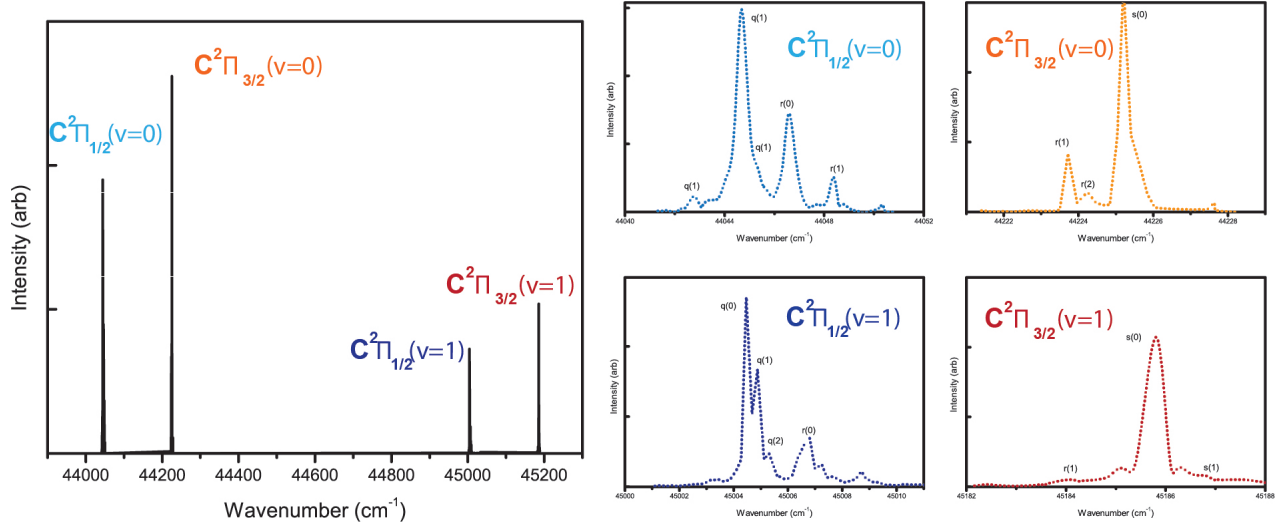


Figure 3.4: Spectrum taken after pumping SiO^+ molecules to the ground rotational state, a small fraction is in the first excited rotational state of $X^2\Sigma^+(v=0)$. The transitions are to $C^2\Pi_{\Omega=1/2,3/2}(v=0,1)$. The spectrum was obtained using Scanmate dye laser.

reflects the partially thermalized distribution due to loading via the 1+1 REMPI transition [71]. Spectra recorded using the rotationally cooled samples were used to extract band origins for all transitions that were not recorded using the more accurately and precisely determined dye laser spectrum. The red hot-bands were generated after pumping SiO^+ into the $X, v=1$ state. Upper spin orbit bands were obscured by the $X, v=0$ lower spin orbit bands and are therefore not shown. The hot-bands confirm the existence of a bound $v=4$ level for at least the lower spin orbit state. Two known Ba^+ lines, $5D_{1/2} \rightarrow 7P_{1/2}$ and $6P_{1/2} \rightarrow 8D_{3/2}$ are used to calibrate the frequency of the OPO.

Rotational resolution is not possible because the linewidth of the OPO is $\sim 4 \text{ cm}^{-1}$. Furthermore, the number of lines present near the origin depends on which spin orbit state is probed and the distribution of the rotational population. These lines are not resolvable and therefore will contribute to artificial broadening of the spectrum. Most of the lines were recorded using a noisier method instead of the less noisy single frequency method (described

in Sec. 3.4.1) and therefore the ability to fit the spectrum to an expected distribution and extract a linewidth is not feasible. The SNR of the higher vibrational levels was also reduced, likely due to a combination of weaker laser power at those wavelengths and smaller FCFs. Nevertheless, they served the purpose of confirming the existence of the $C^2\Pi$ state and pointed to the need for using lasers with narrower linewidths.

3.4 Resolution of rotational lines and Pumping to ground rotational state

The Scanmate dye laser was used in an attempt to resolve the rotational fine structure. The resulting spectrum is shown in the Fig. 3.3 below. The post-ionization distribution is expected to be clustered around $N = 4$, $N = 11$, and $N = 15$. The probing rate is expected to be comparable to the blackbody redistribution rates for the lowest of these rotational states and somewhat faster for the highest. This means that the probed distribution will be non-thermal and the observed signal size for a given rotational state will be sensitive to the precise timing of the probe laser. Furthermore, the optimal conditions for LCFMS require on order of 100 SiO^+ per sample implying that shot noise will contribute significantly. Thus we could not make sense of the observed spectrum.

By pumping to the ground rotational state using the technique in Sec. 2.4.1, spectra were obtained for transitions originating from $X^2\Sigma^+(v = 0)$ and going to both the spin-orbit states of the $C^2\Pi(v = 0)$ state, $\Omega = 1/2$ and $\Omega = 3/2$ (Fig. 3.4). Ground state preparation allowed for two orders of magnitude signal enhancement compared to thermal on measurement of transitions near the band origin and provided valuable information on the efficiency of dissociation and molecular constants describing the vibrational structure of the $C^2\Pi$ state.

The transitions to $C^2\Pi(v = 1)$ state were also measured. However, transitions to

$C^2\Pi(v = 2)$ state were out of range of the dye and therefore, we did not measure them. As reported in the forthcoming section (Sec. 3.5), they were obtained using the narrow linewidth CW laser.

From these, we were able to get obtain accurate information regarding the band-origin of $C^2\Pi(v = 0)$ and $C^2\Pi(v = 1)$, and a good estimate of the vibrational spacing and the spin-orbit splitting. By systematically measuring and assigning other lines, we were able to improve these constants further. All line assignments were performed using PGOPHER [72–74].

We obtained spectra by pumping SiO^+ to a distribution with $\Delta N = \pm 2$ around $N = 10, 25, 40, 55$ and 65 . The spectra and the expected population distribution from pumping to these target states is shown in Fig. 3.5.

3.4.1 Population in a target-state

The 10 Hz rep rate of the dissociation laser is comparable to the measured rate for achieving steady state for ground state preparation ($9(4) \text{ s}^{-1}$). The SiO^+ motional frequency was excited with a waveform consisting of 8 frequencies separated by 2.5 kHz and centered at 230 kHz.

In the steady-state regime, the observed dissociation rate depends directly on the population fraction n_i in the probed state via the relationship,

$$p_i n_i = 1 - e^{-R_i/10} \approx R_i/10 \quad (3.1)$$

where p_i is the probability of dissociating population in the i^{th} state and R_i is the observed dissociation rate in s^{-1} . To completely ensure that the dissociation rate is sufficiently slow for

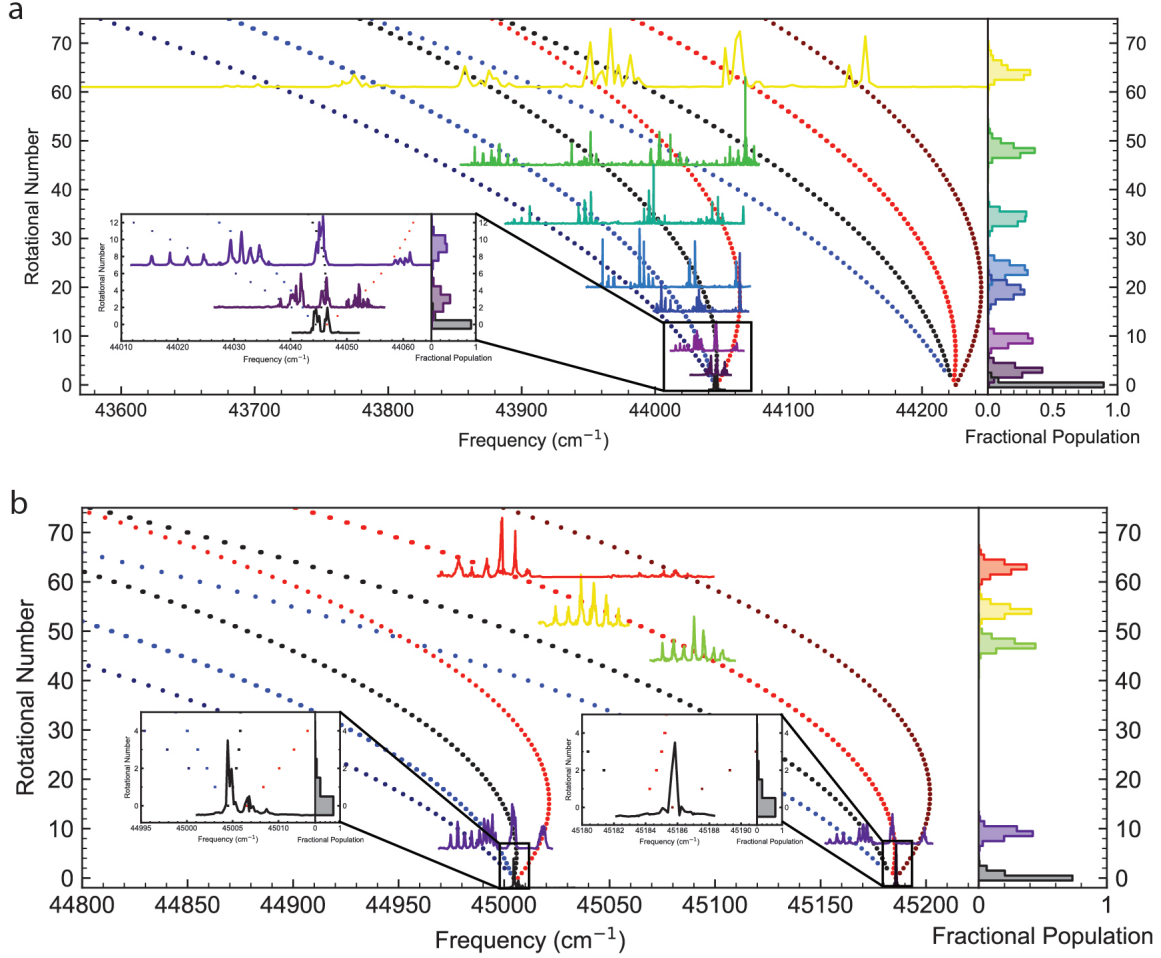


Figure 3.5: Spectrum taken after pumping SiO⁺ molecules to a distribution with $\Delta N = \pm 2$ around $N = 10, 25, 40, 55$ and 65 in $X^2\Sigma^+(v = 0)$. The transitions are to $C^2\Pi_{\Omega=1/2,3/2}(v = 0)$. The spectrum was obtained using Scanmate dye laser.

the full spectrum, the dye laser's fluence was reduced to ensure that the peak dissociation rate R_i was at least an order of magnitude less than the measured equilibration rate. If we assume that the laser intensity does not significantly vary across the spectrum, line strengths of the transitions can be factored out of dissociation probabilities for the purpose of comparing populations. In this way, relative populations can be measured with comparable SNR over

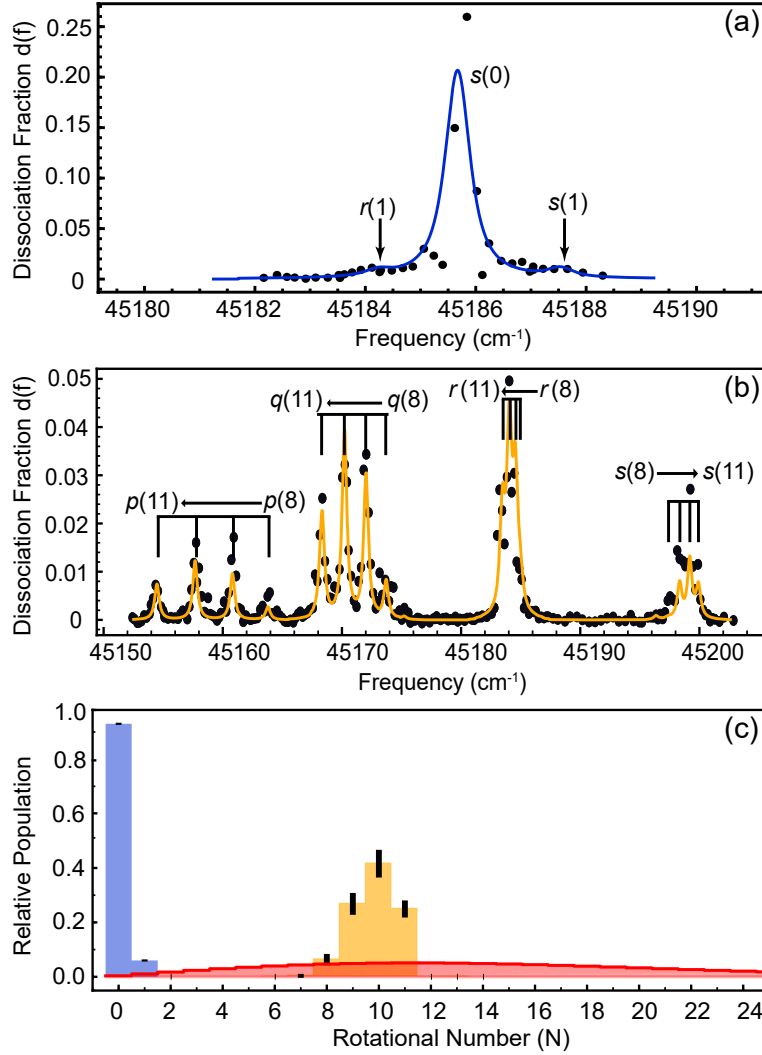


Figure 3.6: **(a)** The $X^2\Sigma^+ \rightarrow C^2\Pi_{3/2}(0, 1)$ dissociation spectrum of SiO⁺ optically pumped by the pulse-shaped spectrum to the ground rotational state. **(b)** The $X^2\Sigma^+ \rightarrow C^2\Pi_{3/2}(0, 1)$ dissociation spectrum of SiO⁺ optically pumped to $N = 8 - 11$. **(c)** The relative rotational state populations inferred by fitting the dissociation spectrum in (a) and (b) using PGO-PHER's contour fit feature are shown and compared to the thermal ($T = 293$ K) distribution in red.

a dynamic range of more than two orders of magnitude.

To obtain relative population distribution, the entire spectrum was fit using the contour

Source	T_e (cm $^{-1}$)	ω_e (cm $^{-1}$)	$\omega_e x_e$ (cm $^{-1}$)	A_e (cm $^{-1}$)
This work	44222(2)	989(3)	14.8(1.6)	181.0(2)
Theory [51]	44680	913.2	15.13	–
Theory [48]	44556	978	–	–
Theory [76]	44468.65	985.462	8.12351	153.63

Table 3.1: Molecular constants for the $C^2\Pi$ state

fit feature of PGOPHER. This only gives the relative population in states that are being fit. We ran several scans for populations in other rotational states and in the vibrationally excited state ($v = 1$) and did not find any discernable peaks in the spectrum. Moreover, we also verified the relative population percentages obtained using the PGOPHER fit with absolute measurements performed using a single-shot dissociation method detailed in Pat Stollenwerk’s thesis as well as in a published paper [75].

The observation that there is no discernable peak anywhere else can be justified on the following grounds: if there is any population in non-target rotational states in the $v = 0$, it is quickly pumped into the target states as a result of broadband optical pumping. The bigger concern is for population that undergo a rare off-diagonal decay into $v = 1$.

The vibrational frequency (ω_e) of the B state (1138 cm $^{-1}$) is slightly less than that of the X state (1162 cm $^{-1}$), which implies that the $X^2\Sigma(v) \rightarrow B^2\Sigma(v)$ band origins are red de-tuned by ~ 25 cm $^{-1}$ for each subsequent v . Consequently, the broadband spectrum we use for optical pumping covers the P -branch as well as the low- N portion of the R -branch for the first few $|X, v\rangle, |B, v\rangle$ bands with $v > 0$. Once a molecule is pumped to $v = 1$, the optical pumping light will continue to drive transitions in the $|X, 1\rangle, |B, 1\rangle$ band. The $v = 1$ lifetime was measured to be greater than 1 second, so off-diagonal decay to $v = 0$ or $v = 2$ is the dominant exit channel from $|X, v = 1\rangle \rightarrow |B, v = 1\rangle$ cycling.

The $|X, v = 2\rangle$ level is only 90 cm $^{-1}$ above $|A, v = 0\rangle$ in energy. Due to this near-

Source	$B_e(\text{cm}^{-1})$	$R_e(\text{\AA})$	$D_e \times 10^6 (\text{cm}^{-1})$	$\alpha_e \times 10^6 (\text{cm}^{-1})$	$\beta_e \times 10^6 (\text{cm}^{-1})$
This work	0.66921(15)	1.57564(18)	1.224(7)	7.15(15)	0.072(5)
Theory [51]	0.66698	913.2	—	—	—
Theory [48]	0.6439	1.604	—	—	—
Theory [76]	0.66773	1.5750	1.2263	6.60150	—

Table 3.2: Molecular constants of the $\text{C}^2\Pi$ state (cont.)

degeneracy and strong coupling, $|B, v = 2\rangle \rightarrow |A, v = 0\rangle$ borrows $\sim 10\%$ of the $(2, 2)$ band intensity. This results in a significant enhancement (calculated, $\Gamma \sim 1 \times 10^6 \text{ s}^{-1}$) over other $|B\rangle \rightarrow |A\rangle$ decay channels ($\Gamma \sim 2 \times 10^3 \text{ s}^{-1}$). From calculations, population in $|A, v = 0\rangle$ subsequently decays to $|X, v = 0\rangle$ in time-scales of a few ms. Since for $|X, v > 2\rangle$ decay to A is also energetically allowed, the calculated transition moments predict that they decay to $|A, v\rangle$ states and from there quickly return to $|X, v < 2\rangle$, with the timescale for both decays being less than 10 ms. In a nutshell, if at all there is any small population in $|X, v > 2\rangle$, it is only transitory in nature, because the rate of pumping to these states is much slower than the rate of their decay. It is highly unlikely that there is any significant steady-state population in $|X, v > 2\rangle$.

Fig. 3.6 shows the relative population in $N = 0$ and in $N = 8 - 11$ as a result of the contour fit using PGOPHER. The fit and a comparison to the thermal distribution at 300 K are also shown in the figure.

3.4.2 Pumping to high-energy super-rotor states

Using the pulse shaping technique described in Sec. 2.4.1.3, we were able to obtain rotational distributions at high energies corresponding to around $N = 170$ onward and also sustain the molecules in such highly non-equilibrium distributions for a long period of time. The spectroscopic constants for the $B - X$ transitions determined in the literature [50] are only

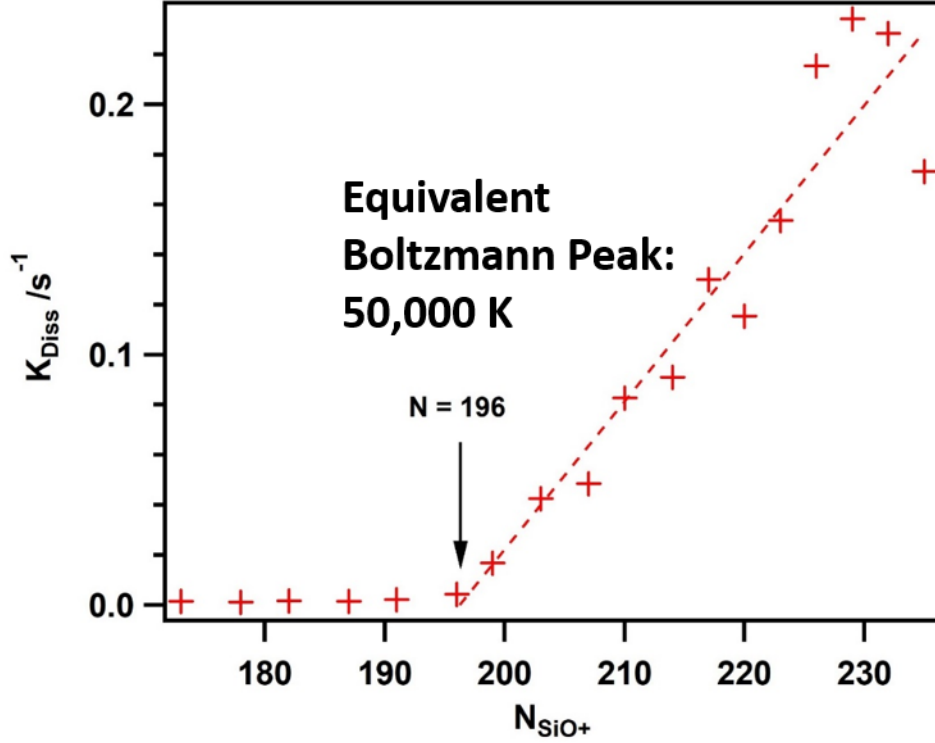


Figure 3.7: The rate of dissociation of super-rotors, the onset of dissociation is $\sim N = 196$. The X and B state Hamiltonian constants are not accurately determined for these energies and thus the rotational state is an estimate using available rotational lines data up to $N = 100$ and fitting them using additional higher order parameters. This matches well ($\Delta N \sim 2$) with the prediction from LEVEL calculations

good to around $N = 100$, thus the energies and rotational state assignments were tentatively made by refitting the data in [50] with higher order terms in the Hamiltonian. This was also corroborated with the values obtained from LEVEL calculations [77] and were found to be consistent with each other to within 4 rotational numbers. Starting from $N = 190$, we observed dissociation of the SiO^+ molecules due to the centrifugal force arising from rotating at very high speeds. We measured the dissociation rates using the LCFMS steady-state technique described in Sec. 3.2.1. This is shown in Fig. 3.7. We never measured directly (i.e. spectroscopically) what super-rotor states we populate. We had to rely on simulations

to provide an understanding of the mechanism by which we create super-rotor states. At these high-rotational energies (beyond $N = 145$), the $A^2\Pi$ is the true ground electronic state. The $A^2\Pi$ state acts as a reservoir which has little interaction with the pump laser. However, at these high rotational states, it does quickly decay to lower rotational states via spontaneous emission. Eventually it gets into more strongly interacting levels where it gets pumped to the B state and eventually lands into the X state after which it undergoes efficient pumping in the direction of higher rotational states. The strongly interacting levels could be either X levels at much lower rotational states where the order of electronic states is reversed back to normal, or perturbed rotational levels of the A state that interact with X due to spin-orbit coupling and borrow intensity from $B \rightarrow X$ transition. Therefore, A state, which is the true ground electronic state at these high rotational states, holds $\sim 90\%$ of total population, also in the form of super-rotors with a peak in the distribution in rotational states 163 – 168.

3.5 High-resolution spectroscopy with narrow linewidth CW laser

The observed linewidths of the spectrum obtained with the *Scanmate dye laser* and the *Ek-spla OPO* are a convolution between the linewidth of the laser and the lifetime of the $C^2\Pi$ state. Tunneling across the energy barrier of the quasi-bound $C^2\Pi$ state may be responsible for pre-dissociation if the life-time for this process is lesser than the radiative decay from the $C^2\Pi$ state. The average lifetime for molecules in the quasi-bound state can be estimated by calculating the classical period of a harmonic oscillator and dividing by the transmission probability at the classical turning point. Essentially, every time the vibrating nuclei reach their maximum separation, there is a probability for tunneling through the barrier and dissociation. Calculated lifetimes and line-widths from Antonio G. S. de Oliveira-Filho

and A. P. de Lima Batista are listed in the table below. With the frequency-doubled light from *Scanmate* being as broad as 0.4 cm^{-1} , it was not possible to determine if the laser was responsible for the broad linewidths or if the pre-dissociation time was faster than the estimates. To better understand, we used a narrow linewidth CW laser (*MSquared SolsTiS*) to perform dissociation spectroscopy measurements and estimate the life-times for the vibrational states of C^2H . For this purpose, we pumped the SiO^+ molecules to the ground rotational state. Since we were now working with a CW laser, it was necessary to modify the setup for dissociation spectroscopy as outlined below.

3.5.1 Setup and timing controls

The M-Squared SolsTiS was frequency-quadrupled to reach wavelengths from 210-225 nm. The laser sits on a table adjacent to the rest of the experiment and propagates in free-space to the trap. There is a quartz AOM to turn on and off the laser beam going to the trap. There are two bow-tie cavities in series that take light from the SolsTiS at near IR wavelengths and quadruple it to deep UV wavelengths. One problem with using crystals to get to frequencies in the deep UV is that the power is often not stable and tends to fall continuously over time. And the decrease is rapid enough that there is a variation of more than 10-15% during the measurement window. To overcome this problem, we setup a layman's version of a power lock where the zeroth order beam from the AOM is picked off and measured continuously using a power-meter. The time for which the AOM remains on is adjusted to ensure that the product of power and time for which the AOM is on remains constant. Since the dye-laser used for measurements previously had a repetition rate of 10 Hz, we use the same repetition rate to turn on and turn off the AOM. The product of the laser power and time

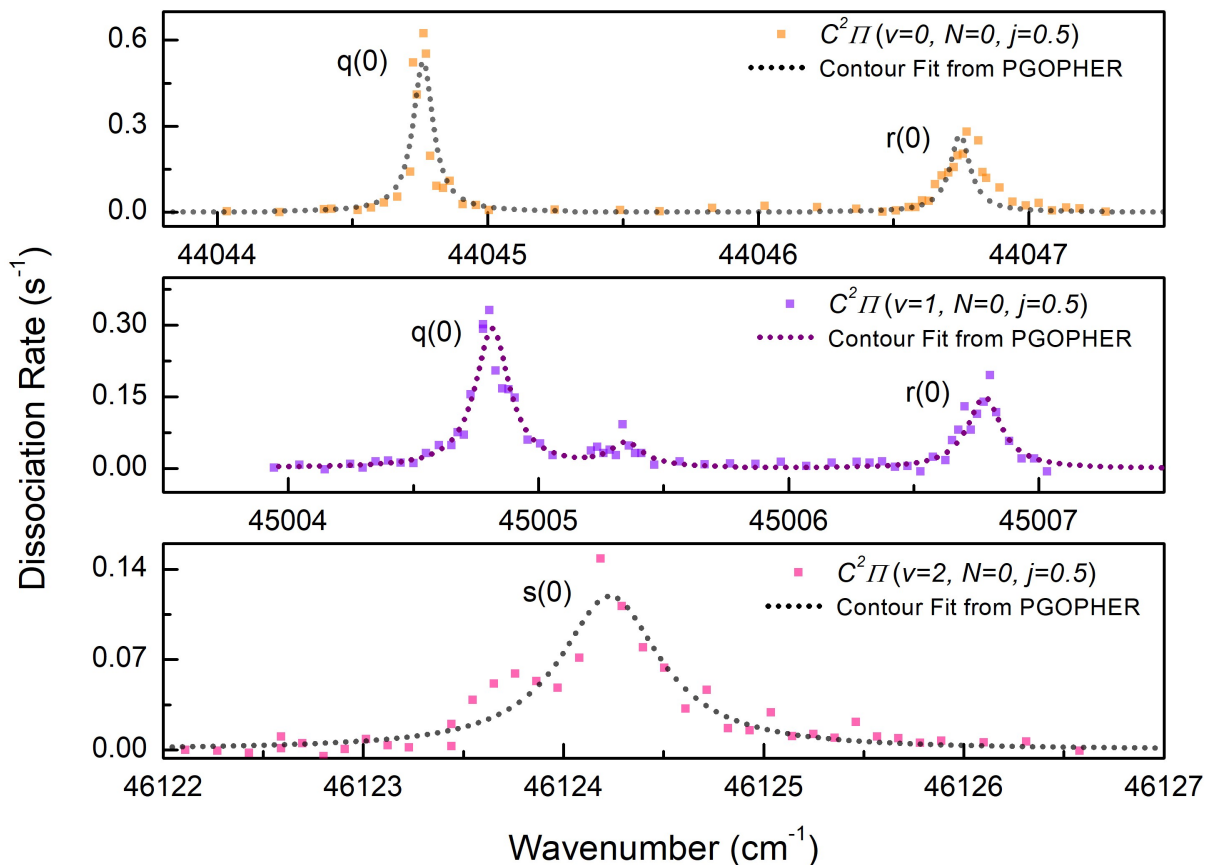


Figure 3.8: Spectrum obtained for the $X, v=0$ to $C(v=0, 1, \text{ and } 2)$ using the M-Squared SolsTiS laser which is frequency quadrupled to the desired wavelength range. Also shown is the contour fit obtained using PGOPHER to extract the line position and linewidth.

was experimentally optimized to determine a close to ideal combination so that the rate of dissociation is small enough to allow the good signal to noise ratio. (See 3.4.1 for why the rate of dissociation needs to be slow enough for a good SNR).

3.5.2 Determination of linewidth and vibrational state lifetimes

We carried out spectroscopy for transitions from $|X, v=0\rangle \rightarrow |C, v=0, 1, 2, 3\rangle$ and fit the obtained spectrum using the contour fit feature of PGOPHER to obtain the linewidth. The

v ($C^2\Pi$)	N ($C^2\Pi$)	Ω	Branch designation	Energy (cm^{-1})
0	0	0.5	q	44045.66
0	0	0.5	r	44046.56
0	0	1.5	s	44225.2
1	0	0.5	q	45004.61
1	0	0.5	r	45006.88
1	0	1.5	s	44185.78
2	0	0.5	q	45942.27
2	0	0.5	r	45944.21
2	0	1.5	s	46123.93

Table 3.3: Line positions obtained via high-resolution spectroscopy

tabulated line-widths are shown in the table alongside the theoretically calculated values.

The disagreement with theory is large and also contradictory. For the higher vibrational states, the experimentally measured value is lower than the theoretical prediction which implies that the barrier for pre-dissociation is larger and therefore the time-scales are longer for the molecules to pre-dissociate, resulting in a smaller line-width. This is also supported by the fact that we see spectral lines to $|C, v = 4\rangle$ from $|X, v = 1\rangle$ in Fig. 3.2. The existence of $|C, v = 4\rangle$ implies that the well-depth is larger than the calculated depth. However, the lifetime for the $|C, v = 0\rangle$ and $|C, v = 1\rangle$ are larger than the calculated values indicating that the predissociation is faster than what is theoretically expected. These experimental findings are at odds which suggest that either the tunnel-widths are smaller at lower energies or that there may be additional mechanisms of pre-dissociation such as via perturbations due to neighboring states.

The $C^2\Pi$ state is overlapped by several other states as seen in calculations, and perturbed interactions with these states may additionally contribute to pre-dissociation. In particular,

v, N	Calculated (cm^{-1})	Experimental (cm^{-1})	
		High-resolution	Broad OPO
0, 0	0.01	0.08(005)	0.08(1)
1, 0	0.1021	0.17(02)	0.237(16)
2, 0	2.640	0.41(03)	1.9(1.1)
3, 0	60.51	3(1)	6(3) 27(9)

Table 3.4: Calculated values of vibrational state lifetimes from Antonio G. S. de Oliveira-Filho and A. P. de Lima Batista and experimentally determined lifetimes.

there are repulsive crossings of the $(1)^2\Delta$ and $(1)^2\Sigma^-$ states in the bound region near the inner turning point around $|C, v = 1\rangle$. The strength of the perturbative interactions are determined by matrix elements.

$$W_{12} = \int \psi_1 W \psi_2 d\tau \quad (3.2)$$

The rigorous conditions for non-vanishing W_{12} are that they must have the same total angular momentum *i.e.* $\Delta J = 0$, and they must both be either positive or negative. This rules out the $(1)^2\Sigma^-1$ state. Perturbed interactions via the $(1)^2\Delta$ state is possible. The selection rules described here do not talk about the vibrational quantum number v . While there is no explicit rule, the overlap integral of the vibrational wave-function (analogous to FCF) determines the extent of perturbation. In other words, two electronic states at similar heights will perturb each other strongly only if there was a possibility to classically go from one state to another without a large alternation of the position and momentum.

The narrow line-widths that we observe using the high-resolution CW laser spectroscopy

as compared to using the pulsed laser is an indication that the line-widths observed previously are largely limited by the laser line-width. It is possible to de-convolute the experimentally obtained peak profiles using the broadband pulsed lasers to account for the laser linewidth. These results are also summarized in Table. 3.4. The values of the lifetimes obtained are consistent within the errors.

3.6 Conclusion

By selectively populating only certain states of the $X^2\Sigma^+$, we were able to de-congest the rotational spectrum and could assign rotational lines, calculate vibrational band-origins and characterize the molecular constants of the $C^2\Pi$ state. The fact that we could pump to as high as $N = 60$ and obtain the spectra associated with it enabled the characterization of higher order constants of the Hamiltonian such as the centrifugal distortion. Also, by pumping all of the SiO^+ molecules to the desired rotational target state, and by virtue of the detection technique used, the SNR of the obtained spectrum was high despite only having 20-100 SiO^+ molecules per measurement. Thus, we have successfully demonstrated the ability to discover, assign and carry out spectroscopy of states far beyond equilibrium bond-lengths by utilizing the ability to control the quantum state of the molecule.

Rotational resolution was obtained via pre-dissociation from the inner well of the $C^2\Pi$ state. The lifetimes of the vibrational states are in disagreement with theoretical calculations. The observed lifetimes indicate that there could be multiple mechanisms responsible for the pre-dissociation. While we were able to identify the lifetimes of the vibrational states with a high-precision spectroscopy laser, we could not make any conclusions on the mechanisms responsible for the pre-dissociation.

CHAPTER 4

TOWARDS FLUORESCENCE AS STATE DETECTION

4.1 Introduction

One of the biggest advantages of optical pumping as a method for control of molecular ions comes from the fact that it is easy to re-prepare a sample of molecular ions and the same set of ions can be recycled over several measurements. To effectively achieve the re-prepare and re-use technique, optical pumping is just one of the two requirements. The other requirement is a non-destructive state-readout technique. A popular form of non-destructive molecular state readout is quantum logic spectroscopy (QLS). This circumvents the issues in molecules concerning the unavailability of cycling transitions that can generate enough photons per second to achieve reasonable detection efficiencies. QLS started out as a detection technique for the single-ion Al^+ clock, where Al^+ did not have suitable transition for the electron shelving part of the state-readout process. Since then several groups working on molecular ion control have adopted variations on the QLS method for molecular state detection. Fluorescence, on the other hand, is simpler than QLS provided that there are enough photons available for a good SNR in the detection scheme. In addition, when there is a cloud of molecular ions, containing anywhere between 50-500 molecules, fluorescence coupled with optical pumping is a promising way forward for applications such as blackbody thermometry. The first attempt at some form of fluorescence on the SiO^+ molecule came from Pat Stollenwerk a long time back, when he tried the dispersed LIF technique as a means

to obtain branching fractions in SiO^+ . The effort was stopped for reasons discussed in detail in his thesis. With the certainty of being able to optically pump, and state-prepare SiO^+ , fluorescence was the next big step for SiO^+ .

4.2 Limits on the existing information on SiO^+

As discussed previously in Table.1.1, there is already substantial information available on the $X \rightarrow B$ transition. However, the big pieces of missing data are the transition wavelengths of interest to us measured at the level of precision of a few 10 MHz. There are two main transitions of interest - the $X \rightarrow B$ $R(0)$ transition and the quasi-cycling $X \rightarrow B$ $P(1)$ transition. Each have their own merits and de-merits. For a first attempt at fluorescence, we decided to proceed with the $R(0)$ transition for reasons I explain in later sections. Since the wavelength of the transition was unknown to the required accuracy, we had to make an estimate of the transition wavelength using a 6^{th} degree polynomial fit of the already existing transitions data. The fit yielded a value of 384.34937(5) nm for the $R(0)$ $X|J = 0.5(e)\rangle \rightarrow B|J = 1.5(f)\rangle$ transition.

4.3 Additions and modifications to the experimental setup

We had to make several modifications to the general experimental setup described in Chapter 2. The MaiTai was used to optically pump the SiO^+ molecules to the ground rotational state. The frequency doubled light from the M-Squared SolsTis was used to pump the SiO^+ on the $X \rightarrow B$ $R(0)$ transition.

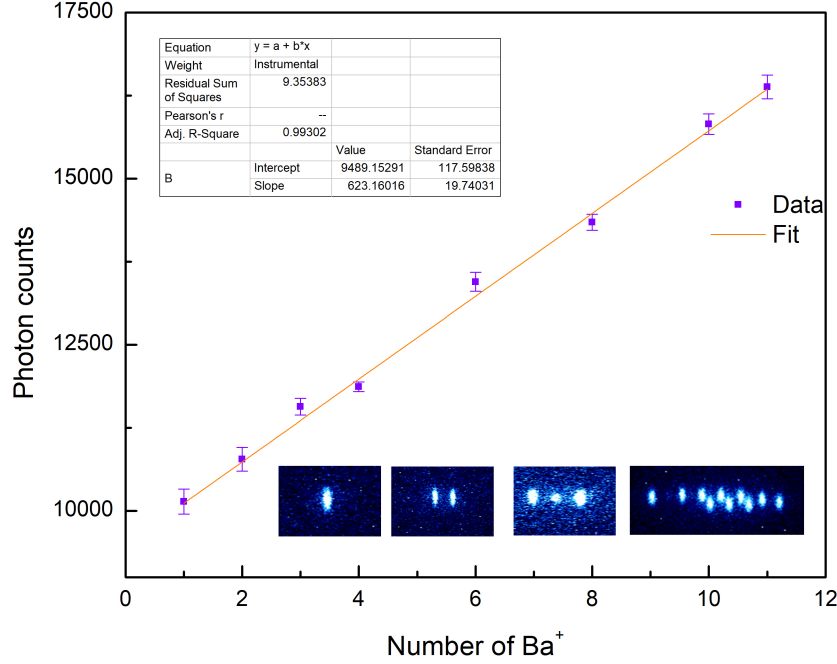


Figure 4.1: Number of photons collected as a function of Ba^+ ions in the trap. The total number of measurements were 1,000,000. The fit gives the detection efficiency of the system as 0.0623%. It should be noted that there is a 50-50 beam splitter that splits the light collected using the imaging optics to the camera and the PMT. The Hamamatsu PMT has a quantum efficiency of $\sim 25\%$ at 385 nm and $\sim 19\%$ at 493 nm. Inset shows the fit parameters and the figures at the bottom are images of 1, 2, 3, and 10 Ba^+ loaded in the trap.

4.3.1 Determination of detection efficiency

To detect the fluorescent photons, we used a Time to Digital converter attached to a PMT to obtain time-resolved measurement of the photons detected by the PMT. Before proceeding to obtain fluorescence, we determined the detection efficiency of our system using the method of deterministic pumping. In this scheme, we load a pre-determined and countable number of Ba^+ into the trap. We turn off the 650 nm laser for a period of $5\mu\text{s}$, during this time,

only the 493 nm laser is on, this results in the Ba^+ getting accumulated into the dark $5\text{D}_{3/2}$ state. After 5 μs , the 493 nm laser is turned off and the 650 nm laser is turned on for 5 μs to re-pump the Ba^+ ions to the $6\text{P}_{1/2}$ state. From the $6\text{P}_{1/2}$ state, the photons then fall back to the ground state emitting a single photon during the process. If they go back to the $5\text{D}_{3/2}$ state then they are pumped back to the $6\text{P}_{1/2}$ state. Once they fall back to the ground state they stay there as the 493 nm laser is turned off. Therefore, the number of photons emitted is then equal to the number of Ba^+ present as every Ba^+ emits only one 493 nm photon when it decays from $6\text{P}_{1/2}$ to $6\text{S}_{1/2}$. After a total time of 10 μs , both the 493 nm and 650 nm are turned back on and Doppler cooling takes place continuously for the next 90 μs . This cycle is repeated 50000 times to get enough statistics. We count the total photons detected during the window when 493 nm is turned off and plot it as a function of the number of Ba^+ to obtain the detection efficiency. The PMT is fitted with a band-pass filter of ~ 10 nm centered around 493 nm so that we do not detect photons of any other wavelength. This also gives us an estimate of the photon counts we can expect for SiO^+ .

4.3.2 Alignment of the M-Squared laser into the trap

To align a focused beam of the M-Squared laser into the trap, we use the 389.288 nm $6\text{P}_{1/2} \rightarrow 6\text{D}_{3/2}$ transition for Ba^+ . This causes the Ba^+ to go dark and we continuously repeat the process of reducing the power followed by improving the alignment to cause the Ba^+ cloud to go dark until no further optimization on the alignment can be obtained. The M-Squared beam passes through an AOM before going into the trap, and changing wavelengths changes the AOM alignment. So, after using the 389.288 nm to align, moving to other wavelengths for fluorescence measurements causes the beam to walk and thereby lose the alignment obtained with the 389.288 nm transition. This can be overcome by placing two 100 μm sized pin-holes

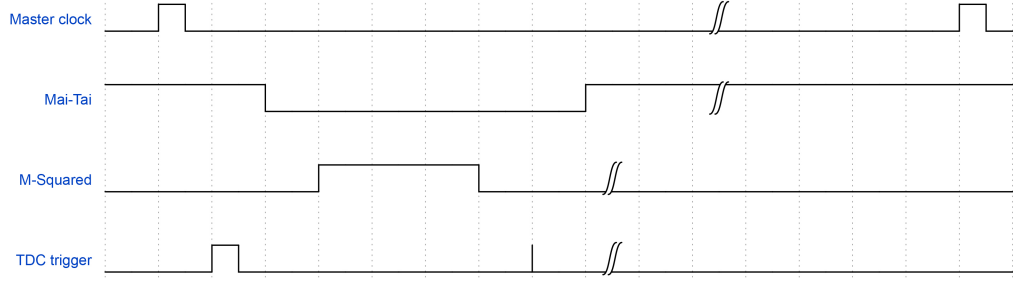


Figure 4.2: Timing diagram for fluorescence detection. M-Squared is parked at a particular wavelength and fired at an interval of 10 ms using an AOM. During the time M-Squared is on, the Mai-tai is shut off to prevent it from overwhelming the detector photon counts. The TDC is triggered before the M-Squared is turned on and provides a time-resolved measurement of the photons.

in the beam path after the AOM once the alignment to the Ba^+ crystal has been obtained at 389.288 nm. This ensures mirrors before the AOM can be used to compensate for the beam walking so that they can pass through the two pinholes before going into the trap and thereby preserving the alignment referenced using the Ba^+ crystal.

4.3.3 Locking the M-Squared Laser

The wavemeter purchased with the M-Squared laser system has an accuracy of 600 MHz and is therefore not sufficient for our purpose. To lock the laser, we used the existing wavemeter setup along with a switching AOM in the laser farm and fed back signal into the slow resonator port of the SolsTiS. This gave us a resolution of 10MHz. To lock the M-Squared laser to the laser farm wavemeter setup, we manually adjust the etalon and the resonator until the wavelength is within 50-100 MHz of the set point and then allow the PID control to take it from there and keep it within ± 2 MHz.

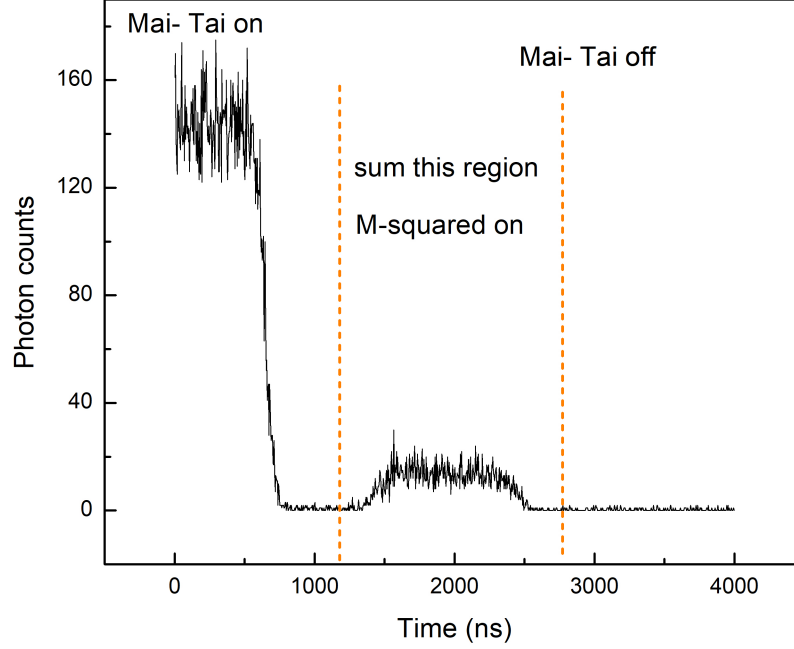


Figure 4.3: Data taken at a fixed wavelength using Method 1 for fluorescence detection. The TDC starts counting just before the Mai-Tai turns off. The photon counts registered by the TDC when the M-Squared laser is on is summed up and plotted as a function of wavelength.

4.4 Search for fluorescence

4.4.1 Method 1: M-Squared laser parked at a fixed wavelength

We adopted two different approaches to search for the fluorescence from the $R(0)$ transition. In the first method, we parked the M-Squared laser at a fixed wavelength and looked for fluorescence by cooling to $N(0)$ using the Mai-Tai and then exciting the SiO^+ on the $R(0)$ transition to look for fluorescence. During the photon-detection window the Mai-Tai is turned off. The M-Squared is kept on for a period of about $1 \mu\text{s}$, and the Mai-Tai is turned

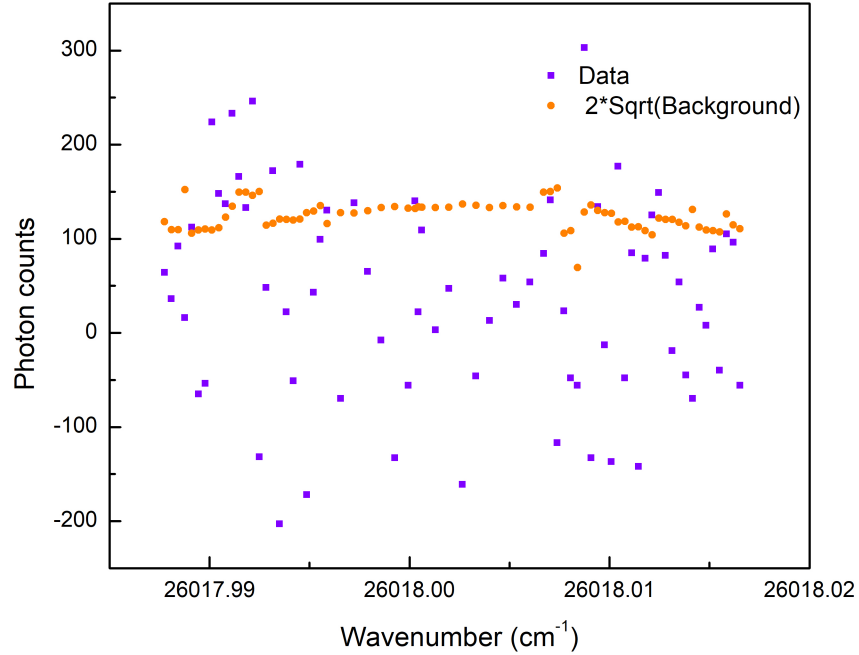


Figure 4.4: The sum of the photon counts when the M-Squared is on is plotted after background subtraction. Background is obtained in the absence of SiO^+ and accounts for the scattered photons from the M-Squared laser. The plot also shows the fluctuations in the background photons.

back on again. This is repeated at a frequency of 100 Hz for a total of 30000 times. The photon counts during the period when M-Squared is left on is inspected and compared to the background counts when there is no SiO^+ . We plot the difference between the photon counts in the presence and absence of SiO^+ as a function of the M-Squared laser excitation wavelength. The saturation intensity of SiO^+ is calculated to be $50 \mu\text{W}/\text{mm}^2$. Using the Ba^+ ions, we characterized our collection efficiency and expected an efficiency of 0.06% for SiO^+ .

This also includes the quantum efficiency of the PMT for the SiO^+ fluorescence wave-

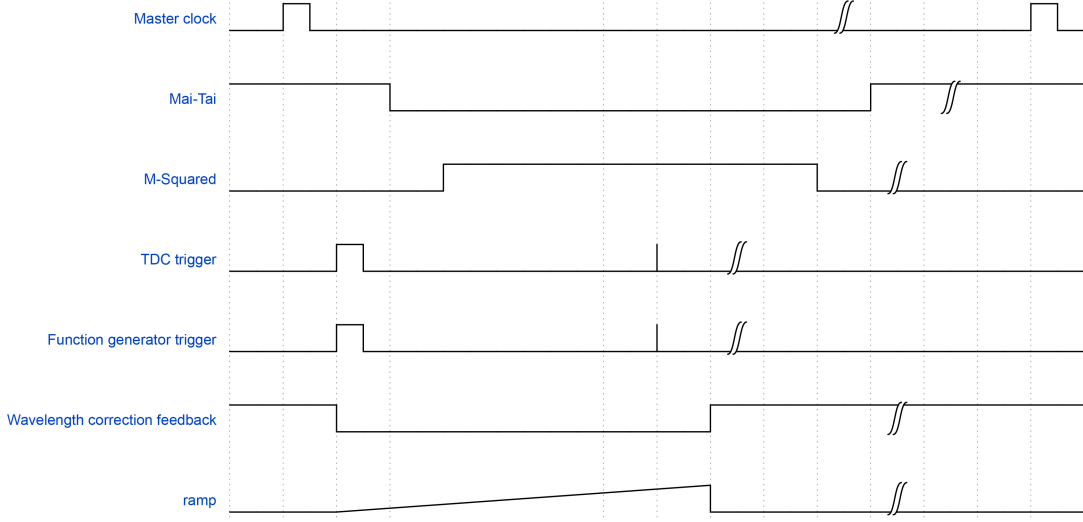


Figure 4.5: Timing diagram for fluorescence detection. M-Squared is parked at a particular wavelength and fired at an interval of 10 ms using an AOM. During the time M-Squared is on, the Mai-tai is shut off to prevent it from overwhelming the detector photon counts. The TDC is triggered before the M-Squared is turned on and provides a time-resolved measurement of the photons.

lengths (385 nm). We used an unfocused beam of $10 \mu\text{W}$ and a beam diameter of 1mm. This is roughly 20 times higher than I_{sat} (saturation intensity) of the transition, and we expect a broadening of the linewidth by 4.5 times, or roughly a linewidth of ~ 10 MHz. On average, we expect to load around 100 SiO^+ molecules into the trap and we expect to collect about 1800 photons over the course of the 30000 cycles of measurement. Our background is about 3500 photons and the fluctuations on that is about 120 photons. Thus, we expect to see a decent signal provided we hit the transition. We searched a total parameter space of about 1 GHz with a step size of 10 MHz over the course of 2-3 weeks and did not find any signal.

4.4.2 Method 2: Scanning the M-Squared

To ensure that we don't miss the transition, we decided to sweep the M-Squared laser using the fast piezo resonator input. The slow resonator input maintains the center wavelength

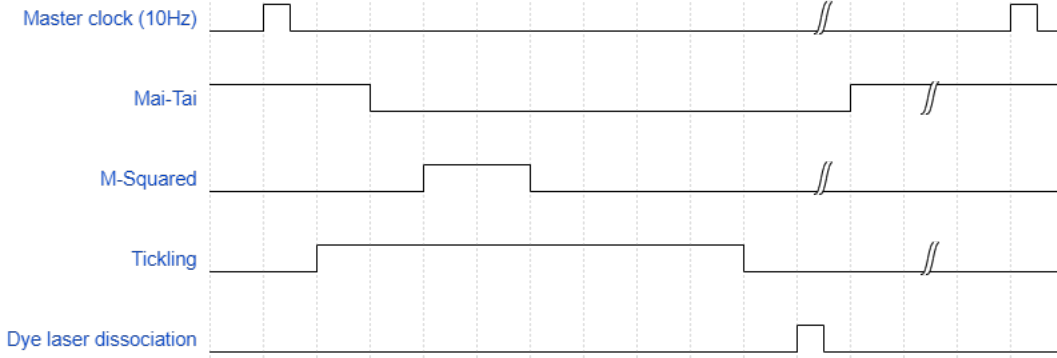


Figure 4.6: Timing diagram for the detection of $R(0)$ and $P(1)$ lines using a double resonance method - wherein, the dye laser is used to dissociate out of a state different from the initial state provided the excitation on the $R(0)$ or $P(1)$ transition using the M-Squared laser is successful.

of the scan to within ± 5 MHz and the fast resonator then scans the M-Squared by ± 50 MHz from the center wavelength. During the fast piezo scan, the slow resonator input that corrects the wavelength with feedback from the wavemeter is momentarily stopped. The fast piezo scan is achieved with the help of a trigger to the function generator and this trigger also sends in a command to the wavemeter to stop reading and correcting for the M-Squared wavelength during the scanning period. Just like the previous method, we repeat this for 30,000 times. Each cycle is 10 ms long and the sweep rate of the M-Squared is 65 MHz/ms. Each time interval recorded by the TDC corresponds to a different frequency. Furthermore, we also reduced the power in the beam significantly and focused it to reduce our background. We searched a parameter space spanning 1 GHz and did not find any signal with this method as well.

4.5 Double resonance spectroscopy - finding $R(0)$ and $P(1)$ lines

In the previous method, we were trying to hit two birds with one stone, (*i.e.*), look for fluorescence as well as get the spectral line positions of $R(0)$ and $P(1)$ lines. However, this

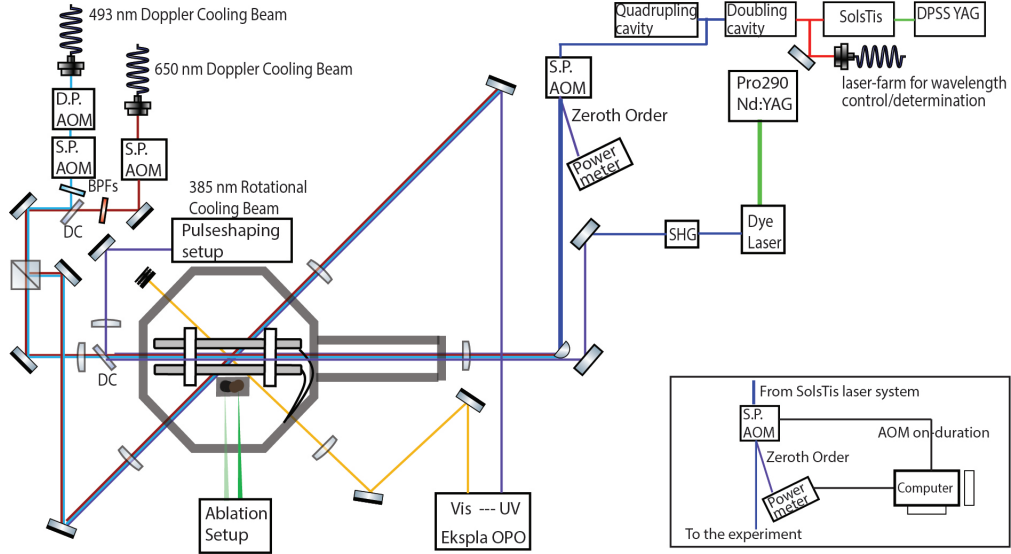


Figure 4.7: The M-Squared beam is used to excite the SiO^+ atoms either on the $R(0)$ or the $P(1)$ transition. The M-Squared is locked to an accuracy of ± 2 MHz using the wavelength locking system in the laser-farm. Since the M-squared as well as the dye-laser are required for the double resonance spectroscopy, and we propagate both the lasers axially, we use a D-mirror on the path of the dye-laser to ensure that we can also get the M-Squared laser go through the trap. To keep the power from the M-Squared beam stable, we have a layman version of a power-lock. The zeroth order beam from the AOM is continuously read and the first order power is calculated using a pre-determined factor. This is then fed into a LabView code that determines the on-duration for the AOM so that the product of power and on-duration remains a constant. This setup is shown as an inset on the bottom left.

was not very successful. In this section, we try and address the issue of finding the $R(0)$ and $P(1)$ lines using a double resonance method where the M-Squared is used to search for the $R(0)$ line. If the laser is stationed on the line, then the SiO^+ molecules will be driven either to $N = 2$ or they will fall back to $N = 0$. The SiO^+ that falls into $N = 2$, is dissociated with the Scanmate dye laser on the $|X, v = 0\rangle$ to $|C, v = 0\rangle$ transition. If the M-squared is not successful in moving the ions from $N = 0$ to $N = 2$ on the $R(0)$ transition, then there would be no molecules in $N = 2$ that can be dissociated using the Scanmate dye laser.

We looked for a dissociation signal from the dye laser using the Single Frequency method

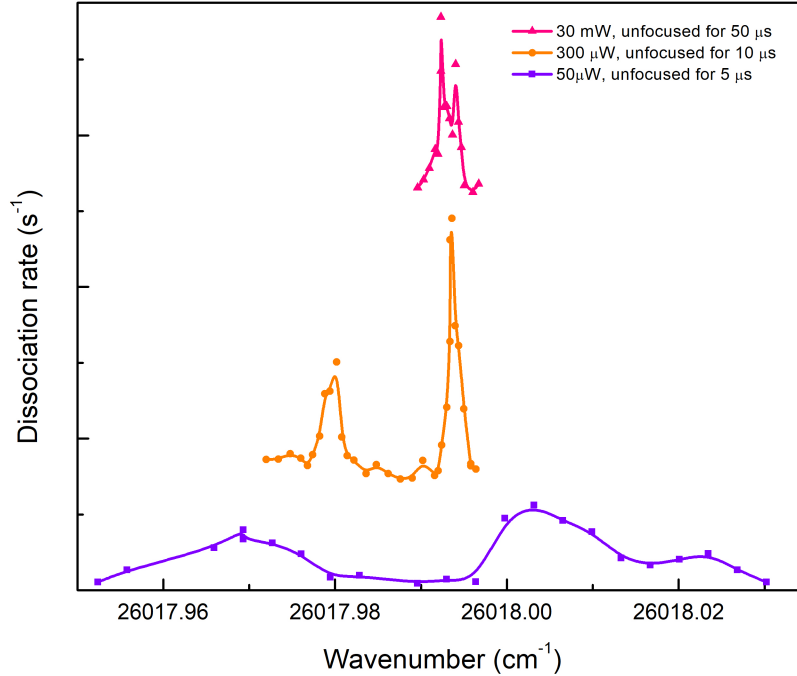


Figure 4.8: The line positions obtained for $R(0)$ using double resonance spectroscopy. The spectrum obtained using $50\mu\text{W}$ for $10\mu\text{s}$ shows a splitting in the peak. We do not understand the origin of this peak and cannot point it to any particular fine structure that we expect. One possibility is that the AOM could be causing it, however, we have not verified it.

described in 3.2. We started out with higher power on the M-Squared ($\sim 30\text{ mW}$, unfocused beam) and gradually lowered it once the transition was found. Over the course of the power reduction, the peak shifted as would be expected.

We used a similar approach to determine the $P(1)$ transition. We dissociated out of $N = 2$ in the $|X, v = 0\rangle$ state. For this purpose, the SiO^+ has to undergo a parity flipping transition via the low-lying $A^2\Pi$ state. To ensure that there is sufficient population in $N = 1$ state, we deliberately created a poor mask for the $N = 0$ state so that the opportunity for a parity flipping transition is low. This gave us about 50 % of the population in $N = 1$.

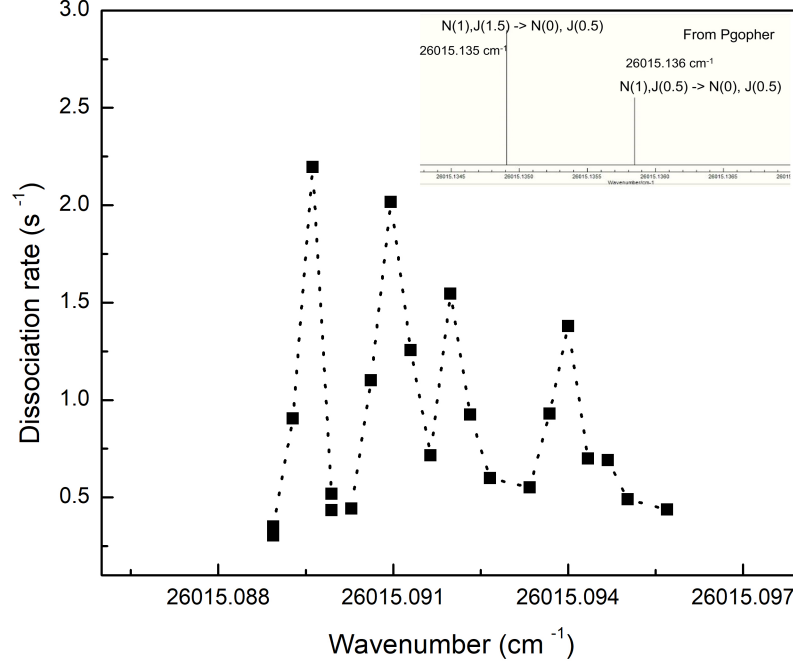


Figure 4.9: The line positions obtained for $P(1)$ using double resonance spectroscopy. The spectrum shows a splitting in the peak. We do not understand the origin of this peak and cannot point it to any particular fine structure that we expect. The inset shows the Pgopher simulation for the $X \rightarrow B$ transition and the expected lines originating from $N = 1$. We only expect to see two lines, however, there is an unexplained doubling of the lines similar to our observation in the $R(0)$ spectrum.

4.6 Summary and Further Work

Direct detection of fluorescence has proved difficult and despite some success in location the $R(0)$ and $P(1)$ transitions, it likely going to be difficult to detect fluorescence and use it as a tool for state detection. An improved imaging system with light baffles, or a more advanced trap design such as blade traps can make it a lot easier to detect fluorescence from a cloud of SiO^+ molecules co-trapped with Ba^+ in an ion trap. Once fluorescence is in place, the

next steps would be to add re-pump lasers to take optical pumping of SiO^+ into the Doppler cooling regime where enough photons are scattered per second that it can slow down the molecular motion significantly. Doppler cooling of molecular ions is perhaps not a distant imagination any more. With every small step, we are getting closer to that goal.

CHAPTER 5

REACTION KINETICS OF SiO^+ IN AN ION TRAP

5.1 Introduction

One among many long-standing goals in chemical physics has been to control chemical reactions and understand reaction pathways. Scientific curiosity backed by a plethora of possible applications have pioneered efforts towards the study of chemical reactions where all initial conditions of the reactants are known. To get to this goal, the strategy in the scientific community has been multi-pronged. Success has been obtained by cooling the reactants to ultra-cold temperatures where the speed with which molecules move around slows to the extent that it is possible to capture a reaction at its most critical stage - bond-breaking and bond-formation [78–81]. Varying the internal and external energy of the reactants and studying its effect on reaction rates is another dimension that warrants scientific understanding. Several important developments, most notably, buffer gas cooling and supersonic expansion of molecular beams have made it possible to obtain a good measure of control over the translational, electronic, and vibrational degrees of freedom in molecules. However, control of rotational motion in molecules has been a rather challenging affair. With some effort, these techniques can be used for rotational control to a certain extent but, to study chemical reactions as a function of the quantum states of the reactants, one would like to prepare the molecule in any rotational state of choice including very high “super-rotor” state energies. In other words, we would like to manipulate the molecules precisely enough to understand

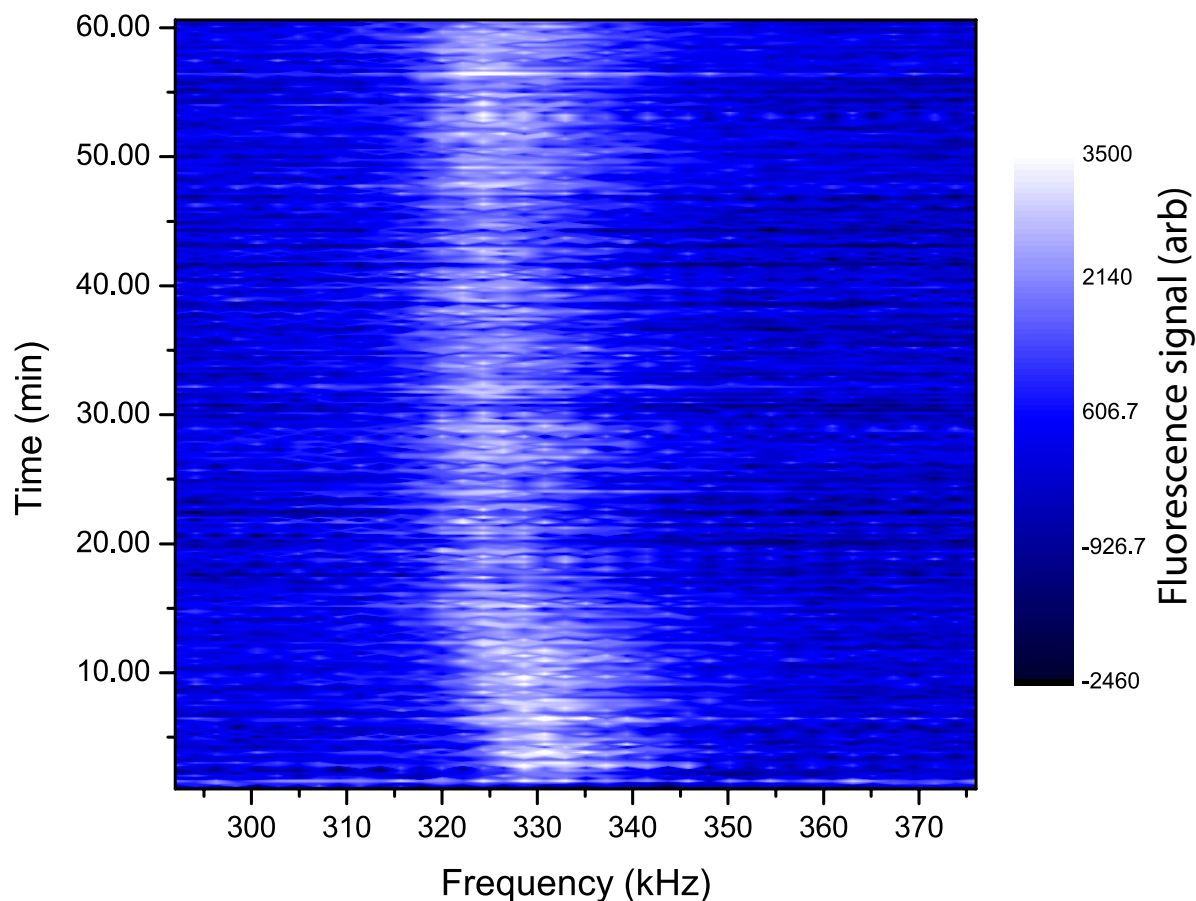


Figure 5.1: The shift in excitation frequency of the Ba^+ fluorescence dip indicates a shift in the mass over time due to H_2 reaction with SiO^+ . Each horizontal time slice is modeled by the sum of two Gaussians, one at the mass of SiO^+ ($m = 44 \mu$) and one at SiOH^+ ($m = 45 \mu$)

how an increased rotational energy of the reactants affects reaction kinetics. In a somewhat related effort, several studies have looked at collision dynamics [82–87] of molecules with high rotational energies via the use of an optical centrifuge to energize molecules to super-rotor states. Since the experiments are carried out in a dense beam, it is limited to collision dynamics only and not chemical reactions. Furthermore, being a non-dissipative technique, the efficiency of populating a target rotational state in an optical centrifuge is limited by

the spread in the initial distribution. In contrast, ion traps are an excellent place to study chemical reactions because of the long storage times of trapped ions. We recently reported results on the preparation of SiO^+ molecules centered around a target rotational state and with a narrow distribution in an ion trap [25, 75]. The target states can range from the ground state all the way to super-rotor states. With the ability to confine as well as control the quantum states of the molecular ions for a long enough duration, we now have a tool to study the dependence of chemical reaction kinetics on the internal energy of a reactant.

Extensive information about chemical kinetics and reaction rate constants, specifically at low temperatures, are required to develop chemical models that explain the composition of stars and planets and the evolution of molecules responsible for life-processes; and these often come from laboratory experiments and theoretical calculations. Neutral SiO is one of the few molecules that can survive in the interstellar medium and was first detected in interstellar clouds and subsequently from supernovae explosions. The reaction of SiO^+ with H_2 is of significance because it could play an important role in the production of interstellar SiO [88]. This was first observed by Fahey et.al [89] and the bi-molecular rate constant was measured to be $3.2(1.0) \times 10^{-10} \text{cm}^{-3} \text{s}^{-1}$.

Driven by motivations from astrochemistry and ultra-cold chemistry, we report experimental and theoretical results on the reaction kinetics of $\text{SiO}^+ + \text{H}_2 \rightarrow \text{SiOH}^+ + \text{H}$ in low rotational states of SiO^+ and compare it with the kinetics in super-rotor states.

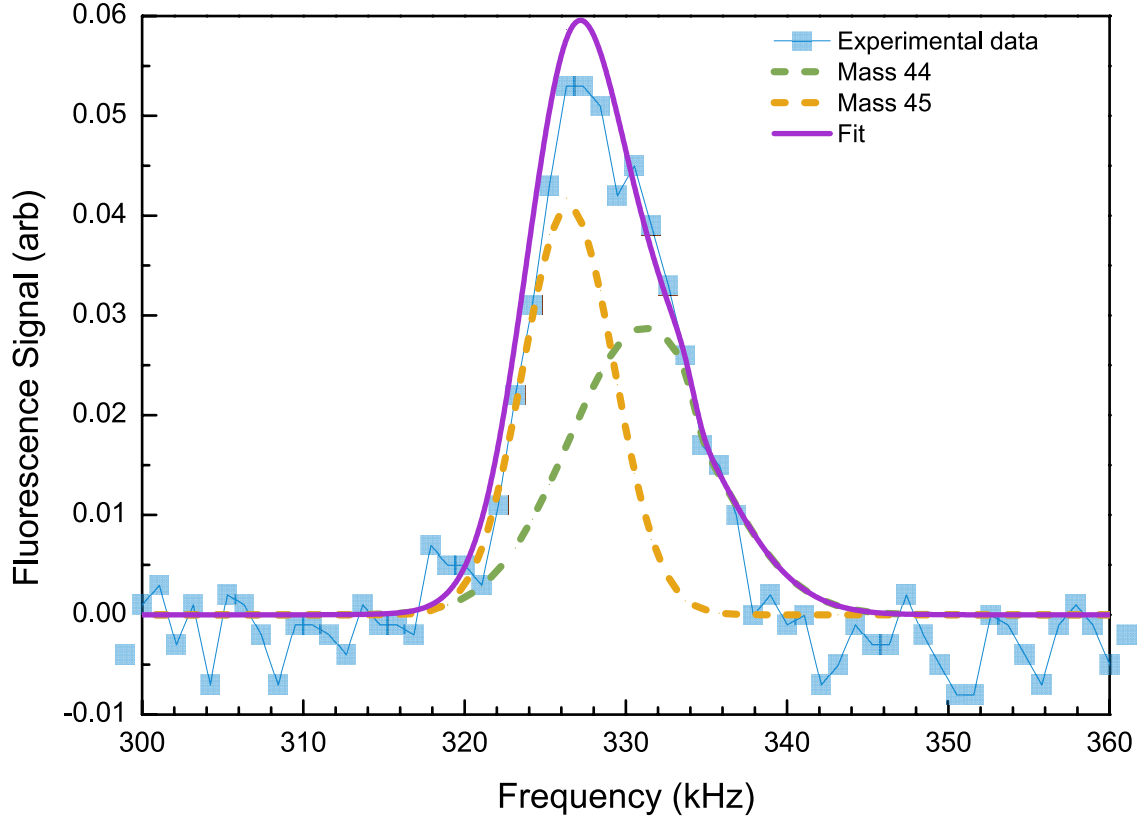


Figure 5.2: Each measurement of the secular frequency spectrum contains reacted and unreacted SiO^+ that is modeled by the sum of two Gaussians.

5.2 Setup and Data analysis

Besides using LCFMS as a tool to confirm loading of SiO^+ into the trap (Sec. 2.2.1), we also used it to monitor the reaction rate of SiO^+ with H_2 . Being small in size, H_2 gas molecules diffuse through the vacuum chamber walls more than any other gas and therefore it is the most difficult gas to remove from the vacuum chamber. As a result at ultra high vacuum levels in the chamber, H_2 typically represents 70 - 95% of the background gas in the system.

As SiO^+ reacts away to form SiOH^+ , the dip in fluorescence shifts to lower frequencies, reflecting an increase in SiOH^+ concentration (Fig. 5.1). The resolving power of LCFMS

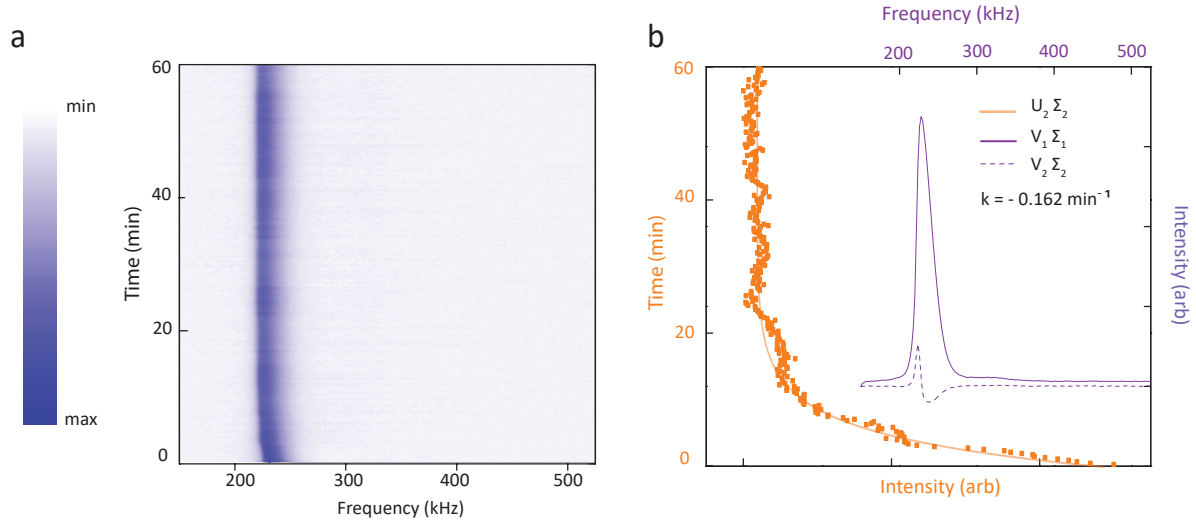


Figure 5.3: **a**: The data set obtained from the experiment. **b**: Components of the Singular value matrix that depict the overall spectrum and the change in the spectrum as a function of time.

technique in our ion trap is $\frac{m}{\Delta m} \approx 30$ and thus it cannot resolve SiO^+ (mass 44) and SiOH^+ (mass 45). However, with sufficient averaging we can detect the shift in the peak to lower frequencies.

5.2.1 Gaussian Global Fit method

We tried a few different approaches to analyzing the data from reactions. The first round of data analysis was done using a fitting routine that involved de-convolution of the fluorescence peak into two Gaussians centered around the secular frequency of SiO^+ and SiOH^+ . We fitted mass-spectra using a sum of two Gaussians, and the time dependence of the Gaussian amplitudes was fitted to an exponential rise of the one centered at the SiOH^+ frequency (corresponding to an increase in SiOH^+) and an exponential decay of the Gaussian amplitude centered around the secular frequency of SiO^+ (corresponding to a decrease in SiO^+). The exponential rise and decay were assumed to have the same time-constant reflecting the

conversion of SiO^+ to SiOH^+ . We then plotted the exponential rise/decay time constant as a function of H_2 pressure and the slope of the linear fit was used to determine the second-order rate which is the slope of the linear dependence. The method of extracting the rate constant from the slope of the linear fit of the reaction rate Vs concentration of H_2 is known as Stern-Vollmer plot. This is done because H_2 is in large excess over SiO^+ and we expect the kinetics to be (pseudo)first order.

However, we found this method to be unreliable as there were often large swings in the Ba^+ fluctuations due to drifts in frequency, on the order of a few MHz, of the lasers used to Doppler-cool Ba^+ . On rare occasions, this also led to a loss of SiO^+ ions from the trap if the drift was larger than 5 MHz and often led to estimated reaction rates that were higher than expected rates.

5.2.2 Singular Value Decomposition

To deal with the noise from fluorescence fluctuations, we used singular value decomposition (SVD) of the data to effectively isolate amplitude variations in fluorescence and mass-dependent frequency shift of the fluorescence spectrum. With sufficient averaging, and by appropriately employing SVD analysis, we inferred the rate of reaction of SiO^+ . The 2-D matrix ($\mathbf{R}$) (Fig. 5.3a) is the experimental data; it represents the depletion in Ba^+ fluorescence as function of the frequency of the chirp and time. $\mathbf{R}$ has dimensions $m \times n$, m for chirp frequency and n for time. SVD factorizes $\mathbf{R}$ such that $\mathbf{R} = \mathbf{U} \Sigma \mathbf{V}^*$ where $\mathbf{U}$ has the dimensions of $m \times m$ and $\mathbf{V}$ has dimensions of $n \times n$ and $\mathbf{U}$ and $\mathbf{V}$ are unitary matrices. Σ is a diagonal $m \times n$ matrix with the diagonal entries being ordered from the largest to smallest values. SVD of any matrix can be used to obtain a weighted and ordered sum of several constituent matrices. We now rewrite $\mathbf{R}$ as $\mathbf{R} = \sum_i \sigma_i \mathbf{U}_i \otimes \mathbf{V}_i$, where σ_i

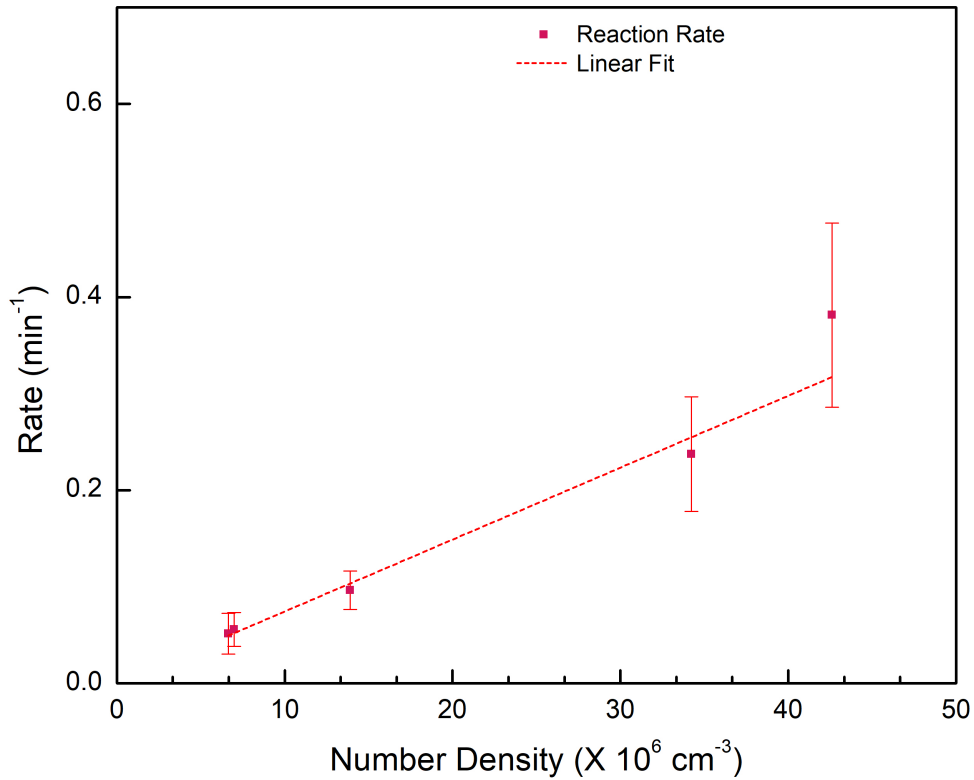


Figure 5.4: Stern-Volmer plot depicting the reaction rate as a function of H_2 number density; slope obtained from the linear fit gives us the bi-molecular rate constant for the reaction.

are the ordered values from the diagonal of Σ and $\mathbf{U}_i$ and $\mathbf{V}_i$ are i^{th} columns of $\mathbf{U}$ and $\mathbf{V}^*$ respectively. σ_i s weigh the contribution of each of the separable matrices $\mathbf{U}_i \otimes \mathbf{V}_i$ to the original matrix. Writing the original matrix in terms of its SVD decomposition reveals characteristic patterns in data that may otherwise not be noticeable due to noise and size of the data. In our case, we would like to understand the kinetics of SiOH^+ production and the consequent shift in the fluorescence spectrum to lower frequencies by isolating it from the intensity and linewidth fluctuations in fluorescence. The first few values of σ_i are

of appreciable intensity, the rest are very small positive numbers indicating that the first few elements of $\Sigma_i \sigma_i \mathbf{U}_i \otimes \mathbf{V}_i$ contribute to the actual data and the rest can be discarded without affecting the information in the data. In our case, we choose to work with the first two singular values. Fig. 5.3b represents the first two columns of $\mathbf{V}$, the blue trace is $\sigma_1 \mathbf{V}_1$ and shows the fluorescence depletion spectrum as a function of frequency. The dotted lines show $\sigma_2 \mathbf{V}_2$ which represents the change in the shape of the spectrum - the spectrum shifts to lower frequencies. The orange line is the time dependence of the frequency shift in the spectrum and that is given by plotting $\sigma_2 \mathbf{U}_2$. We fit this using an exponential function of the form $y = y_0 e^{-kt}$. The decay constant gives the rate of formation of SiOH^+ .

5.3 Experimental Results

With the SVD analysis yielding reliable reaction rates, we were able to measure the reaction rates of SiO^+ with H_2 both using uncontrolled SiO^+ as well as SiO^+ which was pumped to specific rotational states.

5.3.1 Rate constant measurement using a sample of rotationally uncontrolled SiO^+

$\text{SiO}^+ + \text{H}_2 \rightarrow \text{SiOH}^+ + \text{H}$ is a pseudo-first order reaction. The bi-molecular reaction rate constant may be obtained by plotting the reaction rates as a function of concentration of the more abundant reaction species, which in our case is H_2 . In Fig. 5.4, we plot the measured reaction rate and their uncertainties as a function of estimated H_2 concentration in the trap, also known as Stern-Volmer plot in literature. For these measurements, we did not pump the SiO^+ to any specific distribution. When we load SiO^+ into the trap, the rotational distribution is centered around $N = 12 - N = 20$. Over the course of the measurement, it is

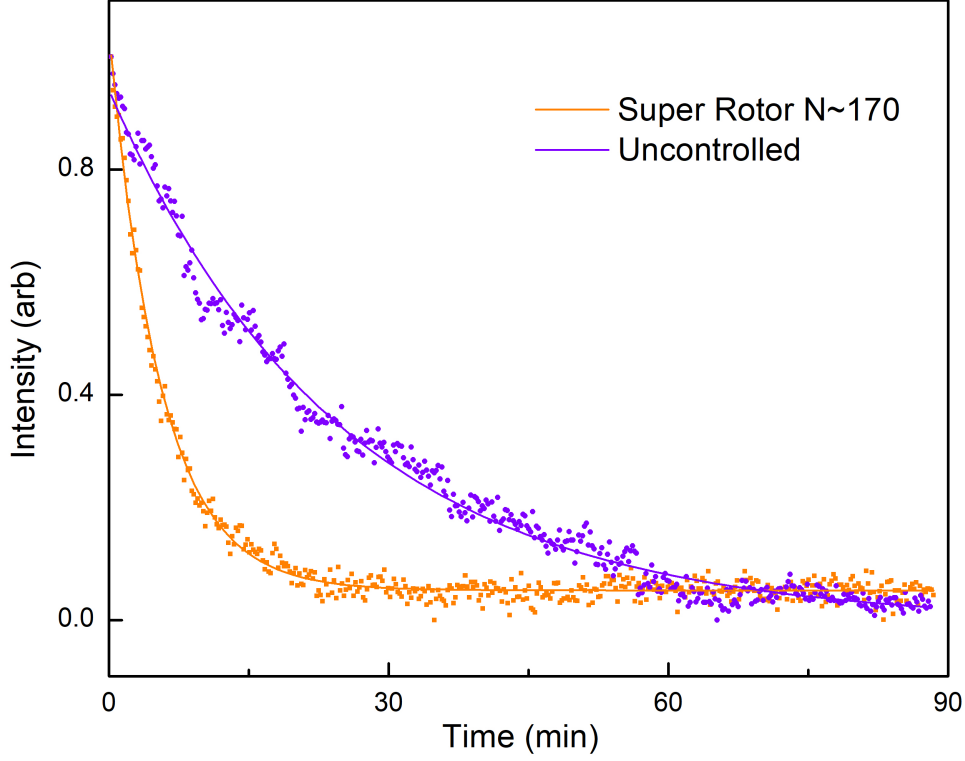


Figure 5.5: Reaction rates for SiO^+ pumped to super-rotor states compared to an uncontrolled rotational distribution of SiO^+ . A higher exponential decay constant indicates that the reaction rate is faster.

expected to equilibrate to a thermal distribution at room temperature. H_2 is the background gas in the trap and is at room temperature. The uncertainties for data points at low H_2 densities, *i.e.* at $7 \times 10^6 \text{ cm}^{-3}$ and $1.4 \times 10^7 \text{ cm}^{-3}$ are obtained from standard deviations in the sample data; for higher number densities (which were obtained by firing the titanium sublimation pump to increase H_2 concentration), only one data set was available to measure the estimated reaction rate. The error bars for these have been conservatively estimated at

30% based on the standard deviation from the data sets take an lower H_2 pressure. The slope of the straight-line extracted from the linear fit graph gives us the rate of the reaction: $1.26(\pm 0.6) \times 10^{-10} cm^{-3} s^{-1}$. The measured rate constant reported previously by Fahey et.al lies outside the 2σ value of our measurement and therefore the two measurements appear to be in discrepancy with each other. However, this is not completely surprising given that we assume the background gas in the trap to be 100% H_2 for the purposes of the calculation. There may be other Hydrogen containing gases such as CH_4 that could contribute to the reaction rate. Moreover, even if we do assume that the gas composition is by and large only H_2 , the accuracy of the ion gauge measurements could be severely limited by H_2 that desorbs and adsorbs from the walls of the trap. During the course of such adsorption/desorption process, there is a possibility that some of the H_2 may react with SiO^+ molecules. The ion gauge sensitivity to such H_2 molecules is rather low. The uncertainty in the ion-gauge is 4% at a pressure of 10^{-8} torr. At lower pressures such as at 10^{-10} torr, there could be a certain fraction of this error that stays constant regardless of the pressure and another component which could increase with a decrease in pressures. As such, we made no attempt to characterize the long term stability and uncertainty of the pressure gauge. Moreover, at UHV levels, there is also a significant portion of other molecules in the system such as water (H_2O) which have a higher gas correction factor compared to H_2 . Thus, we predict that our measurements suffer from uncertainties in these two fronts - presence of other molecules in the chamber and the uncertainty in the ion gauge reading.

5.3.2 Reaction rate of super-rotor SiO^+

We also measured the reaction rates at a number density of $7 \times 10^6 cm^{-3}$ for the uncontrolled distribution and compared it to the reaction rates when SiO^+ molecules are pumped to

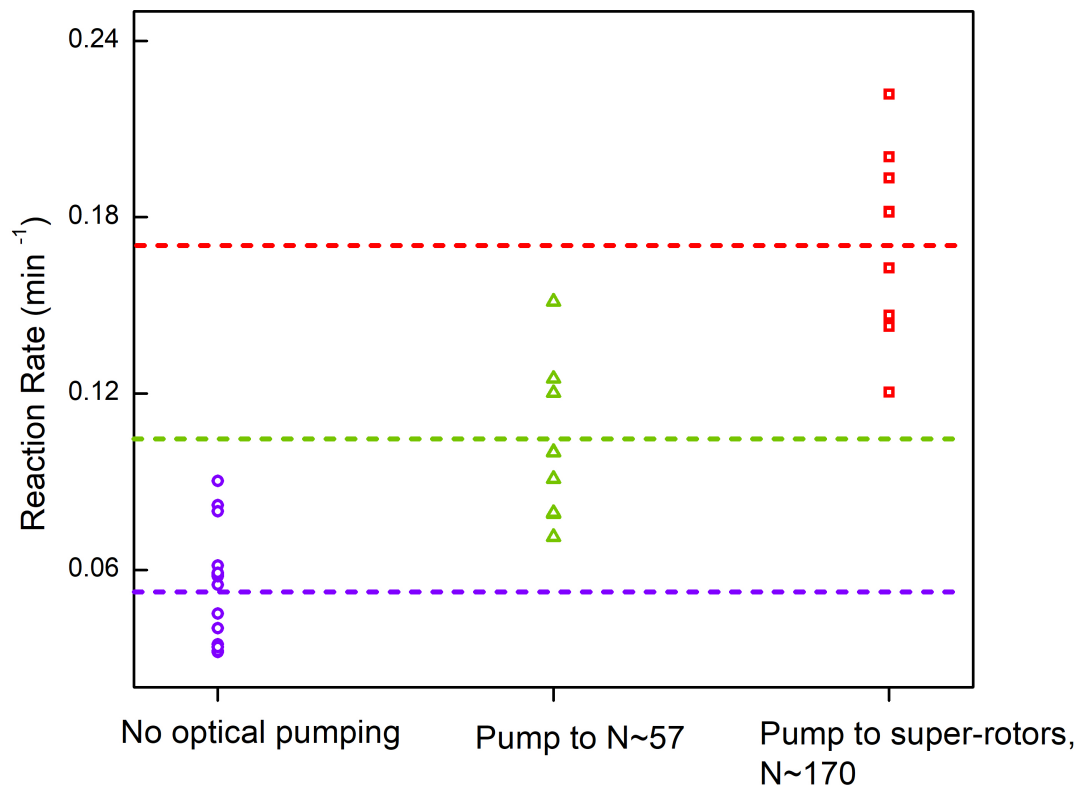


Figure 5.6: Scatter plot showing the reaction rate outcomes from repeated measurements for uncontrolled and super-rotor SiO^+ . The dotted lines indicate the average of all the measurements.

super-rotor states ($N \approx 170$) in Fig. 5.5. The reaction proceeds significantly faster when the SiO^+ is pumped to super-rotor states. We repeated this measurement several times over the course of 5 days (the variation in the pressure of H_2 during the 5-day window was within the error of the gauge). A scatter plot of the rates obtained is shown in Fig. 5.6. The average rate of reaction (indicated by the dotted lines) when the SiO^+ is pumped to super-rotor states is 0.18 min^{-1} compared to 0.05 min^{-1} for the case of the uncontrolled

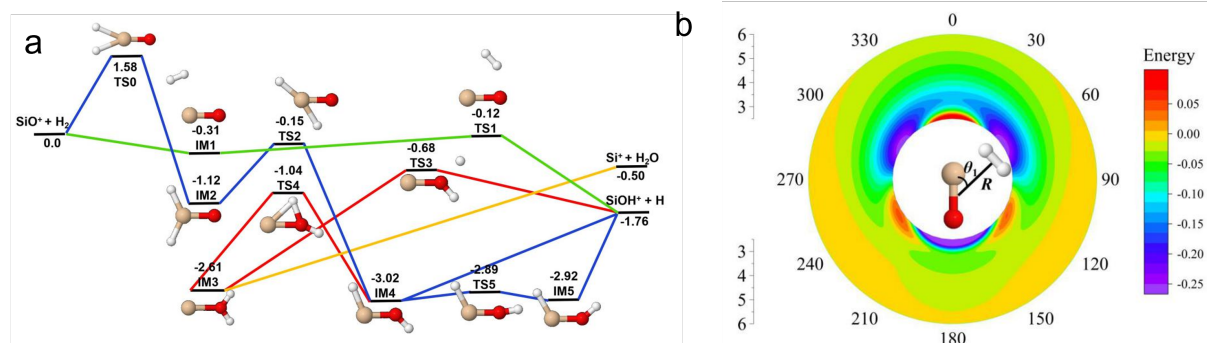


Figure 5.7: **a:** Energetics of the ground state reaction pathways for the $\text{SiO}^+ + \text{H}_2$ reaction in potential energy surface(PES), the relative energies are in eV. **b:** Contours of the PES in reactant Jacobi coordinates along R and θ_1 with fixed $r_{HH} = 0.74$ at H_2 equilibrium distances and optimized r_{SiO} , θ_2 and ϕ . The attractive potential is isotropic until $R = 4$ Å.

SiO^+ sample.

5.4 Simulations and theoretical understanding - adapted from the summary of the work done by Prof. Anyang Li and Hua Guo

The adiabatic potential energy surface (PES) for the ground electronic state of the SiOH_2^+ (X^2A) system is obtained from 20147 ab initio points at the explicitly correlated unrestricted coupled cluster singles, doubles, and perturbative triples level of theory (UCCSD(T)-F12) [90] with the explicitly correlated correlation-consistent polarized core-valence triple-zeta basis set (pCVTZ-F12),2 using MOLPRO [59]. The quasi-classical trajectory (QCT) calculations were performed using the standard technique implemented in VENUS [91].

The PES for the $\text{H}_2 + \text{SiO}^+$ has a complex topography, with multiple minima and saddle points, as shown in Fig. 5.7a. However, there is a dominant dynamics pathway leading to the abstraction of H by SiO^+ . This pathway, illustrated by the green line in Fig. 5.7a, featuring a loose pre-reaction well (IM1) with a depth of merely 0.31 eV, in which the H_2 and SiO^+

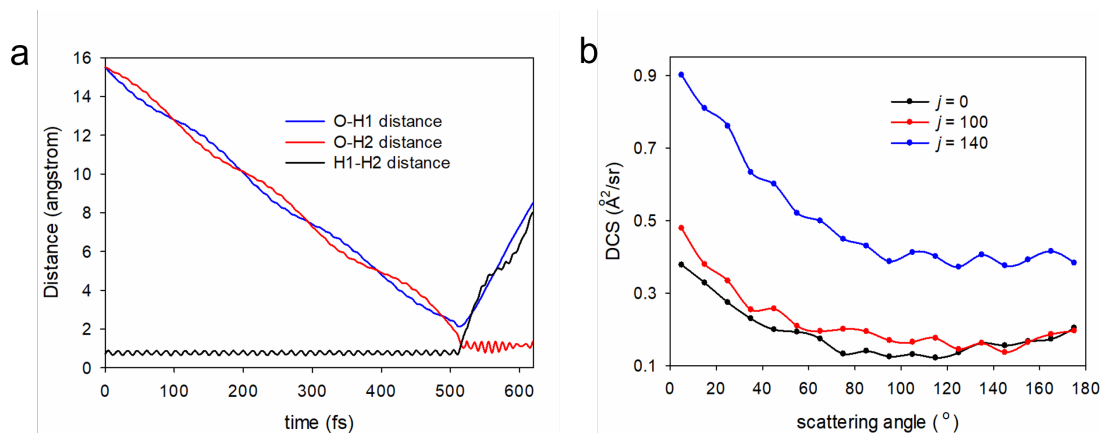


Figure 5.8: **a:** The evolution of the O-H1, O-H2 and H1-H2 distances with time from an exemplary reactive trajectory. **b:** Differential cross sections at three $J = 0, 100$ and 140

form a complex. This shallow well is present nearly isotropically around the SiO^+ moiety, as shown in Fig. 5.7b, suggesting an electrostatic nature. The H-abstraction barrier (TS1) is only 0.12 eV below the reactant asymptote, which features a partially broken H-H bond and an incipient H-O bond. Apparently, this reaction path is barrier-less with an attractive long-range interaction potential, although the submerged TS1 serves as a reaction bottleneck for large impact parameters. Beyond the barrier, the SiOH^+ product is formed exoergically. Fig. 5.8a illustrates an exemplary trajectory with the H-H and O-H distances plotted with time. The differential cross section (DCS) for the reaction is shown for three J (SiO^+) values and all indicates a forward bias in Fig. 5.8b. Most trajectories show a stripping mechanism in which the two reactants pass each other as the SiO^+ picks up the H from H_2 , leading to forward scattering.

The calculated rate coefficient as a function of the rotational excitation of SiO^+ is shown in Fig. 5.9. In agreement with experimental trend, the excitation of SiO^+ , particular above $J=120$, greatly enhances the reactivity. Quantitatively, the calculated rate overestimates the experimental values at both low and high J values but the agreement is better at intermediate

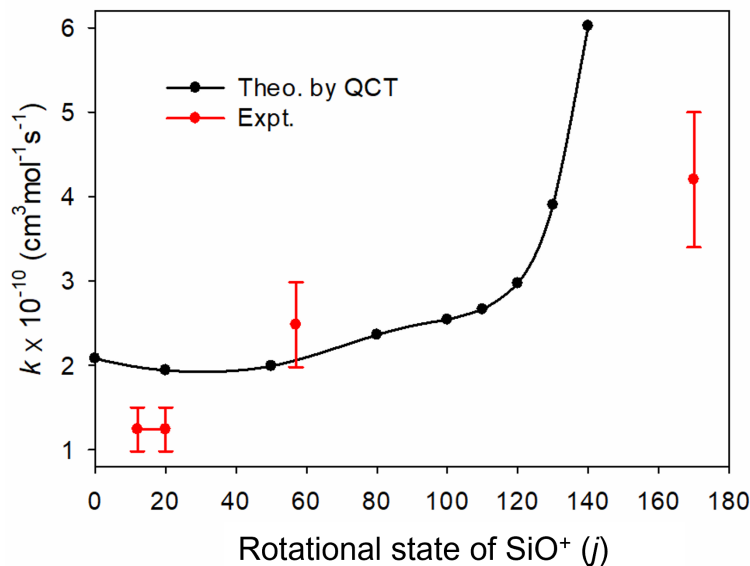


Figure 5.9: The calculated rate constants as a function of J (rotational quantum number of SiO^+), experimental data is indicated in red

value of J . The discrepancy could have several possible sources, including possible ro-vibrational coupling at high J values, involvement of excited electronic states, and remaining errors in the PES. To explain this behavior, we resort to the sudden vector projection (SVP) model [92]. In the SVP model, the ability of a reactant mode to enhance the reactivity is attributed to a large projection of its normal mode onto the reaction coordinate at the relevant transition state, in this case TS1. Table. 5.1 lists the SVP values ($0 < \zeta_i < 1$) for all the reactant modes ($i=1-5$) and it is clear that the rotation of SiO^+ has a very large value. This implies that the SiO^+ rotation is strongly coupled with the reaction coordinate at TS1 which allows facile energy flow into the reaction coordinate. Excitation of this mode thus enhances the reactivity.

mode	TS1	TS2	TS3	TS4
Rot (SiO ⁺)	0.42	0.23	0.13	0.12
Rot (H ₂)	0.08	0.32	0.32	0.02
Vib (SiO ⁺)	0.05	0.02	0.01	0.26
Vib (H ₂)	0.12	0.24	0.05	0.10
Translational	0.15	0.55	0.02	0.16

Table 5.1: SVP values for rotational and vibrational modes of SiO⁺ and H₂ projected onto the reaction coordinates at different transition states

5.5 Conclusions and Future Work

As of the day this thesis was submitted, we are characterizing the uncertainties in our analysis and our experiment. They will be a part of the journal article that is currently under progress and the article will discuss the results described in this chapter.

This work can really benefit from a more accurate determination of the chemical kinetics rates. The rates obtained here have an uncertainty in determining the concentration of Hydrogen from the ion gauge pressure. Despite that, there is clearly a relative effect in the reaction rates as a function of the rotational state of SiO⁺. Using a residual gas analyzer in conjunction with the experiment may perhaps give an accurate representation of the gas in the chamber.

CHAPTER 6

FUTURE WORK

6.1 Blackbody thermometry

Blackbody radiation (BBR) causes AC Stark shifts to clock transition states and is the largest contributors to uncertainty in most clock transitions. The frequency shift due to BBR is proportional to the difference in static polarizabilities of the clock transition states and the fourth power temperature of the trap environment [93]. For ion clocks, current best standards of uncertainty are in the Al^+ single-ion clock [94], but Al^+ is a unique system where static polarizabilities for the clock transitions are nearly equal and cancel each other to a very good extent. However, Al^+ is not easy to Doppler cool. For simpler ion based frequency references which can easily be Doppler cooled, such as Ca^+ , Yb^+ , the BBR induced Stark shift causes uncertainty on the 10^{-16} level. Knowing the BB radiation environment and temperature can bring down the uncertainty by another order of magnitude.

Diatomic molecules are good candidates for BBR thermometry as the rotational and vibrational transitions provide an opportunity to measure the BBR spectral density on resonance [95]. In SiO^+ , there is an additional low-lying electronic state, $A^2\Pi$ whose $v = 0$ lies very close to $v = 2$ in $X^2\Sigma^+$ indicated in Fig.1.1. Therefore, blackbody can also drive transitions to the A state in addition to excited vibrational levels and rotational levels in $X^2\Sigma^+$ state.

Fig.6.1 compares time-scales for various BBR in SiO^+ . For rotational levels from 0 to 15, the dominant mechanism is the electronic blackbody redistribution via the A state.

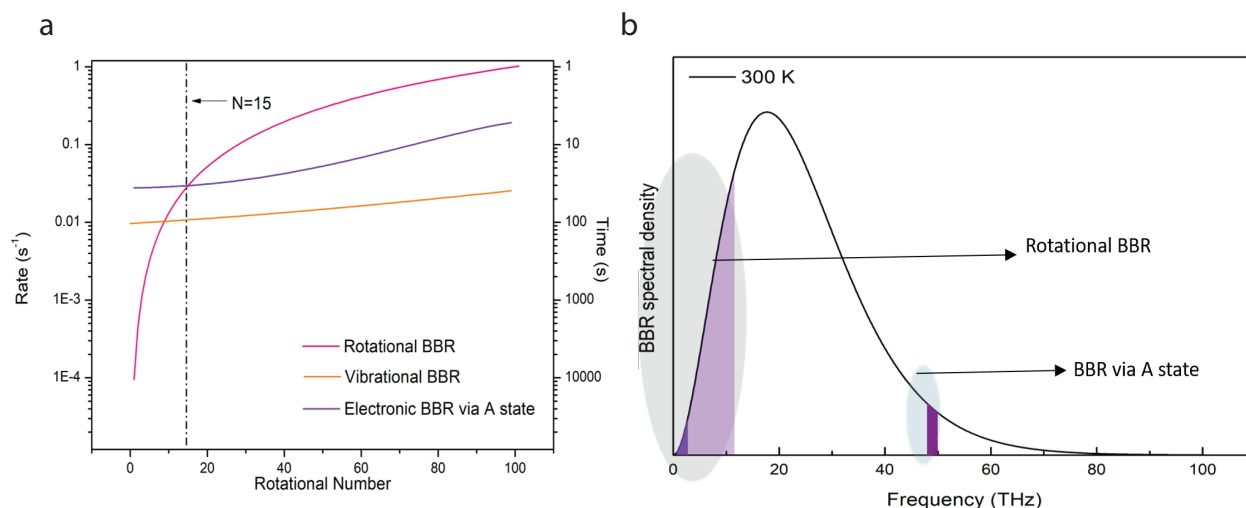


Figure 6.1: **a:** Comparison of time-scales for blackbody redistribution as a function of the rotational state occupied by SiO^+ . **b:** BBR spectrum at 300K overlapped with regions where the rotational blackbody transitions are accessible and where BBR via A state is accessible.

However from $N = 15$ on-wards, rotational blackbody redistribution is the fastest of them all. Rotational blackbody timescales being large implies that we cannot hope to equilibrate our rotational population but the control we have in terms of being able to put them into states of our choice, implies that we can probe different parts of the BBR spectrum. This has the added advantage that we may be able to say if the BBR spectrum is due to a single temperature or has multiple temperature components to it. So, the bottom line is, the sensitivity to BBR temperature is going to be much better with the ability to individually probe the BBR rate from different levels than when probing the equilibrium population distribution and fitting a single temperature spectrum.

The rotational blackbody redistribution allows us to probe the low frequency end of the BBR spectrum whereas the electronic blackbody redistribution to the A state allows us to probe the higher frequencies of the BBR spectrum. This implies that we can now create a

better spectral map and possibly provide insights on whether the blackbody spectrum in the trap is a single temperature spectrum or has multiple temperature components.

In order to probe the BBR induced-transitions, we need a state-selective method which could either be destructive probing via the C state or using fluorescence on $X - B$ channel. In addition to being a slow method, dissociation via the C state could also have problems due to the linewidth of the transition. As of now, the transition linewidth of 0.3 cm^{-1} that we observe could be due to the dye laser which is used for probing or as a consequence of the lifetime of the C state. Transition from $N = 1$ is roughly about one linewidth away. If the linewidth is due to the latter reason, then probing via dissociation could mean taking into account systematics due to off-resonant Lorentzian contribution from the neighboring $N = 1$ transition. In that case, the state-selective probing technique would have to be fluorescence measurement on the $X - B$ transition. The B state has a lifetime of $\sim 70 \text{ ns}$ and the transitions are well-separated to avoid the problem of non-resonant Lorentzian contributions. Fluorescence is however more challenging to achieve and needs further development of instrumentation and detection capabilities.

6.2 Summary and Conclusion

To summarize, the first year of my Ph.D. was devoted to working on setting up the lasers for rotational state control and detection. I then progressed to work on the applications of state control and as a part of that effort, I have demonstrated spectroscopy, progress towards fluorescence and rotational state dependent chemistry of SiO^+ . Blackbody thermometry is yet another exciting application of state control in molecular ions and is something that can be achieved once fluorescence as state detection is possible.

REFERENCES

- ¹S. Haroche, “Essay: fifty years of atomic, molecular and optical physics in physical review letters”, Phys. Rev. Lett. **101**, 160001 (2008).
- ²W. Ketterle and D. E. Pritchard, “Atom cooling by time-dependent potentials”, Physical Review A **46**, 4051 (1992).
- ³D. DeMille, “Diatomic molecules, a window onto fundamental physics”, Physics Today **68**, 34–40 (2015).
- ⁴E. R. Hudson and W. C. Campbell, “Dipolar quantum logic for freely rotating trapped molecular ions”, Physical Review A **98**, 040302 (2018).
- ⁵W. C. Campbell and E. R. Hudson, “Dipole-phonon quantum logic with trapped polar molecular ions”, arXiv preprint arXiv:1909.02668 (2019).
- ⁶R. Schmidt and M. Leshchko, “Rotation of quantum impurities in the presence of a many-body environment”, Physical review letters **114**, 203001 (2015).
- ⁷R. Schmidt and M. Leshchko, “Deformation of a quantum many-particle system by a rotating impurity”, Physical Review X **6**, 011012 (2016).

- ⁸K. R. Hazzard, B. Gadway, M. Foss-Feig, B. Yan, S. A. Moses, J. P. Covey, N. Y. Yao, M. D. Lukin, J. Ye, D. S. Jin, et al., “Many-body dynamics of dipolar molecules in an optical lattice”, *Physical review letters* **113**, 195302 (2014).
- ⁹J. Hudson, B. Sauer, M. Tarbutt, and E. Hinds, “Measurement of the electron electric dipole moment using ybf molecules”, *Physical Review Letters* **89**, 023003 (2002).
- ¹⁰D. DeMille, S. B. Cahn, D. Murphree, D. A. Rahmlov, and M. G. Kozlov, “Using molecules to measure nuclear spin-dependent parity violation”, *Physical Review Letters* **100**, 023003 (2008).
- ¹¹D. DeMille, S. Sainis, J. Sage, T. Bergeman, S. Kotochigova, and E. Tiesinga, “Enhanced sensitivity to variation of m_e/m_p in molecular spectra”, *Physical review letters* **100**, 043202 (2008).
- ¹²V. Flambaum and M. Kozlov, “Enhanced sensitivity to the time variation of the fine-structure constant and m_p/m_e in diatomic molecules”, *Physical review letters* **99**, 150801 (2007).
- ¹³M. G. Kokish, P. R. Stollenwerk, M. Kajita, and B. C. Odom, “Prospects for a polar-molecular-ion optical probe of varying proton-electron mass ratio”, *Physical Review A* **98**, 052513 (2018).

- ¹⁴V. Andreev, D. G. Ang, D. DeMille, J. M. Doyle, G. Gabrielse, J. Haefner, N. R. Hutzler, Z. Lasner, C. Meisenhelder, B. R. O’Leary, C. D. Panda, A. D. West, E. P. West, X. Wu, and A. C. M. E. Collaboration, “Improved limit on the electric dipole moment of the electron”, *Nature* **562**, 355–360 (2018).
- ¹⁵J. Kobayashi, A. Ogino, and S. Inouye, “Measurement of the variation of electron-to-proton mass ratio using ultracold molecules produced from laser-cooled atoms”, *Nature communications* **10**, 1–5 (2019).
- ¹⁶T. Zelevinsky, S. Kotochigova, and J. Ye, “Precision test of mass-ratio variations with lattice-confined ultracold molecules”, *Physical review letters* **100**, 043201 (2008).
- ¹⁷I. Manai, R. Horchani, H. Lignier, P. Pillet, D. Comparat, A. Fioretti, and M. Allegrini, “Rovibrational cooling of molecules by optical pumping”, *Physical review letters* **109**, 183001 (2012).
- ¹⁸J. M. Hutson, “Ultracold chemistry”, *Science* **327**, 788–789 (2010).
- ¹⁹M. T. Bell and T. P. Softley, “Ultracold molecules and ultracold chemistry”, *Molecular Physics* **107**, 99–132 (2009).
- ²⁰N. Balakrishnan, “Perspective: ultracold molecules and the dawn of cold controlled chemistry”, *The Journal of chemical physics* **145**, 150901 (2016).

- ²¹L. D. Carr, D. DeMille, R. V. Krems, and J. Ye, “Cold and ultracold molecules: science, technology and applications”, *New Journal of Physics* **11**, 055049 (2009).
- ²²S. Ospelkaus, K.-K. Ni, D. Wang, M. De Miranda, B. Neyenhuis, G. Quémener, P. Julienne, J. Bohn, D. Jin, and J. Ye, “Quantum-state controlled chemical reactions of ultracold potassium-rubidium molecules”, *Science* **327**, 853–857 (2010).
- ²³B. Roth, P. Blythe, and S. Schiller, “Motional resonance coupling in cold multispecies coulomb crystals”, *Physical Review A* **75**, 023402 (2007).
- ²⁴Y.-P. Chang, K. Długołęcki, J. Küpper, D. Rösch, D. Wild, and S. Willitsch, “Specific chemical reactivities of spatially separated 3-aminophenol conformers with cold Ca^+ ions”, *Science* **342**, 98–101 (2013).
- ²⁵I. O. Antonov, P. R. Stollenwerk, S. Venkataramanababu, A. P. de Lima Batista, A. G. S. de Oliveira-Filho, and B. C. Odom, “Precisely spun super rotors”, *Nature Communications* **12**, 2201 (2021).
- ²⁶M. Sinhal, Z. Meir, K. Najafian, G. Hegi, and S. Willitsch, “Quantum-nondemolition state detection and spectroscopy of single trapped molecules”, *Science* **367**, 1213–1218 (2020).
- ²⁷G. Herzberg, “Molecular spectra and molecular structure. vol. 1: spectra of diatomic molecules”, New York: Van Nostrand Reinhold, 1950, 2nd ed. (1950).

- ²⁸X. Tong, A. H. Winney, and S. Willitsch, “Sympathetic cooling of molecular ions in selected rotational and vibrational states produced by threshold photoionization”, *Physical review letters* **105**, 143001 (2010).
- ²⁹Y. Shagam and E. Narevicius, “Sub-kelvin collision temperatures in merged neutral beams by correlation in phase-space”, *The Journal of Physical Chemistry C* **117**, 22454–22461 (2013).
- ³⁰A. K. Hansen, O. Versolato, S. B. Kristensen, A. Gingell, M. Schwarz, A. Windberger, J. Ullrich, J. C. López-Urrutia, M. Drewsen, et al., “Efficient rotational cooling of coulomb-crystallized molecular ions by a helium buffer gas”, *Nature* **508**, 76 (2014).
- ³¹A. Korobenko, A. A. Milner, and V. Milner, “Direct observation, study, and control of molecular superrotors”, *Physical review letters* **112**, 113004 (2014).
- ³²K.-K. Ni, S. Ospelkaus, M. De Miranda, A. Pe’Er, B. Neyenhuis, J. Zirbel, S. Kotochigova, P. Julienne, D. Jin, and J. Ye, “A high phase-space-density gas of polar molecules”, *science* **322**, 231–235 (2008).
- ³³P. F. Sta anum, K. Højbjerg, P. S. Skyt, A. K. Hansen, and M. Drewsen, “Rotational laser cooling of vibrationally and translationally cold molecular ions”, *Nature Physics* **6**, 271 (2010).

- ³⁴J. Barry, D. McCarron, E. Norrgard, M. Steinecker, and D. DeMille, “Magneto-optical trapping of a diatomic molecule”, *Nature* **512**, 286 (2014).
- ³⁵C.-Y. Lien, S. R. Williams, and B. Odom, “Optical pulse-shaping for internal cooling of molecules”, *Physical Chemistry Chemical Physics* **13**, 18825–18829 (2011).
- ³⁶T. Schneider, B. Roth, H. Duncker, I. Ernsting, and S. Schiller, “All-optical preparation of molecular ions in the rovibrational ground state”, *Nature Physics* **6**, 275–278 (2010).
- ³⁷D. Sofikitis, S. Weber, A. Fioretti, R. Horchani, M. Allegrini, B. Chatel, D. Comparat, and P. Pillet, “Molecular vibrational cooling by optical pumping with shaped femtosecond pulses”, *New Journal of Physics* **11**, 055037 (2009).
- ³⁸D. Sofikitis, R. Horchani, X. Li, M. Pichler, M. Allegrini, A. Fioretti, D. Comparat, and P. Pillet, “Vibrational cooling of cesium molecules using noncoherent broadband light”, *Physical Review A* **80**, 051401 (2009).
- ³⁹M. Viteau, A. Chotia, M. Allegrini, N. Bouloufa, O. Dulieu, D. Comparat, and P. Pillet, “Optical pumping and vibrational cooling of molecules”, *Science* **321**, 232–234 (2008).
- ⁴⁰C.-Y. Lien, C. M. Seck, Y.-W. Lin, J. H. Nguyen, D. A. Tabor, and B. C. Odom, “Broadband optical cooling of molecular rotors from room temperature to the ground state”, *Nature communications* **5**, 4783 (2014).

- ⁴¹P. S. H.J. Metcalf, *Laser cooling and trapping* (Springer-Verige, New York, 1999).
- ⁴²Y.-W. Lin, “Towards the precision spectroscopy of a single molecular ion”, PhD thesis (Northwestern University, 2016).
- ⁴³J. Nguyen and B. Odom, “Prospects for doppler cooling of three-electronic-level molecules”, *Physical Review A* **83**, 053404 (2011).
- ⁴⁴R. Nicholls, “Franck-condon factor formulae for astrophysical and other molecules”, *The Astrophysical Journal Supplement Series* **47**, 279–290 (1981).
- ⁴⁵E. Shuman, J. Barry, D. Glenn, and D. DeMille, “Radiative force from optical cycling on a diatomic molecule”, *Physical review letters* **103**, 223001 (2009).
- ⁴⁶T. Chen, W. Bu, and B. Yan, “Structure, branching ratios, and a laser-cooling scheme for the baf 138 molecule”, *Physical Review A* **94**, 063415 (2016).
- ⁴⁷Y. You, C.-L. Yang, M.-S. Wang, X.-G. Ma, and W.-W. Liu, “Theoretical investigation of the laser cooling of a libe molecule”, *Physical Review A* **92**, 032502 (2015).
- ⁴⁸S. Chattopadhyaya, A. Chattopadhyay, and K. K. Das, “Electronic spectrum of SiO^+ : a theoretical study”, *Journal of Molecular Structure: THEOCHEM* **639**, 177–185 (2003).

- ⁴⁹R. Cameron, T. Scholl, L. Zhang, R. Holt, and S. Rosner, “Fast-ion-beam laser spectroscopy of the $b^2\Sigma^+-x^2\Sigma^+$ and $b^2\Sigma^+-a^2\Pi$ systems of SiO^+ : deperturbation analysis”, *Journal of Molecular Spectroscopy* **169**, 364–372 (1995).
- ⁵⁰S. Rosner, R. Cameron, T. Scholl, and R. Holt, “A study of the $x^2\Sigma^+$ and $a^2\Pi$ states of SiO^+ using fast-ion-beam laser spectroscopy”, *Journal of molecular spectroscopy* **189**, 83–94 (1998).
- ⁵¹Z.-L. Cai and J.-P. François, “Ab initio study of the $x^2\Sigma^+$ and $a^2\Pi$ states of the SiO^+ cation including the effect of core correlation”, *Chemical physics* **234**, 59–68 (1998).
- ⁵²R. S. Mulliken, “The isotope effect in band spectra, iv: the spectrum of silicon nitride”, *Physical Review* **26**, 319 (1925).
- ⁵³U. Bressel, A. Borodin, J. Shen, M. Hansen, I. Ernsting, and S. Schiller, “Manipulation of individual hyperfine states in cold trapped molecular ions and application to H_2^+ frequency metrology”, *Physical review letters* **108**, 183003 (2012).
- ⁵⁴R. Cameron, T. Scholl, L. Zhang, R. Holt, and S. Rosner, “Fast-ion-beam laser spectroscopy of the $b^2\Sigma^+-x^2\Sigma^+$ and $b^2\Sigma^+-a^2\Pi$ systems of SiO^+ : experiment”, *Journal of Molecular Spectroscopy* **169**, 352–363 (1995).
- ⁵⁵A. Lagerqvist, I. Renhorn, and N. Elander, “The spectrum of SiO in the vacuum ultraviolet region”, *Journal of Molecular Spectroscopy* **46**, 285–315 (1973).

- ⁵⁶E. Colbourn, J. Dyke, E. Lee, A. Morris, and I. Trickle, “The vacuum ultra-violet photoelectron spectrum of the SiO^+ ($x1\Sigma^+$) molecule”, *Molecular Physics* **35**, 873–882 (1978).
- ⁵⁷P. K. Ghosh, *Ion traps* (1995).
- ⁵⁸R. Li, X. Yuan, G. Liang, Y. Wu, J. Wang, and B. Yan, “Laser cooling of the SiO^+ molecular ion: a theoretical contribution”, *Chemical Physics* **525**, 110412 (2019).
- ⁵⁹H. Werner, P. Knowles, G. Knizia, F. Manby, M. Schütz, P. Celani, W. Györffy, D. Kats, T. Korona, R. Lindh, et al., “Molpro, version 2015.1, a package of ab initio programs, 2015”, University of Cardiff Chemistry Consultants (UC3): Cardiff (2017).
- ⁶⁰P. Stollenwerk, “Rovibrational control of a diatomic molecule”, PhD thesis (Department of Physics Northwestern University, 2020).
- ⁶¹P. R. Stollenwerk, I. O. Antonov, and B. C. Odom, “Ip determination and $1+1$ rempi spectrum of SiO^+ at 210-220 nm with implications for $\text{SiO}^+ \Gamma\{+\}$ iontraploading”, arXiv preprint arXiv:1710.08905 (2017).
- ⁶²M. Drewsen, C. Brodersen, L. Hornekær, J. S. Hangst, and J. P. Schiffrer, “Large ion crystals in a linear Paul trap”, *Phys. Rev. Lett.* **81**, 2878–2881 (1998).
- ⁶³C.M.Seck, “Quantum state control of trapped atomic and molecular ions”, PhD thesis (Department of Physics Northwestern University, 2016).

- ⁶⁴T. Baba and I. Waki, “Cooling and mass-analysis of molecules using laser-cooled atoms”, Japanese journal of applied physics **35**, L1134 (1996).
- ⁶⁵T. Baba and I. Waki, “Laser-cooled fluorescence mass spectrometry using laser-cooled barium ions in a tandem linear ion trap”, Journal of Applied Physics **89**, 4592–4598 (2001).
- ⁶⁶J. Li, J. T. Bahns, and W. C. Stwalley, “Scheme for state-selective formation of highly rotationally excited diatomic molecules”, The Journal of Chemical Physics **112**, 6255–6261 (2000).
- ⁶⁷A. N. Fletcher, R. A. Henry, M. E. Pietrak, D. E. Bliss, and J. H. Hall, “Laser dye stability, part 12. the pyridinium salts”, Applied Physics B **43**, 155–160 (1987).
- ⁶⁸K.-K. Ni, H. Loh, M. Grau, K. C. Cossel, J. Ye, and E. A. Cornell, “State-specific detection of trapped hff^+ by photodissociation”, Journal of Molecular Spectroscopy **300**, 12–15 (2014).
- ⁶⁹C. M. Seck, E. G. Hohenstein, C.-Y. Lien, P. R. Stollenwerk, and B. C. Odom, “Rotational state analysis of alh^+ by two-photon dissociation”, Journal of Molecular Spectroscopy **300**, 108–111 (2014).
- ⁷⁰K. Chen, S. J. Schowalter, S. Kotochigova, A. Petrov, W. G. Rellergert, S. T. Sullivan, and E. R. Hudson, “Molecular-ion trap-depletion spectroscopy of bacl^+ ”, Physical Review A **83**, 030501 (2011).

- ⁷¹P. R. Stollenwerk, I. O. Antonov, and B. C. Odom, “Ip determination and 1+ 1 rempi spectrum of sio at 210–220 nm in an ion trap: implications for sio+ ion trap loading”, *Journal of Molecular Spectroscopy* **355**, 40–45 (2019).
- ⁷²C. M. Western, “Pgopher: a program for simulating rotational, vibrational and electronic spectra”, *Journal of Quantitative Spectroscopy and Radiative Transfer* **186**, Satellite Remote Sensing and Spectroscopy: Joint ACE-Odin Meeting, October 2015, 221–242 (2017).
- ⁷³C. M. Western and B. E. Billinghurst, “Automatic and semi-automatic assignment and fitting of spectra with pgopher”, *Phys. Chem. Chem. Phys.* **21**, 13986–13999 (2019).
- ⁷⁴C. M. Western, “Pgopher: a program for simulating rotational, vibrational and electronic spectra”, *Journal of Quantitative Spectroscopy and Radiative Transfer* **186**, 221–242 (2017).
- ⁷⁵P. R. Stollenwerk, I. O. Antonov, S. Venkataramanababu, Y.-W. Lin, and B. C. Odom, “Cooling of a zero-nuclear-spin molecular ion to a selected rotational state”, *Phys. Rev. Lett.* **125**, 113201 (2020).
- ⁷⁶D. Shi, W. Li, W. Xing, J. Sun, Z. Zhu, and Y. Liu, “Mrci study on electronic spectrum of several low-lying electronic states of the sio+ cation”, *Computational and Theoretical Chemistry* **980**, 73–84 (2012).

- ⁷⁷R. J. Le Roy, “Level: a computer program for solving the radial schrödinger equation for bound and quasibound levels”, *Journal of Quantitative Spectroscopy and Radiative Transfer* **186**, 167–178 (2017).
- ⁷⁸M.-G. Hu, Y. Liu, D. D. Grimes, Y.-W. Lin, A. H. Gheorghe, R. Vexiau, N. Bouloufa-Maafa, O. Dulieu, T. Rosenband, and K.-K. Ni, “Direct observation of bimolecular reactions of ultracold krb molecules”, *Science* **366**, 1111–1115 (2019).
- ⁷⁹M.-G. Hu, Y. Liu, M. A. Nichols, L. Zhu, G. Quémener, O. Dulieu, and K.-K. Ni, “Nuclear spin conservation enables state-to-state control of ultracold molecular reactions”, *Nature Chemistry* **13**, 435–440 (2020).
- ⁸⁰Y. Liu, M.-G. Hu, M. A. Nichols, D. Yang, D. Xie, H. Guo, and K.-K. Ni, “Precision test of statistical dynamics with state-to-state ultracold chemistry”, *Nature* **593**, 379–384 (2021).
- ⁸¹Y. Liu, M.-G. Hu, M. A. Nichols, D. D. Grimes, T. Karman, H. Guo, and K.-K. Ni, “Photo-excitation of long-lived transient intermediates in ultracold reactions”, *Nature Physics* **16**, 1132–1136 (2020).
- ⁸²X. Tong, D. Wild, and S. Willitsch, “Collisional and radiative effects in the state-selective preparation of translationally cold molecular ions in ion traps”, *Physical Review A* **83**, 023415 (2011).

- ⁸³A. A. Milner, A. Korobenko, J. W. Hepburn, and V. Milner, “Effects of ultrafast molecular rotation on collisional decoherence”, *Physical review letters* **113**, 043005 (2014).
- ⁸⁴A. Korobenko, A. A. Milner, and V. Milner, “Direct observation, study, and control of molecular superrotors”, *Physical review letters* **112**, 113004 (2014).
- ⁸⁵L. Yuan, S. W. Teitelbaum, A. Robinson, and A. S. Mullin, “Dynamics of molecules in extreme rotational states”, *Proceedings of the National Academy of Sciences* **108**, 6872–6877 (2011).
- ⁸⁶H. M. Ogden, T. J. Michael, M. J. Murray, Q. Liu, C. Toro, and A. S. Mullin, “The effect of co rotation from shaped pulse polarization on reactions that form c2”, *Phys. Chem. Chem. Phys.* **21**, 14103–14110 (2019).
- ⁸⁷M. J. Murray, H. M. Ogden, and A. S. Mullin, “Importance of rotational adiabaticity in collisions of co2 super rotors with ar and he”, *The Journal of Chemical Physics* **148**, 084310 (2018).
- ⁸⁸J. Turner and A. Dalgarno, “The chemistry of silicon in interstellar clouds”, *The Astrophysical Journal* **213**, 386–389 (1977).
- ⁸⁹D. Fahey, F. Fehsenfeld, E. Ferguson, and L. Viehland, “Reactions of si+ with h2o and o2 and sio+ with h2 and d2”, *The Journal of Chemical Physics* **75**, 669–674 (1981).

- ⁹⁰G. Knizia, T. B. Adler, and H.-J. Werner, “Simplified ccsd(t)-f12 methods: theory and benchmarks”, *The Journal of Chemical Physics* **130**, 054104 (2009).
- ⁹¹X. Hu, W. L. Hase, and T. Pirraglia, “Vectorization of the general monte carlo classical trajectory program venus”, *Journal of Computational Chemistry* **12**, 1014–1024 (1991).
- ⁹²H. Guo and B. Jiang, “The sudden vector projection model for reactivity: mode specificity and bond selectivity made simple”, *Accounts of Chemical Research* **47**, 3679–3685 (2014).
- ⁹³M. S. Safronova, “The search for variation of fundamental constants with clocks”, *Annalen der Physik* **531**, 1800364 (2019).
- ⁹⁴S. M. Brewer, J.-S. Chen, A. M. Hankin, E. R. Clements, C. W. Chou, D. J. Wineland, D. B. Hume, and D. R. Leibbrandt, “ $^{27}\text{Al}^+$ quantum-logic clock with a systematic uncertainty below 10^{-18} ”, *Phys. Rev. Lett.* **123**, 033201 (2019).
- ⁹⁵J. Koelemeij, B. Roth, and S. Schiller, “Blackbody thermometry with cold molecular ions and application to ion-based frequency standards”, *Physical Review A* **76**, 023413 (2007).

VITA

Journal Publications

- ***Sruthi Venkataramanababu***, Ivan Antonov et.al, Reaction kinetics of a rotating molecular ion, manuscript under preparation
- Ivan Antonov, Patrick Stollenwerk, ***Sruthi Venkataramanababu***, Ana P. de Lima Batista, Antonio G. S. de Oliveira-Filho, Brian Odom, Precisely Spun Super Rotors, Nature Communications, 2021
- Patrick Stollenwerk, Ivan Antonov, ***Sruthi Venkataramanababu***, Yen-Wei Lin, Brian Odom, Cooling of a Zero-Nuclear-Spin Molecular Ion to a Selected Rotational State, Phys.Rev.Lett, 2020

Conference presentations (Talks)

- ***Sruthi Venkataramanababu***, Ivan Antonov, James Dragan, Patrick Stollenwerk, Anyang Li, Hua Guo, Brian Odom, Reaction Kinetics of SiO^+ and H_2 in an ion trap, MCAW, Purdue University, 2021
- ***Sruthi Venkataramanababu***, Ivan Antonov, Patrick Stollenwerk, Brian Odom, Quantifying rovibrational control in a molecular ion, APS DAMOP 2020, Portland (Talk, virtual)
- ***Sruthi Venkataramanababu***, Ivan Antonov, Patrick Stollenwerk, Brian Odom, Black-body Thermometry with Quantum State Control of Trapped SiO^+ , APS DAMOP 2019, Milwaukee (Talk)
- ***Sruthi Venkataramanababu***, Ivan Antonov, Patrick Stollenwerk, Brian Odom, Characterizing Molecular Ions for Laser Control, 73rd International Symposium on Molecular Spectroscopy, 2018, University of Illinois Urbana-Champaign (Talk)

Leadership Positions

- **2018 - 2021:** Applied physics graduate student council, Northwestern University

- **2020 - 2021:** Applied physics diversity and inclusion committee member, Northwestern University
- **2018 - 2022:** Lab safety manager, Odom molecular ion and atom trapping group, Northwestern University
- **September 2018 - Jan 2019:** Lead photographer and organizing committee member: APS CUWiP 2019, Northwestern University

Certifications and Volunteering

- Science Writing Program jointly offered by the Medill School of Journalism and Science in Society, Fall 2020
- Certificate in Research Communication from Research Communication Training Program at Northwestern University, Summer 2019
- Volunteer at Serve 901, Memphis, Tennessee. Alternate spring break spent in various activities such as organizing the libraries at public schools, cleaning a graveyard, helping Streets Ministries, Memphis organize an event, help with planting at Landmark urban farms.
- Volunteer at Splash, Northwestern - short courses on fascinating topics not usually taught in schools offered to high-school students in Chicagoland. I designed and taught a course called, 'Of Quantum Among Other Things'