University of Nevada, Reno

Rotation, Rotation, Rotation

A study of rotational motion for the purpose of selectivity, control, and application

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Physics

by

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Abstract

This thesis describes three projects related to the general study of control of molecular rotation.

The first project discussed probes the preferred sense of rotation of NO fragments generated from the UV photodissociation of nitrosobenzene. Photodissociation experiments involving nitrosoalkanes show the rotational orientation of the generated fragments has a significant preference for $\mathbf{v} \perp \mathbf{j}$ velocity-angular momentum vector correlation. Experiments by Keßler et al. proposed the possibility that the aryl compound nitrosobenzene may show a preference for the opposite $\mathbf{v} \parallel \mathbf{j}$ vector correlation. Experimental testing of this proposal here shows a measurable preference for the NO fragment to emerge from the parent molecule with a $\mathbf{v} \parallel \mathbf{j}$ recoil trajectory after the UV photodissociation of nitrosobenzene. Determination of the bipolar moment, $\beta_0(22)$, which quantifies the degree of $\mathbf{v} \perp \mathbf{j}$ correlation, gave an average value of 0.22, with an average standard deviation of 0.11. This demonstrates an uncommon $\mathbf{v} \perp \mathbf{j}$ fragment trajectory for UV photodissociation experiments.

The second project investigated the possibility of directly controlling the sense of rotation of molecules by imparting rotational orientation via absorption of circularly polarized light. Simulations which calculated the degree of rotational orientation and alignment of model, symmetric, prolate rigid rotors demonstrated theoretical feasibility. As part of the same simulation, the amount of internal vibrational energy stored over the course of many photon absorptions predicted significant photodecomposition in a simple two-electronic state model having one vibrational mode. The results highlighted a concern for photostability in practical experiments. When the laser dye molecule Rhodamine 575 was held in an ion trap and continuously irradiated with circularly polarized 514 and 488 nm laser light, it demonstrated a propensity for photodecomposition. Detection of the polarization of the emitted fluorescence also
showed a slight rotational alignment of the molecules, though the data were inconclusive. The concept of directly controlling the rotational orientation of an ensemble of molecules by irradiation with circularly polarized light shows promise.

The final project quantified the efficiency of internal rotation about a double bond during UV photoisomerization of a model molecular motor prototype. The family of dibenzofulvene derivatives investigated showed significant photoisomerization quantum yields, as high as 0.5 in the case of the iodo substituted dibenzofulvene rotor. While theoretical calculations of fulvene predict little to no photoisomerization, experimental evidence of the photoisomerization of these dibenzofulvene rotors suggests addition of aromatic benzene rings alters the potential energy surfaces of the ground and excited electronic states involved in photoisomerization to the extent that surface crossing from the excited state to the ground state occurs at nuclear coordinates much more favorable to isomerization in dibenzofulvene. The photoisomerization quantum yields showed a dependence on the substituent group, with $t$-butyl $<$ nitro $<$ cyano $<$ iodo. The cyano and iodo substituted compounds showed evidence of a small degree of photodecomposition, which did not significantly affect the photoisomerization quantum yields. The substituent groups also affected the absorption spectrum of the molecule, with the nitro substituted compound absorbing into the near visible region at $\sim 400$ nm.

These three projects, while not directly related to each other, add to the overall understanding of molecular rotation and give insight into the issues involved in selectively generating a specific sense of rotation in molecules, whether by harnessing the preferred sense of rotation in UV photodissociation fragments, directly imparting specific angular momentum via absorption of circularly polarized light, or custom designing a molecular rotor for efficient photoisomerization.
Acknowledgments

Many special thanks go to my research advisor Prof. Joseph Cline whose patience and guidance cannot be measured. Also to the members of the Cline research group: James Barr, Jordan Mantha, Ali Ismail, and Udaya Jayasundara who have offered their collaboration and support in many ways. In addition, this thesis covers work on three separate projects, and there are many people to whom I owe considerable appreciation and thanks for their contributions.

Velocity-angular momentum vector correlations of nitrosobenzene
I would like to thank Prof. Jeffery Bartz who allowed me to assist him in the study of NO photofragment vector correlations from which I learned a great deal.

Rotational orientation of trapped chromophores
Much appreciation is given to Nicholas Sassin for his collaborative work on the ion trapping project; for his running of the ion trap and the modeling of rhodamine photodissociation dynamics. Prof. Kent Ervin was kind enough to grant us use of his ion trap, and contributed much to our insight and understanding of the data collected. After the departure of Nick Sassin, Beni Dangi continued his work running the ion trap, and is still pursuing the project. Additional thanks are given to Dr. Wayne Stanbery who helped with the initial design of the fluorescence collection apparatus and laser excitation setup.

Photoisomerization of a molecular motor prototype
The molecular motor project was a large collaborative effort on the part of many people. Dr. Nicholas Hext, Rolando Procupez, HyunJong Kim, and others under the leadership of Prof. Thomas Bell worked on the synthesis of the molecular motor prototype. My predecessors James Barr and Dr. Wayne Stanbery are responsible for preliminary work on the amino and nitro substituted motor molecule prototypes. Dr. Stanbery especially guided me in continuing the work already begun. Clay Mishler and Udaya Jayasundara contributed their time and effort in the collection experimental data, and Udaya will be continuing work on this project. I would also like to thank Prof. Christine Cremo for her participation in collaborative discussions.
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Preface

The topic of molecular rotation is considerably broad and has numerous realized and potential applications. Even narrowing the scope of interest to molecular rotation driven by photochemical processes still leaves too much for one to consider in depth. Still, the study in this field has yet to be exhausted. Here we conduct further investigations into molecular rotation with three separate, but related, projects with the ultimate goal of being able to selectively generate specific rotational motion in molecules.

This thesis describes these three projects related to the general study of detection and control of molecular rotation. Beginning with a passive study of the photodissociation of nitrosobenzene, we have measured the rotational alignment preference of the NO photoproduct. From characterization, we move to actively controlling the rotation of molecules by transferring angular momentum from circularly polarized photons to impart a specific sense of molecular rotation. Finally, we engineer a molecule to isomerize by internal rotation about a double bond with the ultimate goal of generating unidirectional rotary motion for application in molecular devices.
Chapter 1

Photodissociation of Nitrosobenzene
1.1 Introduction

There have been a number of previous studies investigating the velocity, $v$, angular momentum, $j$, and transition dipole, $\mu$, vector correlations in the recoil trajectories of fragments from molecular photodissociation.\textsuperscript{1-4} The trajectories reveal valuable information about the bond-breaking energies in the parent molecule and the directionality of the intermolecular forces between the recoiling product species. In combination with theoretical models, measurements of photofragment angular correlations provide some of the most detailed information available of the high-energy regions of molecular potential energy surfaces relevant to chemically reacting systems. In this work we examine the angular correlations of the recoil trajectory of the NO product from the UV photodissociation of nitrosobenzene. Of special interest to this current study is the work by earlier members of the Cline research group who studied the fragment recoil trajectories of NO from nitrosoalkanes.\textsuperscript{1,3-5} In general, most photodissociation reactions produce products having recoil trajectories that preferentially exhibit $v \perp j$ velocity-angular momentum vector correlations. In contrast, this study of nitrosobenzene photodissociation provides the first angular correlation measurements for an aryl nitroso compound. Indirect evidence has suggested that these compounds may show a rare $v \parallel j$ “propeller” recoil trajectory of the NO fragment.

Kessler \textit{et al.} investigated the UV photodissociation of nitrosobenzene (PhNO).\textsuperscript{6} Because NO fragment is a radical with an unpaired electron in a $\pi^*$ orbital, there exists a coupling of the electronic and rotational angular momenta that gives rise to non-degenerate lambda doublet states, labeled $A'$ and $A''$. The symmetric $A'$ state exists with the occupied $\pi^*$ orbital in the plane of molecular symmetry, while the antisymmetric $A''$ state exists with the occupied $\pi^*$ orbital perpendicular to the plane molecular symmetry. Kessler \textit{et al.} found that photodissociation of PhNO shows a preference for the NO fragment to emerge in the $A''$ state. After examining the
molecular orbital geometries of the ground and excited states of the parent PhNO molecule, they concluded that these populations suggest the NO fragment from photodissociated PhNO possibly recoils with a preferred $v \parallel j$ vector correlation, opposite that which is most commonly observed.$^6$

Given the fact that nitrosobenzene has been studied extensively by others,$^7$–$^14$ its electronic structure is well known,$^6$,$^15$ and it is commercially available, we chose to perform direct experimental tests of the proposed $v \parallel j$ NO photofragment trajectory from photodissociated PhNO.

### 1.2 Experiment

The 305 nm photodissociation dynamics of nitrosobenzene (PhNO) was studied in a velocity-map imaging time-of-flight mass spectrometer built by previous members of the Cline group. A schematic representation is given in Fig. 1.1 and discussed in greater detail elsewhere.$^{16}$ The molecular beam of PhNO (Aldrich 97%) was prepared for delivery by flowing ca. 1 atm of He gas over a liquid sample of nitrosobenzene held at 60°C in a temperature-controlled water bath, having a PhNO vapor pressure
of approximately 0.024 atm.\textsuperscript{13,17} The He/PhNO gas mixture was introduced into the differentially-pumped two-chamber vacuum system by a pulsed solenoid valve (General Valve Series 9) and passed through a skimmer to form a molecular beam.\textsuperscript{16} The main chamber had a base pressure of approximately $5 \times 10^{-7}$ Torr. Inside the main chamber, the molecular beam interacted with three laser beams.

PhNO was dissociated with 305 nm laser light. Two different laser wavelengths were used in the $1 + 1'$ REMPI NO excitation scheme: the resonant step through the $A \, ^2\Sigma \leftrightarrow X \, ^2\Pi_{\frac{1}{2}, \frac{3}{2}}$ transition and a non-resonant ionization of the NO photofragment. Figure 1.2 gives a schematic representation of these three steps. The C-N bond dissociation energy in PhNO is 2.45 eV as calculated by Tseng\textsuperscript{18}, consuming the majority of the energy from the 305 nm dissociation photon with energy 4.06 eV. The resulting NO photoproduction is born solely in the ground $X \, ^2\Pi$ state having some excitation of vibrational, $v$, and angular momentum, $j$, internal states. Individual rotational states of the 0-0 vibrational band of the $A \leftrightarrow X$ transition are probed at wavelengths 225-226 nm by scanning the probe laser which has a 0.2 cm\textsuperscript{-1} bandwidth. The resulting NO* is then ionized using 308 nm laser light and detected with velocity-map ion imaging.

The generation of the dissociation, probe, and ionization beams is shown in Fig. 1.3. The 532 nm second harmonic of a pulsed nanosecond Nd:YAG laser (Quanta-Ray GCR 3) pumped a tunable dye laser (Quanta-Ray PDL-3) which was frequency doubled to generate the 305 nm dissociation pulse. A fraction of the 355 nm third harmonic of the Nd:YAG laser was used to pump a second tunable dye laser (Quanta-Ray PDL-3) that was frequency doubled to 226 nm for the probe pulse. The 226 nm probe pulse was tuned to select individual resolvable $A \leftrightarrow X$ transitions of the NO photoproduction with pulse energies $< 100 \, \mu J$ pulse\textsuperscript{-1}. While collecting an image, the probe laser was scanned back and forth over the Doppler profile of the selected
Figure 1.2: Photodissociation of nitrosobenzene (PhNO) and 1+1’ REMPI of the NO photofragment through the A→X transition.

Figure 1.3: Laser excitation setup for photodissociation of PhNO and 1+1’ REMPI probing of the NO photofragment. The λ/2 waveplate and photoelastic modulator set the linear polarization of the 305 nm dissociation and 226 nm probe beams, respectively. The 308 nm ionization beam, generated from the first Anti-Stokes line from a H₂ Raman shifter, is unpolarized. The total time delay between the dissociation and ionization pulses is 25-30 ns.
transition. The remainder of the 355 nm laser light was focused into a Raman shifter containing 25 psi of H\textsubscript{2}. A Pellin-Broca prism separated the first Anti-Stokes line at 308 nm to use as for ionization with pulse energies 1-3 mJ pulse\textsuperscript{-1}. Pulses were 5-10 ns in duration and the total time delay between the dissociation and ionization pulses was approximately 25-30 ns. A photoelastic modulator (Hinds PEM-90) controlled the polarization of the dissociation beam, which was alternated between horizontal and vertical on alternate laser shots. A $\lambda/2$ waveplate set the polarization of the dissociation and probe beams, and the ionization beam was unpolarized. By setting the linear polarization of the dissociation and probe beams as parallel ($\circledcirc$) or perpendicular ($\perp$) to the detector axis in the laboratory frame as shown in Fig. 1.4, four different ion images were recorded for each NO rotational transition probed.

The resulting NO\textsuperscript{+} photofragment was velocity-map imaged using a series of ion lenses located opposite the source region and perpendicular to the molecular beam, as shown in Fig. 1.1. The nascent recoil velocity in the laboratory frame is mapped onto a two-dimensional detector.\textsuperscript{19} The position-sensitive detector (Burle 3075FM) consists of a pair of 40 mm chevron-type multichannel plates fiber-optically coupled
Figure 1.5: NO velocity distribution from 355 nm photodissociated NO$_2$ probing the $Q_{11}$ branch of the A←X transition with $j = 25.5$. Conservation of energy forces a very narrow NO fragment speed distribution which allows determination of the speed scaling factor in the image.

to a phosphor screen (Phosphor P47, response time 50 ns) of the same diameter. The image was collected by a CCD camera (Cooke Sensicam QE) and transferred to a laboratory computer running LabVIEW. To calibrate the velocity scale of the imaging system, the 355 nm photodissociation of NO$_2$ was studied and the NO fragment was probed. An example calibration image is shown in Fig. 1.5, where the NO photofragment has a very narrow speed distribution. Using the known NO-O bond energy and the selected rotational state, conservation of energy calculations by Prof. Jeffery Bartz gave a radial speed scaling factor of 11.31 m s$^{-1}$ per pixel for our imaging apparatus.$^{20}$ During a typical experiment, a set of polarization-selected ion images
was constructed from the sum of 12,000 laser shots in each of the four polarization schemes.

### 1.3 Theoretical parameterizing of vector correlations

Angular correlations among the direction of the photofragment recoil velocity, $\hat{v}$, and angular momentum, $\hat{j}$, vectors can be expanded in a basis of the bipolar harmonics, $B_{KQ}(v,j)$, in the frame of the dissociating parent molecule.\textsuperscript{21} The $z$-axis of the molecular frame is the transition dipole, $\mu$, of the parent molecule on the photodissociation transition. Following the notation of Dixon,\textsuperscript{21} we express the renormalized coefficients of the bipolar harmonic expansion as the bipolar moments, $\beta_{KQ}^k(k_1k_2)$. The renormalized $\beta_{KQ}^k(k_1k_2)$ are physically constrained to specific ranges and quantify the extent of the angular correlation among $v$, $j$, and $\mu$. Of interest in this study are the bipolar moments, $\beta_{00}^2(20)$ and $\beta_{00}^0(22)$, quantifying the $\mu$-$v$ and $v$-$j$ correlations, respectively. For both these moments, the values are physically constrained to the range $\{-0.5, 1.0\}$, where the limiting values of -0.5 and +1.0 indicate a perfect perpendicular (\perp) or parallel (\parallel) vector correlation, respectively. Interpretation of velocity map ion images to extract $\beta_{00}^2(20)$ and $\beta_{00}^0(22)$ bipolar moments is described in detail by Nestorov\textsuperscript{5} and was performed using the program “fimage” developed in the Cline group.

### 1.4 Results

Sets of four velocity map ion images, corresponding to polarization geometries representing combinations of the dissociation and probe beams polarized parallel and
perpendicular to the plane of the detector, were obtained for selected P, Q, and R transitions of the NO photofragment with angular momentum quantum numbers, \( j \), ranging from 16.5 to 33.5. Figure 1.6 shows a typical set of four false-color images. The velocity map ion images from the photodissociation of PhNO show a much broader NO photofragment speed distribution than that measured for the NO fragment photodissociated from NO\(_2\). The significant difference in the speed distribution is due to the phenyl radical fragment having a large number of vibrational modes and additional rotational degrees of freedom capable of absorbing energy during the dissociation process. The NO photofragment from photodissociated PhNO is therefore ejected with a broad range of kinetic energies, in contrast to the NO fragment ejected from photodissociated NO\(_2\) in Fig. 1.5 for which the partner O atom fragment has only one energetically resolved product state. Because of the slow, unstructured velocity distribution, large differences between images obtained using different polarizations are not readily apparent. However, when we examine the difference between normalized images obtained with vertically (\( \uparrow \)) and horizontally (\( \odot \)) polarized dissociation and probe beams, polarization-dependent branch-specific characteristics become evident. In particular the NO photofragment images show a stronger dependence on the probe polarization than on the dissociation polarization.

To obtain quantitative values for the \( \mathbf{v} - \mathbf{j} \) correlation, the set of four images were simultaneously fit in an optimization of the \( \beta_0^0(22) \) bipolar moment using the “fimage” program developed by Prof. Joseph Cline described in detail by Nestorov et al.\(^5\) The fitting parametrizes the \( \mathbf{v}, \mathbf{j} \), and \( \mathbf{\mu} \) vector correlations using the semi-classical bipolar moment scheme proposed by Dixon.\(^5,22\) The measurable bipolar moments are extracted from the images using a forward-convolution scheme which can also take into account the possibility of multiple photodissociation channels. The fragment
Figure 1.6: A set of four images, with combinations of vertically (\(\downarrow\)) and horizontally (\(\bigcirc\)) polarized dissociation and probe pulses, collected from the Q_{11} branch of the A\(\leftarrow\)X transition, with \(j = 33.5\). The differences between vertically and horizontally polarized probe and dissociation pulses are shown on the bottom and right, respectively, with red representing a positive difference and blue a negative difference. The small dependence on the dissociation polarization is consistent with the small \(\mu - \nu\) correlation, \(\beta_0^2(20) = 0.03\) fit to the images. The larger probe polarization dependence gives rise to a fitted value of \(\beta_0^0(22) = 0.26\) for the Q_{11} transition. The “fimage” fits to this data are shown in Fig. 1.7.
Table 1.1: Optimized $\beta_0^0(22)$ values for the NO (A, $v = 0$) photoproduct obtained from the simultaneous fit of four images probed on the indicated transition, with $\beta_0^0(20) = 0.03$ used for all transitions. Also reported are the average speed, $\langle v \rangle$, and the FWHM of the anisotropic speed distribution, $w$.

<table>
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<th>Branch</th>
<th>$j$</th>
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<th>$\langle v \rangle$ (m s$^{-1}$)</th>
<th>$w$</th>
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<td>-0.25</td>
<td>770</td>
<td>1138</td>
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recoil velocity is fit using two Maxwell-like speed distributions of the form

$$P(v) = N v^2 e^{-\ln^2 \left( \frac{w}{v} \right) / 2},$$

(1.1)

with a normalization factor, $N$, such that the integral over all velocities, $v$, is unity and $w$ defines the width of the distribution. The average speed of the distribution is

$$\langle v \rangle = \int_0^{\infty} v \ P(v) \ dv .$$

(1.2)

For the experiments described here, the NO speed function included a Maxwell isotropic speed distribution to account for background NO. This speed component included no lab-frame anisotropy. The background NO contribution varied from experiment to experiment and showed no consistent width, $w$. A small $\mu \parallel v$ vector correlation was observed that was relatively consistent through all experiments, so the average experimentally determined corresponding $\beta_0^0(20)$ bipolar moment value was fixed in the optimization of $\beta_0^0(22)$. Table 1.1 reports the optimized $\beta_0^0(22)$ bipolar
moment values for the nascent NO photoproduct and the $\langle v \rangle$ and $w$ of the anisotropic speed distribution for the rotational transitions investigated. Figure 1.7 shows calculated images from parameters optimized in the simultaneous fit of the experimental data shown in Fig. 1.6.

The transitions investigated show a significant $\beta_0^0(22) > 0$ value, with the exception of two outlier cases. We were unable to determine the cause of the discrepancy, however. The broad velocity profile makes determination of $\beta_0^0(22)$ difficult; however, the data does show an average $\beta_0^0(22) = 0.22$ (excluding outliers), and an average standard deviation of 0.11. The average $\langle v \rangle$ and $w$ are $840 \pm 100$ and $1270 \pm 180$ m s$^{-1}$, respectively.

1.5 Discussion

Figure 1.8 demonstrates the two limiting NO photofragment $v - j$ angular correlations with their corresponding values of $\beta_0^0(22)$. The first case, where $v \perp j$, can be rationalized as arising from the impulse force in the C-N bond breakage giving the NO fragment torque in the molecular plane, causing the fragment to be ejected in a “cartwheel” fashion. The second case, $v \parallel j$, requires an out-of-plane torque applied to the NO prior to C-N bond breakage in order to acquire the “propeller” recoil trajectory. The $\beta_0^0(22)$ measurements in this study show a preference for NO to dissociate from PhNO in a propeller fashion. We explore the origin of this out-of-plane torque by considering the symmetries of the relevant electronic states.

The 305 nm dissociation photon excites PhNO to the second excited electronic state, $S_2$, which has an excited state lifetime of less than 100 fs.$^6$ Although the 305 nm photon with 4.06 eV exceeds the 2.45 eV C-N bond energy in PhNO,$^{18}$ it is not energetically possible to dissociate on the $S_2$ surface. Instead, there is a non-radiative transition to either the first excited, $S_1$, or ground, $S_0$, electronic state from which
Figure 1.7: Velocity map images calculated from the optimized parameters in a simultaneous fit to the four experimental images collected for the $Q_{11}$ branch transition of the $A-X$ transition with $j = 33.5$ shown in Fig. 1.6. The difference images shown on the bottom and right are obtained from the calculated fit images, with red representing a positive difference and blue a negative difference.
Figure 1.8: Velocity, \( \mathbf{v} \), and angular momentum, \( \mathbf{j} \), vector correlations for a) cartwheel style, \( \beta_i(22) = -0.5 \), and b) propeller style, \( \beta_i(22) = +1 \), NO photofragment recoil trajectory.
dissociation occurs. The NO moiety has an unpaired electron residing in a $\pi^*$ orbital, which gives rise to the lambda doublet states A' and A" mentioned in Sec. 1.1. The A' state has an unpaired electron occupying the $\pi^*$ orbital that lies in the molecular symmetry plane and the A" state exists with the unpaired electron occupying the $\pi^*$ orbital that is perpendicular to plane of molecular symmetry. Keßler et al. report that both the S_0 and S_2 electronic states of PhNO have A' symmetry, while the first excited state, S_1, has A" symmetry. Figure 1.9 shows a schematic representation of the PhNO excitation to the S_2 excited state, relaxation to S_1 or S_0, and subsequent dissociation from either the first excited, S_1, or ground, S_0, electronic states.

Figure 1.9 also shows the nascent molecular frame orientation of the NO HOMO born from the S_1 and S_0 states if the molecular symmetry of the parent PhNO molecule is preserved through the photodissociation process. For the NO fragment, the plane of molecular rotation (perpendicular to $\hat{j}$) defines the reference plane for reflection symmetry; NO in the A' lambda doublet state has its unpaired electron in the $\pi^*$ orbital in the plane of rotation, and the A" lambda doublet state has the unpaired electron in the $\pi^*$ orbital perpendicular to the plane of rotation. For the two limiting case $\mathbf{v} - \mathbf{j}$ correlations for the NO product, Fig. 1.9 shows the corresponding A' and A" lambda doublet symmetries for NO with $\mathbf{v} \parallel \mathbf{j}$ and $\mathbf{v} \perp \mathbf{j}$. The PhNO UV photodissociation experiments of Keßler et al. report that the NO fragment shows a preference for the A" lambda doublet state (highlighted in Fig. 1.9), as much as 4:1 A":A'. The result can be combined with our measured preference for the NO fragment to be ejected with $\mathbf{v} \parallel \mathbf{j}$ to deduce the surface on which PHNO dissociates. Photodissociation from the first excited, S_1, state leads to an NO fragment with the preferred A" lambda doublet symmetry having $\mathbf{v} \perp \mathbf{j}$, a $\mathbf{v} - \mathbf{j}$ correlation opposite the preference measured here. On the other hand, photodissociation from the S_0 ground state leads to an NO fragment with A" lambda doublet symmetry having $\mathbf{v} \parallel \mathbf{j}$. 
Figure 1.9: Schematic representation of the PhNO excitation to the second excited, \( S_2 \), electronic state, non-radiative relaxation, and subsequent dissociation from the first excited, \( S_1 \), or ground, \( S_0 \), electronic states. The lambda doublet symmetry states, \( A' \) and \( A'' \), are shown for the parent PhNO molecule and the nascent NO fragment dissociated from either \( S_1 \) or \( S_0 \) with \( \mathbf{v} \parallel \mathbf{j} \) and \( \mathbf{v} \perp \mathbf{j} \). Image adapted from Kessler et al, who reported an \( A'' \) (highlighted) preference for NO photodissociated from PhNO under UV excitation.\(^6\)
Considering the results of the UV PhNO photodissociation experiments by Keßler et al. and those reported here, it can be concluded that PhNO dissociates on the $S_0$ ground electronic state. Furthermore, ground and excited state energy calculations of the phenyl radical by Radziszewski et al. show that dissociation from the $S_1$ state is not energetically possible with the 1.61 eV remaining energy of the 4.06 eV from the 305 nm dissociation photon.\textsuperscript{10}

An additional question is the origin of the out-of-plane torques that rotationally excites the product NO. PhNO, in the ground state, has a planar geometry. To investigate the torques, time-dependent density functional theory (TDDFT) calculations were performed by our collaborator Prof. Bartz.\textsuperscript{20} They showed that the $S_2$ excited state, to which the PhNO is excited prior to dissociation, decreases in energy as NO is rotated out of the plane of the phenyl ring, as shown in Fig. 1.10. Additionally, the vibrational period of the out-of-plane Ph-NO bend is approximately 100 fs, similar to the excited state lifetime. The concurrence of the energetically favorable PhNO non-planar geometry of the $S_2$ excited state coupled with the NO out-of-plane bend in the ground $S_0$ state may give rise to Ph-NO bond angle torsions during the dissociation event which supply the appropriate torque to generate $\mathbf{v} \parallel \mathbf{j}$ NO fragment recoil trajectories.

\section*{1.6 Conclusion}

A classical picture of the photodissociation of nitrosobenzene might predict a $\mathbf{v} \perp \mathbf{j}$ NO fragment trajectory by reason of the direction of impulse given the NO during Ph-NO bond breakage. In fact, the $\mathbf{v} \perp \mathbf{j}$ photofragment trajectory is the most common occurrence in photodissociation experiments. However, the experimental results given here show significant preference for PhNO dissociating with an uncommon $\mathbf{v} \parallel \mathbf{j}$ NO trajectory, in agreement with the postulation made by Keßler et al.\textsuperscript{6}
Figure 1.10: The energies of the ground, $S_0$, and first two excited, $S_1$ and $S_2$, electronic states as a function of the PhNO dihedral angle. TDDFT calculations were performed by our colleague Prof. Jeffery Bartz. Image courtesy of Prof. Bartz.
Bibliography


Chapter 2

Imparting Rotational Orientation by Circularly Polarized Light

\[ \text{Diagram showing absorption and emission processes.} \]
2.1 Introduction

Having observed that products from photodissociation reactions can show preferred planes of rotation after being expelled from their parent molecule, we now consider the possibility of controlling the laboratory-frame orientation and alignment of molecular rotational angular momentum using irradiation with circularly polarized light.

The premise of controlling the angular momentum of a population of molecular absorbers is analogous to the control of linear momentum using “optical molasses”. Figure 2.1 gives a pictorial view of the following discussion. The photons in a beam of circularly polarized light have an angular momentum vector, \( \mathbf{j}_p \) either parallel (left circularly polarized, LCP) or anti-parallel (right circularly polarized, RCP) to the light propagation direction, \( \mathbf{k} \). When a molecule absorbs a photon, its angular momentum changes in accordance with conservation laws. In the case of circularly polarized light, this gives rise to a \( \Delta m = +1 \) (LCP) or \( \Delta m = -1 \) (RCP) selection rule, where \( m \) is the projection of the molecule’s rotational angular momentum vector, \( \mathbf{j} \), onto \( \mathbf{k} \). The spatial symmetry of the photon emission process results in an average change to the molecule’s angular momentum of zero. Over multiple absorption/emission events, each molecule’s angular momentum vector will become oriented with respect to the \( \mathbf{k} \) vector of the beam of circularly polarized light.

2.2 General considerations

To obtain a quantitative understanding of this process, it is helpful to examine the process as it occurs in both the body-fixed frame (Fig. 2.2a) and the space-fixed frame (Fig. 2.2b). Here we restrict our attention to an initially thermal sample of symmetric top molecules irradiated by a unidirectional beam of circularly polarized light. We could irradiate the molecules with a broadband light source so that energy resonance
Figure 2.1: Conceptual schematic of how repetitive absorption of left circularly polarized light imparts rotational orientation to an absorber with rotational angular momentum vector $\mathbf{J}$ and a $\mathbf{k}$-projection $M$. Following absorption of a photon with an angular momentum quantum number $j_p = 1$ and $m_p = +1$ (LCP), the molecule's subsequent total angular momentum is $J'$, with $M' = M + 1$. Averaging over all directions of emission, there is no net preference for the sign of $\Delta M$, so that emission results in an averaged zero net effect on $M$, and the angular momentum $J$ becomes oriented with respect to $\mathbf{k}$ after many absorption/emission cycles.
between the molecules and the source photons is maintained as the sample becomes rotationally oriented during successive absorption/emission cycles. In practice, we might imagine the light source as a narrow bandwidth, circularly polarized laser beam and use molecules having a large number of vibrational degrees of freedom such that they have a broad, structureless absorption spectrum. This ensures that every molecule in the sample has some vibronic transition accessible at the fixed wavelength of the light source.

The probability, $P_{ij}$, of an electric-dipole transition between an initial state $i$ and a final state $f$ for absorption of a single photon is given by

$$P_{ij} = C |\langle \psi_f | \hat{e} \cdot \hat{r} | \psi_i \rangle|^2.$$  \hspace{1cm} (2.1)

The operator representing the transition is $\hat{e} \cdot \hat{r}$, where $\hat{e}$ is, in general, a complex vector representing the electric polarization of the absorbed light and $\hat{r}$ is the direction of the transition dipole moment depicted in Fig. 2.2a. Here these are defined as unit vectors so that the magnitudes of the electric field and the transition dipole become scaling factors in the probability expressions below. In Eq. 2.1, $C$ contains scaling constants such as the magnitude of the electric field, the electronic transition dipole moment, and Franck-Condon factors.

We restrict our attention to the absorption probability for a rotational-electronic transition of a rigid, symmetric top molecule on a “parallel” transition; i.e., the electronic transition dipole is oriented along the cylindrical symmetry axis, $z$, of the molecule, as shown in Fig. 2.2a. Considering only rotational angular momentum, the relevant angular momentum quantum numbers in each electronic state are $J$, $K$, and $M$, where $J$ is the total angular momentum quantum number, $K$ gives the projection of the total angular momentum onto the body-fixed $z$-axis, and $M$ gives
Figure 2.2: Schematic representation of the absorption process of an LCP photon by a prolate symmetric top molecule on a parallel transition in the (a) body-fixed \((x, y, z)\) and (b) space-fixed excitation \((X, Y, Z)\) frames. For prolate symmetric tops, multiple absorptions of LCP photons will successively increase \(\mathbf{J}\) while the \(\mathbf{J}\) projection onto the body-fixed transition dipole, \(K\) is unchanged (a). However, the \(\mathbf{J}\) projection onto the the space-fixed \(Z\) axis, \(M\), always increases (b). After multiple absorptions, \(\mathbf{J}\) has become oriented parallel to the \(Z\) axis with all the transition dipoles, \(\mathbf{r}\), lying in the \(XY\) plane. A detector set \(90^\circ\) to the axis of the laser beam observes fluorescence polarized in the \(XY\) plane. Comparison of fluorescence polarized in the \(XY\) plane to fluorescence polarized in the \(YZ\) plane experimentally quantifies the degree of rotational alignment attained.
the projection onto the space-fixed $Z$-axis (Fig. 2.2b). Eq. 2.1 then becomes

$$ P(JKM; J'K'M') = |\langle J'K'M'|\hat{e} \cdot \hat{r}|JKM\rangle|^2. $$  \hspace{1cm} (2.2)

For simplicity, the proportionality constant $C$ in Eq. 2.1 has been set equal to unity in Eq. 2.2 and the expressions below. The values of $P(JKM; J'K'M')$ are then interpreted as relative absorption probabilities for $|JKM\rangle \rightarrow |J'K'M'\rangle$ in an electronic transition between two specified vibrational-electronic states.

For a one-photon, parallel transition, the general symmetric top rotational selection rules for unpolarized, isotropic excitation are well known:

$$ \Delta K = 0 \quad \Delta J = 0, \pm 1 \quad \text{if} \, K \neq 0 $$  \hspace{1cm} (2.3)

$$ \Delta K = 0 \quad \Delta J = \pm 1 \quad \text{if} \, K = 0 $$  \hspace{1cm} (2.4)

Beyond these rigorous selection rules, rotational line-strengths, or “Hönl-London factors”, are commonly used to quantify the relative probabilities of the allowed transitions for a given set of initial and final rotational quantum numbers $J, K,$ and $J',K'$. However, the Hönl-London factors are valid only for unpolarized, non-directional absorption of randomly oriented rotors. They are calculated by summing Eq. 2.2 over all $M$ and $M'$, and averaging over all polarization directions by making $\hat{e} \equiv 1$, setting $\hat{r} = r_z$, and multiplying by 3 to account for each direction. Here we instead want to derive the relative probabilities for absorption of directional, circularly polarized excitation of rotationally oriented/aligned molecules. This means that the relative probability for each $|JKM\rangle \rightarrow |J'K'M'\rangle$ transition must be separately calculated, and $\hat{e}$ is no longer a scalar.
2.2.1 Fully-resolved rotational transition probabilities

The transition dipole operator, \( \mathbf{\hat{r}} \), is most conveniently defined in the “molecule-fixed” or body-fixed (BF) frame (Fig. 2.2a). The BF frame is defined in the customary way such that the \( z \)-axis is along the cylindrical symmetry axis of the molecule. If the transition dipole, \( \mathbf{\hat{r}} \), lies along the symmetry axis, its BF Cartesian representation is \( \mathbf{\hat{r}} = \mathbf{\hat{z}} = (0, 0, 1) \). However, it is more convenient to work in a spherical tensor basis.\(^4\)

The vector \( \mathbf{\hat{r}} \) becomes a first-rank tensor with three components proportional to the familiar \( l = 1, m = 0, \pm 1 \) spherical harmonics. In the spherical tensor basis, the case of \( \mathbf{\hat{r}} = \mathbf{\hat{z}} \) is analogous to the \( l = 1, m = 0 \) spherical harmonic. Using the spherical tensor notation of Zare,\(^5\) in the BF frame this is expressed as

\[
\mathbf{\hat{r}} = \mathbf{\hat{z}} = T(1, 0) ,
\]

where \( T(1, 0) \) is a first-rank tensor operator. The other two first-rank tensor components, \( T(1, 1) \) and \( T(1, -1) \) vanish.\(^6\)

We assume absorption from a left circularly polarized (LCP) laser beam. The laser beam is most conveniently defined in the space-fixed (SF) frame and we assume that the beam propagates in the \( +Z \)-direction (Fig. 2.2b). The spherical tensor representation of the LCP light in the SF frame is

\[
\mathbf{\hat{e}} = -T(1, 1) ,
\]

with the other two first-rank tensor components being zero.\(^7\)

Following Zare\(^8\), we choose to evaluate the probability expressions in the BF frame. Using the Wigner rotation functions\(^9\) to rotate the space-fixed \( \mathbf{\hat{e}} \) to the body-fixed
frame, we write

\[ \hat{e} = -T(1,1) \quad \text{in SF basis} \quad (2.7) \]

\[ = - \sum_q D_{iq}^{1s}(\hat{R}) T(1,q) \quad \text{in BF basis} \quad (2.8) \]

\[ = - \left[ D_{11}^{1s}(\hat{R}) T(1,1) + D_{10}^{1s}(\hat{R}) T(1,0) + D_{1-1}^{1s}(\hat{R}) T(1,-1) \right] , \quad (2.9) \]

where \( \hat{R} = (\phi, \theta, \chi) \) represents the Euler angles parameterizing the rotation of the SF frame into the BF frame, and the \( D_{MK}^{J}(\hat{R}) \) are the Wigner rotation functions. \(^{10}\)

The dot product \( \hat{e} \cdot \hat{r} \) can be written as a scalar contraction of the two first-rank tensors \( e^{(1)} = \hat{e} \) and \( r^{(1)} = \hat{r} \). In the spherical tensor basis this gives \(^{11}\)

\[ \hat{e} \cdot \hat{r} = -\sqrt{3} \left[ e^{(1)} \otimes r^{(1)} \right]_0^{(0)} \quad (2.10) \]

\[ = -\sqrt{3} \left[ -e(1,1)r(1,1) + e(1,0)r(1,0) - e(1,-1)r(1,-1) \right] , \quad (2.11) \]

where the \( e(k, q) \) and \( r(k, q) \) are the coefficients of the spherical tensor representations of \( \hat{e} \) and \( \hat{r} \). Using Eqs. 2.5 and 2.9 for the direction of our transition dipole and polarization of the electric field, we have the BF frame coefficients

\[ r(1,0) = 1 \quad (2.12) \]

\[ r(1,\pm 1) = 0 \quad (2.13) \]

\[ e(1,0) = -D_{10}^{1s}(\hat{R}) \quad (2.14) \]

\[ e(1,\pm 1) = -D_{1\pm 1}^{1s}(\hat{R}) \quad (2.15) \]

Substituting these components into the general dot product expression in Eq. 2.11, the BF frame transition operator becomes

\[ \hat{e} \cdot \hat{r} = \sqrt{3} D_{10}^{1s}(\hat{R}) . \quad (2.16) \]
Ignoring the constant $\sqrt{3}$ in Eq. 2.16 (by absorbing it into the constant $C$), the BF frame relative absorption probability in Eq. 2.2 becomes

$$P(JKM; J'K'M') = \left| \langle J'K'M'|D_{10}^{1s}(\mathbf{R})|JKM \rangle \right|^2 . \quad (2.17)$$

The rigid symmetric top wavefunctions in Eq. 2.17 can also be expressed in terms of Wigner rotation functions of the Euler rotation angles between the space-fixed and body-fixed frames:\(^{12}\)

\[
|\psi_i\rangle = |JKM\rangle \\
= \left[ \frac{2J + 1}{8\pi^2} \right]^{1/2} D_{MK}^{J*}(\mathbf{R}) \quad (2.19)
\]

\[
|\psi_f\rangle = |J'K'M'\rangle \\
= \left[ \frac{2J' + 1}{8\pi^2} \right]^{1/2} D_{M'K'}^{J'*}(\mathbf{R}) . \quad (2.21)
\]

The integral in the probability expression in Eq. 2.17 then becomes

\[
\langle J'K'M'|D_{10}^{1s}(\mathbf{R})|JKM \rangle = \langle JKM|D_{10}^{1s}(\mathbf{R})|J'K'M'\rangle^* = \left\{ \int \left[ \frac{2J' + 1}{8\pi^2} \right]^{1/2} D_{MK}^{J'}(\mathbf{R}) D_{10}^{1s}(\mathbf{R}) \\
\times \left[ \frac{2J + 1}{8\pi^2} \right]^{1/2} D_{M'K'}^{J'*}(\mathbf{R}) d\Omega \right\}^* \quad (2.23)
\]

\[
= \left[ (2J + 1)(2J' + 1) \right]^{1/2} \frac{8\pi^2}{\sqrt{8\pi^2}} \\
\times \int D_{MK}^{J'}(\mathbf{R}) D_{10}^{1s}(\mathbf{R}) D_{M'K'}^{J'*}(\mathbf{R}) d\Omega \quad (2.24)
\]

Using standard formulas,\(^{13}\) the integral over a triple product of rotation functions
in Eq. 2.24 reduces to a product of Clebsch-Gordan coefficients,

$$\langle JKM | D_{10}^{1} (\hat{R}) | J'K'M' \rangle = \frac{[(2J + 1)(2J' + 1)]^{1/2}}{8\pi^2} \left( \frac{8\pi^2}{2J' + 1} \right) \langle JK, 10 | J'K' \rangle \langle JM, 11 | J'M' \rangle$$

$$= \left[ \frac{2J + 1}{2J' + 1} \right]^{1/2} \langle JK, 10 | J'K' \rangle \langle JM, 11 | J'M' \rangle$$

(2.25)

And the transition probability in Eq. 2.17 becomes

$$P(JKM; J'K'M') = \frac{2J + 1}{2J' + 1} |\langle JK, 10 | J'K' \rangle|^2 |\langle JM, 11 | J'M' \rangle|^2 \ .$$

(2.26)

The Clebsch-Gordan coefficients on the right side of Eq. 2.27 vanish unless $J' = J - 1$ ($P$-branch transitions), $J' = J$ ($Q$-branch transitions), or $J' = J + 1$ ($R$-branch transitions). The triangle condition on the Clebsch-Gordan coefficient involving $K$ and $K'$ is zero if both $J = J'$ and $K = K' = 0$. These considerations give rise to the well-known general symmetric top rotational selection rules previously given in Eqs 2.3 and 2.4. In addition, the Clebsch-Gordan coefficient in Eq. 2.27 involving $M$ and $M'$ gives rise to the well-known $\Delta M = +1$ selection rule for absorption of left circularly polarized light.

Taking these selection rules into account, Eq. 2.27 becomes

$$P(JKM; J'KM + 1) = \frac{2J + 1}{2J' + 1} |\langle JK, 10 | J'K' \rangle|^2 |\langle JM, 11 | J'M + 1 \rangle|^2 \ .$$

(2.28)

with $\Delta J = 0, \pm 1$ and all other transitions forbidden.

### 2.2.2 Probabilities for rotational transitions by branch type

Eq. 2.28 allows us to attack the problem of how the rotational state population evolves upon photon absorption. We begin by separately analyzing the detailed relative
absorption probabilities for a beam of LCP light in $P$, $Q$, and $R$-branches of parallel-polarized symmetric top transitions.

**P-branch transitions ($\Delta J = -1$)**

Evaluating the non-zero Clebsch-Gordan coefficients in Eq. 2.28 with $J' = J - 1$ we have

\[
|\langle JK, 10 | J-1 K \rangle|^2 = \frac{(J-K)(J+K)}{J(2J+1)} = \frac{J^2 - K^2}{J(2J+1)}
\]

(2.29)

\[
|\langle JM, 11 | J-1 M+1 \rangle|^2 = \frac{(J-M-1)(J-M)}{2J(2J+1)}
\]

(2.30)

In the high-$J$ (semi-classical) limit, these expressions become

\[
|\langle JK, 10 | J-1 K \rangle|^2 = \frac{J^2 - K^2}{2J^2}
\]

(2.31)

\[
|\langle JM, 11 | J-1 M+1 \rangle|^2 = \frac{(J-M)^2}{4J^2}
\]

(2.32)

and

\[
P(JKM; J-1 K M+1) = \frac{1}{8J^4} \left( J^2 - K^2 \right) (J - M)^2
\]

(2.33)

**Q-branch transitions ($\Delta J = 0$)**

Evaluating the non-zero Clebsch-Gordan coefficients in Eq. 2.28 with $J' = J$ we have

\[
|\langle JK, 10 | JK \rangle|^2 = \frac{K^2}{J(J+1)}
\]

(2.34)

\[
|\langle JM, 11 | JM+1 \rangle|^2 = \frac{(J+M+1)(J-M)}{2J(J+1)}
\]

(2.35)
In the high-$J$ (semi-classical) limit, these expressions become

\[
|\langle JK, 10 | JK \rangle|^2 = \frac{K^2}{J^2} \tag{2.36}
\]

\[
|\langle JM, 11 | JM + 1 \rangle|^2 = \frac{J^2 - M^2}{2J^2} \tag{2.37}
\]

and

\[
P(JKM; JK M + 1) = \frac{1}{2J^4} K^2 \left( J^2 - M^2 \right) . \tag{2.38}
\]

**$R$-branch transitions ($\Delta J = +1$)**

Evaluating the non-zero Clebsch-Gordan coefficients in Eq. 2.28 with $J' = J + 1$ we have

\[
|\langle JK, 10 | J + 1K \rangle|^2 = \frac{(J - K + 1)(J + K + 1)}{(2J + 1)(J + 1)} \tag{2.39}
\]

\[
|\langle JM, 11 | J + 1 M + 1 \rangle|^2 = \frac{(J + M + 1)(J + M + 2)}{(2J + 1)(2J + 2)} . \tag{2.40}
\]

In the high-$J$ (semi-classical) limit, these expressions become

\[
|\langle JK, 10 | J + 1 K \rangle|^2 = \frac{J^2 - K^2}{2J^2} \tag{2.41}
\]

\[
|\langle JM, 11 | J + 1 M + 1 \rangle|^2 = \frac{(J + M)^2}{4J^2} \tag{2.42}
\]

and

\[
P(JKM; J + 1 K M + 1) = \frac{1}{8J^4} (J^2 - K^2) (J + M)^2 . \tag{2.43}
\]
Summary

Multiplying by the common denominator of $8J^4$ gives a qualitative comparison of branch transition probabilities:

<table>
<thead>
<tr>
<th>branch</th>
<th>$(8J^4) \ P(JKM; J'K'M')$</th>
<th>$P$</th>
<th>$(J^2 - K^2)(J - M)^2$</th>
<th>$Q$</th>
<th>$4K^2(J^2 - M^2)$</th>
<th>$R$</th>
<th>$(J^2 - K^2)(J + M)^2$</th>
</tr>
</thead>
</table>

(2.44) (2.45) (2.46)

2.2.3 Qualitative analysis of rotational population evolution

As we have seen, each absorption event from the LCP beam causes $\Delta M = +1$. However, the spontaneous emission process has no such constraint on $\Delta M$, although it is subject to the general $J$, $K$ selection rules in Eqs. 2.3 and 2.4. Therefore, on average, the emission process has no systematic change on the rotational population distribution and we can ignore it here.

Subsequently, each absorption event effectively always increases $M$, regardless of the change in $J$. The physical range of $M$ is $-J \leq M \leq J$, so that $|M|$ cannot increase beyond $J$. Inspection of Eqs. 2.44-2.46 reveals an inherent preference for the transitions that will eventually lead to strong orientation and alignment of the absorbing molecules. Envisioning the extreme case of a molecule with initial $J$, $M$ values of $J \gg 0$ and $M \cong -J$, that is, a molecule strongly oriented opposite to the desired sense of rotation, we see that the probability of $Q$ and $R$ branch transitions is practically non-existent (Eqs. 2.45 and 2.46). As $J$ decreases with multiple $P$ branch absorptions the probability of $P$ transitions decreases while the relative probabilities of $Q$ and $R$ transitions increase. Since $\Delta M = +1$ always, $M$ increases to the point that $M > 0$ and transition probabilities now favor the $R$ branch; $Q$ branch transitions
again become improbable. As $M$ becomes increasingly positive so that $M \approx J$, the $R$ branch dominates. In this way, the constraint of $\Delta M = +1$ causes transition probabilities which favor a move to states where $M \approx J$ with increasingly higher $J$ values. Thus, individual molecules will become rotationally oriented with respect to the propagation direction, $k$, of the circularly polarized light, regardless of their initial rotational orientation, and a population of molecules as a whole will become rotationally strongly oriented and aligned.

The energy of rotation as a function of $J$ and $K$ is

$$E(J, K) = BJ(J + 1) + (A - B)K^2$$

(2.47)

where $A$ and $B$ are the rotational constants. For a prolate, symmetric top, $A \gg B$. Thus, for a room-temperature thermal distribution of these molecules, $K$ will be small. Absorption/emission processes do not affect $K$ (Eqs. 2.3 and 2.4). While it is possible for collisions to affect $K$, very few collisions will be able to do so to any significant degree because the moment arm for exciting rotation about $\hat{r}$ is small and the energy levels for rotation about the $z$-axis are very widely spaced for a prolate top. Thus, $K$ will remain relatively unchanged from the initial distribution of $K \approx 0$, and in the high-$J$ limit where $J \gg K$, the approximation of $K = 0$ can be made and Eqs 2.44 - 2.46 become

<table>
<thead>
<tr>
<th>branch</th>
<th>$(8J^4)P(JK = 0M; J'K' = 0M')$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>$J^2(J - M)^2$</td>
</tr>
<tr>
<td>$Q$</td>
<td>$0$</td>
</tr>
<tr>
<td>$R$</td>
<td>$J^2(J + M)^2$</td>
</tr>
</tbody>
</table>

(2.48) \hspace{1cm} (2.49) \hspace{1cm} (2.50)

so that only $P$ and $R$ branch transitions need be considered for extremely prolate
The rotational alignment of the ensemble of molecules can be detected by analyzing the polarization of emitted light. As molecules emit photons polarized parallel to the transition dipole moment axis, a population that is rotationally aligned will emit light polarized along the plane of rotation of the transition dipole. For symmetric top molecules with parallel transitions (i.e. the electronic transition dipole is parallel to the cylindrical symmetry axis), emitted photons will be polarized in the plane perpendicular to the angular momentum vector. In Fig. 2.2b, a population of molecules with perfect rotational alignment (with \( \mathbf{r} \) rotating in the \( XY \) plane) will emit light polarized only in the \( XY \) plane. Comparing the number of detected photons polarized in the \( XY \) plane with those polarized in the \( YZ \) plane will give a measure of the degree of rotational alignment achieved.

### 2.3 Monte Carlo Simulations

#### 2.3.1 Rotational

Stochastic simulations were made to determine the feasibility of this project prior to experiments. An ensemble of 10,000 absorbing rigid rotors was studied for up to 60,000 iterations of photon absorption according to the scheme depicted in Fig. 2.4. Initial values of \( J \) were randomly selected from a Boltzmann distribution, using the “rejection method”. The probability distribution as a function of \( J \) is

\[
P_{Boltz}(J) = (2J + 1)e^{-\frac{E_{rot}}{kT}},
\]

with the energy of rotation calculated by

\[
E_{\text{rot}} = BJ(J + 1).
\]
Figure 2.3: Perylene dye derivative having a rotational constant $B = 7 \times 10^{-4}$ cm$^{-1}$ which was used in the rotational simulations.

where $B$ and $T$ are the rotational constant and temperature, respectively. The family of perylene dye molecules was chosen as a basis for this model as it has strong absorption well into the visible range, high fluorescence quantum yields, fluorescence lifetimes on the nanosecond timescale, and is extremely photostable.$^{15,16}$ Additionally, the transition dipole moment, $\hat{r}$ for visible light absorption lies along the long axis of this molecule.$^{17}$ Thus, the rotational constant of the perylene derivative shown in Fig. 2.3, $B = 7 \times 10^{-4}$ cm$^{-1}$, was used for the simulations. The initial distribution of $J$ values was calculated for room temperature, $T = 300$ K. The maximum allowed value for $J$ was set to $J_{\text{max}} = 10,000$, which, with the chosen $B$ value, equates to a rotational energy of $70,000$ cm$^{-1}$. The equivalent temperature of a population of molecules whose most probable $J$ value is 10,000 would be over 200,000 K. In practice, molecules would never reach these unrealistic rotational energies.

The initial $Z$ projection of angular momentum of the $i^{th}$ rotor, $M_i$, was selected from a uniform distribution among the possible values $-J_i \leq M_i \leq J_i$. A simulated photon of left circularly polarized light with $j_p = 1$ and $m_p = +1$ is “absorbed”, and the resulting final state, $J'_i, M'_i$, is calculated by the Clebsch-Gordan probabilities

$$P(J_iM_i; J'_iM'_i) = \frac{(-1)^{(J_i-j_p-M'_i)}}{\sqrt{2J+1}} \langle J_iM_i, j_p|J'_iM'_i\rangle^2$$

(2.53)
Figure 2.4: Flowchart depicting the algorithm for the change in the $J$ and $M$ quantum numbers for the $i^{th}$ absorber over one simulation cycle through the absorption of circularly polarized light. The process is calculated for $N = 10,000$ absorbers and repeated for $n = 60,000$ iterations of photons absorbed. For a given number of photons absorbed ($n$), the ensemble average $\langle J \rangle$ and $\langle M \rangle$ values are calculated, along with the alignment parameters $A_0^1$ and $A_0^2$. 

\[
\begin{align*}
J_i &= J'_i \\
M_i &= M'_i
\end{align*}
\]

no

\[
\begin{align*}
J_i = J'_i \\
M_i &= M'_i
\end{align*}
\]

yes

$P_{\text{col}}(J'M' \rightarrow J \ M)$

repeat for $N$ absorbers

repeat for $n$ photons absorbed
which, substituting in \( j_p = 1 \) and \( m_p = +1 \) for LCP, becomes

\[
P(J_i M_i; J'_i M'_i) = \frac{(1)}{2J + 1} |\langle J_i M_i, 11|J'_i M'_i\rangle|^2.
\]

(2.54)

which is proportional to Eq. 2.28 for a \( K = 0 \) rigid rotor. Collisions with neighboring molecules have an effect on the total \( J \) and \( M \) values and may impede the build-up of angular momentum orientation; therefore, a collisional step is included to phenomenologically account for thermalization of rotation. The collision probability, \( K_{col} \) defines the average number of collisions per photon absorbed. If a collision occurs, \( J_i \) and \( M_i \) are allowed to change according to a Gaussian transfer function with a FWHM of \( w_{col} \). \( J \) and \( M \) values after collision are assigned according to the probabilities

\[
P_{col}(J' \to J) = P_{Boltz}(J)e^{-\frac{4(ln 2)(\frac{J-J'}{w_{col}})^2}{Q}}
\]

(2.55)

\[
P_{col}(M' \to M) = e^{-\frac{4(ln 2)(\frac{M}{w_{col}})^2}{Q}},
\]

(2.56)

where \( Q \) is a partition function used to normalize the probabilities. If \( |M'| > J' \), then the program sets \( |M'| = J' \). Multiplication by \( P_{Boltz}(J) \) in Eq. 2.55 forces the colliding absorbers to return to a Boltzmann-like thermal distribution in the absence of optical pumping. The width parameter, \( w_{col} \), was set to a value of 10, which is much narrower than the width of the Boltzmann rotational distribution, for which \( \langle J \rangle = 1220 \) at 300 K.

Values for \( J \) and \( M \) are constrained to be \( 0 \leq J_i \leq J_{\text{max}} \) and \( -J_i \leq M_i \leq J_i \). The ensemble average values \( \langle J \rangle \) and \( \langle M \rangle \) can be calculated after each iterative cycle of photon absorption and possible collision. The evolution of \( J \) for different \( K_{col} \) values is shown in Fig. 2.5. For the lowest \( K_{col} \) shown (0.005), the population of \( J \) values becomes quite high and some absorbers reach the maximum allowed value,
Figure 2.5: The evolution of $J$ values in the population of absorbers for different collisional probabilities, $K_{\text{col}}$. The population of $J$ values starts in a Boltzmann distribution with $B = 7 \times 10^{-4} \text{ cm}^{-1}$, $T = 300$ K. After successive absorptions, $\langle J \rangle$ increases and the rotational population distribution broadens. Higher $K_{\text{col}}$ values dampens this effect.
Figure 2.6: Calculated evolution of the ensemble-average $J$ and $M$ values as a function of the number of photons absorbed for various collisional probabilities, $K_{\text{col}}$. The inset shows progression of $\langle J \rangle$ and $\langle M \rangle$ in the first 6,000 absorptions.

$J_{\text{max}}$. However, for higher collisional frequencies, such as $K_{\text{col}} = 0.1$, the population of $J$ values shows little to no increase away from the room-temperature thermal Boltzmann distribution even after 60,000 photons are absorbed. Figure 2.6 shows how $\langle J \rangle$ and $\langle M \rangle$ increase with the number of absorbed photons for various values of $K_{\text{col}}$. Initially, $\langle J \rangle$ corresponds to a room-temperature thermal distribution of $J$ values and $\langle M \rangle$ is zero, corresponding to a uniform distribution of all $M$ values. In all cases, the ensemble reaches some photostationary value of both $\langle J \rangle$ and $\langle M \rangle$ which decreases with increasing $K_{\text{col}}$. For $K_{\text{col}}=0.01$ or 0.005, $\langle M \rangle$ matches $\langle J \rangle$ after
absorbing roughly 1,000 photons, after which the majority of the absorbers have their angular momentum vector nearly perfectly aligned with the Z axis. Under higher collisional frequency conditions ($K_{col} = 0.05$ or 0.1), the alignment is noticeably less.

In theoretical treatments of angular momentum distributions, it is common to expand the anisotropy of the spatial distribution of $J$ in the moments of a spherical harmonic basis. These moments can be used to quantitatively predict the degree of absorption or emission polarization. The moments $A_0^1$ and $A_0^2$ quantify the degree of rotational orientation and alignment and are quantities that can be extracted from experimental polarized spectroscopy measurements. In terms of $J$ and $M$ values, these moments are classically expressed as:

$$A_0^1 = \frac{1}{n_{rotors}} \sum_i \frac{M_i}{\sqrt{J_i(J_i + 1)}}$$

$$A_0^2 = \frac{1}{n_{rotors}} \sum_i \frac{3M_i^2 - J_i(J_i + 1)}{J_i(J_i + 1)}$$

where the orientation moment $A_0^1$ has values physically constrained to lie in the range $\{-1,1\}$ and the alignment moment $A_0^2$ has values in the range $\{-1,2\}$. In both cases, the limiting values indicate perfect orientation or alignment while a value of zero represents an isotropic distribution of the angular momentum vector. Figure 2.7 shows the evolution of orientation and alignment in the absorber population for various values of $K_{col}$. For the cases of $K_{col}=0.01$ or 0.005, the population reaches near perfect $\hat{J} \parallel Z$ rotational orientation ($A_0^1 = +1$) and alignment ($A_0^2 = +2$). In all cases, the population reaches a photostationary rotational orientation and alignment, notably showing significant orientation before photostationary alignment is fully achieved. It is interesting to note that $A_0^1$ and $A_0^2$ reach photostationary values more quickly than $\langle J \rangle$ and $\langle M \rangle$, indicating that the absorbers become oriented and aligned long before they have reached their maximum photostationary $\langle J \rangle$. For larger $K_{col}$ values (0.05
Figure 2.7: Calculated rotational orientation, $A_1^0$, and alignment, $A_0^2$, moments for the ensemble of molecules as a function of the number of photons absorbed displayed as absolute moment value (top) and percent of limiting value (bottom) where a value of 100% indicates perfect orientation or alignment. Evolution of rotational orientation and alignment is shown for the first 3,000 absorptions (right) and the full 60,000 absorptions (left).
Figure 2.8: The ensemble “photostationary” average value of a) $\langle J \rangle$ and $\langle M \rangle$, b) $A^1_0$ and $A^2_0$ shown as percent of limiting value reached after 60,000 photons absorbed as a function of the collisional probability, $K_{col}$.

or 0.1), the maximum photostationary orientation and alignment is diminished due to the thermalizing effect of collisions on $J$ and $M$. Figure 2.8 shows the effect of $K_{col}$ on the final photostationary values of $\langle J \rangle$, $\langle M \rangle$, $A^1_0$, and $A^2_0$.

As seen in Fig. 2.5, for $K_{col}$=0.005, after 60,000 iterations, the absorbers reach very high $J$ values, with significant population occupying $J = J_{max}$. For this case, $\langle J \rangle$=7,500, which, with $B = 7 \times 10^{-4}$ cm$^{-1}$, equates to a rotational temperature of 100,000 K. It is reasonable to assume that, in reality, molecules would not reach such high rotational levels with also experiencing other effects of increased internal energy. It is likely that these molecules will have built up significant internal vibrational energy and centrifugal distortion effects before reaching such high rotational levels.

Also seen in Fig. 2.8, higher collision rates destroy rotational orientation and alignment. Therefore, the number of collisions must be minimized if there is to be significant buildup of angular momentum orientation. A supersonic molecular
beam like the one used in Chapter 1 offers near collision-free conditions; however, the molecules in a molecular beam spend a short time interacting with the laser, preventing the absorption and emission of many photons. (A dilute sample in a light carrier gas such as H₂ with a beam velocity of approximately \(3 \times 10^3 \text{ m s}^{-1}\) would traverse a 1 mm diameter beam in about 300 ns.) A gas cell may also be considered, though a similar drawback of too brief an amount of time spent in the laser beam applies as well, in addition to a high collision frequency. An ion trap allows molecular ions to be held in the laser beam for seconds to minutes while still minimizing collisions by working in high vacuum.

We must also consider how to detect rotational orientation. The number of trapped molecular ions will be small, and therefore monitoring absorption would be impractical. As discussed above, the degree of rotational alignment can be monitored through the polarization of the emitted photons. Detection of emission from the trapped ions is more practical; however, the sensitivity of detection is strongly dependent on low background signal.

### 2.3.2 Vibrational

A second simulation was performed to monitor the vibrational levels of these absorbers as they cycled between the two electronic states coupled by absorption and emission. For simplicity, only one vibrational mode was considered, as might be expected if the molecule has only one Franck-Condon active vibration progression in the electronic absorption spectrum. The system was arbitrarily modeled after Cl₂ because of its absorption in the spectral region of interest and its relatively small vibrational spacings that could qualitatively correspond to those found in polyaromatic hydrocarbons. For the \(X \ 1\Sigma^+_g \rightarrow B \ 3\Pi^+_u\) transition of Cl₂, the spectroscopic constants are \(\omega''_{e} = 559.7, \omega''_{e}x_{e} = 2.67, \omega'_{e} = 259.5, \omega'_{e}x'_{e} = 5.38 \text{ cm}^{-1},\) and a \(T_e=17809 \text{ cm}^{-1}.\)
Figure 2.9: A three dimensional representation of the matrix of Franck-Condon factors for transitions between vibrational levels in the ground, $v''$, and excited, $v'$, states of the $X \, ^1\Sigma_g^+ \rightarrow B \, ^3\Pi_u^+$ transition of Cl$_2^{18}$ with $\Delta R = 0.112$ Å.

A matrix of Franck-Condon probabilities was calculated using Mathematica for the transitions between the vibrational levels in the ground, $v''$, and excited, $v'$, electronic states according to

$$ q_{FC}(v', v'') = |\int \Psi_{v'} \Psi_{v''} \, dr|^2, $$

(2.59)

where the Morse oscillator wavefunctions for the ground, $\Psi_{v''}$, and excited, $\Psi_{v'}$, state vibrational levels are described by Rong et al.$^{19}$ and further discussed in Sec. A.2. The equilibrium bond length of both the ground and excited electronic states were varied, with bond length in the ground state being approximately 2.0 Å and the
repeat for \( n \) photons absorbed

Figure 2.10: The flowchart shows the algorithm for the change in the ground vibrational quantum number, \( v'' \), for the \( i^{th} \) absorber over one simulation cycle through the absorption of circularly polarized light. The process is calculated for \( N = 10,000 \) absorbers and repeated for \( n = 60,000 \) iterations of photons absorbed.

difference of the equilibrium bond lengths, \( \Delta R \), varied to investigate how \( \Delta R \) affects the transition probabilities, \( q_{FC} \). Figure 2.9 shows the three dimensional plot of the Franck-Condon factors calculated for a \( \Delta R = 0.112 \).

The light source was assumed to have a Gaussian photon energy distribution centered on an assigned photon energy in the visible region with a FWHM of \( \Gamma = 150 \) cm\(^{-1} \). Figure 2.10 provides a flowchart of the simulation method. The population of absorbers begin with \( v'' = 0 \), and the probability of absorbing a photon, \( P_{abs} \), is determined by the overlap of the energy of the exciting photon, \( E_{photon} \), and the energy of the transition, \( E_{abs}(v'',v') \), multiplied by the Franck-Condon probability for that transition:

\[
P_{abs} = q_{FC}(v', v'') e^{-\frac{4ln2}{\Gamma^2}(E_{abs}(v'',v')-E_{photon})},
\]

(2.60)
and

\[
E_{\text{abs}}(v'', v') = \left[ \omega_e \left( v' + \frac{1}{2} \right) - \omega_e x_e \left( v' + \frac{1}{2} \right)^2 \right] - \left[ \omega_e \left( v'' + \frac{1}{2} \right) - \omega_e x_e \left( v'' + \frac{1}{2} \right)^2 \right] + T_e .
\] (2.61)

To simulate emission, the excited absorber subsequently relaxes to the ground state in some vibrational level \( v'' \) determined purely by Franck-Condon probabilities. On each time step, after absorption and emission, the absorber is allowed to collisionally relax with some probability \( P_{\text{col}} \). If a collision occurs, \( v'' \) is reset to the ground vibrational level \( (v'' = 0) \). Should absorption occur when \( E_{\text{photon}} > E_{\text{abs}}(v'', v'_{\text{max}}) \), the absorber “dissociates” and is removed from the population of simulated absorbers from that point forward.

Figure 2.11 shows the evolution of the population distribution of \( v'' \) over the course of irradiation, taking into account dissociation; Fig. 2.12 shows the total population of absorbers over the course of simulated irradiation. For the case shown, \( \Delta R = 0.10 \) Å and \( E_{\text{photon}} = 19000 \) cm\(^{-1} \), 1040 cm\(^{-1} \) higher than the 0-0 vibrational origin transition.

The most-likely transitions as dictated by the Franck-Condon factors keep the absorbers cycling between \( v'' = 0 \overset{\text{abs}}{\longleftrightarrow} v' = 1 \) levels. Despite this, Fig. 2.5 shows that a significant population of absorbers transition to higher vibrational levels and eventually dissociate. When the evolution of a single absorber was followed, it was found that it did not repetitively cycle between the preferred vibrational levels in the excited and ground electronic states. The large number of Franck-Condon allowed transitions means that occasionally an absorber will emit to a higher ground vibrational level. Absorption of another photon excites the absorber to a higher vibrational level in the excited state, where there is an increased probability of emitting to the ground state in a still higher vibrational level. Figure 2.13 depicts the one-dimensional potential
Figure 2.11: Population distribution of $v''$ values over the course of simulated irradiation for $\Delta R$ values of 0.05 and 0.10 Å, and various probabilities of collisional relaxation, $K_{col}$. 
Figure 2.12: The total population of absorbers as a function of the number of absorption events for $\Delta R=0.05$ and $0.10$ Å at various probabilities of collisional relaxation, $K_{\text{col}}$. 
energy surface and vibrational levels used for this model based on the $X \: ^1\Sigma_g^+ \rightarrow B \: ^3\Pi_u^+$ transition of Cl$_2$ and the path taken by a molecule if every transition occurred according to the second most-likely event. In this case, enough vibrational energy has built up that absorption of the fifth photon causes dissociation. Each individual molecule will follow its own random path of vibrational levels among the ground and excited electronic states; however, this figure demonstrates how quickly dissociation can be achieved once an absorber undergoes a less likely transition and begins to “walk” to higher vibrational levels. Figures 2.11 and 2.12 show that the lower $\Delta R$, i.e. the more vertical transition, shows progression to high $v''$ levels, and subsequently, slower population decay.

While the ground vibrational levels of the two electronic states, $v'' = v' = 0$, may not be ideal for repetitive absorption and emission cycles, it could be possible that some higher pair of vibrational state, $v', v > 0$, exist between which the system cycles more efficiently. Exploring this possibility, varying the photon energies through $v' > 0$ vibrational transitions showed that exciting to higher $v'$ vibrational levels caused the dissociation threshold to be reached more quickly. Alternatively, if the photon energy is decreased to excite a lower energy $v'' > 0 \rightarrow v' > 0$ transition in the attempt to slow the vibrational heating, the absorbers can also slowly “walk” to lower $v''$ vibrational levels until they reach the point where the photon energy is no longer sufficient to excite them to the upper electronic state. Investigation of the effect of $\Delta R$ on the dissociation of these absorbers showed that, in general, a smaller $\Delta R$ value, i.e., a more vertical transition, increased the relative probability of a $v'' = 0 \leftarrow v' = 0$ emission, making transitions to $v'' > 0$ less likely. Unfortunately, the end result was the same; eventually the absorbers would undergo a transition to higher vibrational levels and begin their “walk” to dissociation.

Therefore, for the two-state model investigated, “Franck-Condon walking” pre-
Figure 2.13: The one-dimensional potential energy surfaces of the ground, $v''$, and excited, $v'$, electronic states and their vibrational levels used in the simulation, using potential parameters for the $X^1\Sigma_g^+ \rightarrow B^3\Pi_u$ transition of Cl$_2$. A molecule initially in the $v'' = 0$ level is excited by a photon of $E_{photon} = 19000$ cm$^{-1}$. The largest Franck-Condon factors favor excitation to $v' = 1$ and then emission back to $v'' = 0$. The most probable state evolution is not shown. Instead, the vertical arrows here depict the path of a molecule following the second most probable transition for each individual excitation and relaxation step.
vented the molecule from continuously absorbing and emitting photons indefinitely; either the molecule accumulated vibrational energy over the course of multiple absorption/emission events to the point of dissociation, or a vibrationally hot molecule irradiated with lower photon energy to excite a $v'' > 0 \rightarrow v' > 0$ transition would cool to the point where the photon energy was insufficient to excite $v''$ levels with appreciable Franck-Condon factors. The collisional frequency $K_{col}$ was increased to allow for complete relaxation between absorption cycles more often. This did serve to quench the “Franck-Condon walking”.

2.4 Discussion

The vibrational dynamics simulation used a simple, two-electronic state model with a single vibrational mode, whereas molecules experimentally considered would have a high density of vibrational modes and levels to access, providing more ways to distribute vibrational energy. Vibrational simulations with this simple model showed significant dissociation occurring within 50-100 photon absorptions, and rotational simulations showed the molecules requiring 5 times that amount to build up significant orientation and alignment under similar collisional frequencies. These results are not favorable for the molecular rotation orientation experiments proposed earlier. However, the results did show that the effect of “Franck-Condon walking” can be decreased by collisional relaxation and by electronic transitions which are more vertical in nature, \textit{i.e.} a larger Franck-Condon factor for the 0-0 transition relative to the other possible transitions. The vibrational simulations reveal concerns about vibrational heating in the molecular absorbers, but the promising results of the rotational simulations justify an experimental attempt.
Bibliography


5. R. N. Zare, chapter 5.

6. R. N. Zare, eq. 5.4.

7. R. N. Zare, eq. 5.118.

8. R. N. Zare, sec. 6.5.

9. R. N. Zare, eq. 5.9.

10. R. N. Zare, eq. 6.114.

11. R. N. Zare, eq. 5.41.

12. R. N. Zare, eq. 3.125.

13. R. N. Zare, eq. 3.114.


Chapter 3

Chromophores in an Ion Trap
3.1 Introduction

The laser dye molecule Rhodamine 575 was selected to attempt an experimental test of imparting specific molecular rotational orientation using circularly polarized light as simulated in the previous chapter. Shown in Fig. 3.1, Rhodamine 575 is a large molecule with a large number of vibrational degrees of freedom. It is known to have a large absorption cross section and a high fluorescence quantum yield, making it a good candidate for long-term irradiation studies. Additionally, it is readily available commercially and has been used in other previous ion trapping fluorescence experiments.

3.2 Experimental Setup

A quadrupole ion trap with electrospray ionization source is discussed in further detail elsewhere;\(^1\,^2\) a brief description is given below for context. My contribution focused on the light excitation and detection optics, which is the focus of the following instrumentation description.
Figure 3.2: Ion trapping apparatus designed by Nicholas Sassin, including the electrospray ionization (ESI) source, commercial quadrupole ion trap (QIT), time-of-flight (TOF) region, and multichannel plate (MCP) detectors. Image courtesy of Nicholas Sassín.

3.2.1 Ion Trapping and Detection

The ion trapping apparatus, consisting of an electrospray ionization (ESI) source, quadrupole ion trap (QIT), and time-of-flight (TOF) mass spectrometer, was assembled by Nicholas Sassin and shown in Fig. 3.2, with Fig. 3.3 showing laboratory view of the actual instrument. The QIT and TOF were obtained commercially (R.M. Jordan models C1251 and D850, respectively), and the ESI was custom built using a Kd Scientific syringe pump (model 100) and 0.11 mm diameter needle held at 3.5-5.0 kV (Glassman High Voltage Inc., EL series). The QIT is cylindrically symmetric with a hyperbolic geometry and is comprised of three electrodes: two end cap electrodes 0.71 cm from the center, and a ring electrode with radius 1.00 cm. The ring electrode is applied with a 983 kHz, 900 V electric field which traps the ions while the two
end electrodes are held at ground potential during ion trapping. Ions enter and exit the trap through a 2.97 mm diameter hole bored into each of the end electrodes. Four evenly spaced apertures, 2.36 mm in diameter, in the ring electrode allow the transmission of the laser irradiation beam and collection of fluorescence emitted by trapped ions. He buffer gas introduced into the ion trap region is controlled using a variable leak valve (Granville Phillips series 203). Ion fill into the trap region is controlled by an electric field deflector, gated using a dc voltage pulser (R.M. Jordan D-1040), while ion extraction from the trap is accomplished by applying a 10 μs long 500 V pulse to one of the end electrodes, transferring the ion cloud to the TOF mass spectrometer with a multichannel plate (MCP) detector.\textsuperscript{1,2}

The QIT chamber is kept at 30 μTorr pressure by an oil-diffusion pump, though the pressure inside the trap is higher than the base pressure due to the limited conductance out of the trap. Adjustment of the He flow rate by a variable leak valve allows some control over the buffer gas pressure inside the ion trap. Estimated operational trap pressures range from 0.27 to 0.95 mTorr with 10% uncertainty of the relative pressure and 50% uncertainty of the absolute pressure. Once the dye molecular cations are trapped, they are irradiated for a period of time, after which the extraction pulse empties the ion trap and directs the ion cloud to the TOF mass spectrometer where the composition of the ion cloud population is mass analyzed.\textsuperscript{1,2}

### 3.2.2 Laser Excitation and Fluorescence Detection

A continuous beam of 514 nm radiation was generated by an Ar\textsuperscript{+} laser (Coherent Innova 100) and was directed through apertures in the QIT ring electrode into the interaction region at the center of the ion trap after passing through a spatial filter, polarization optics, and light baffles as shown in Fig. 3.4. The spatial filter selected out the fundamental transverse mode (TEM\textsubscript{00}) and was comprised of an 11 mm
Figure 3.3: Vacuum Chamber showing ESI source on the left, the TOF chamber on the right, the light baffles which are perpendicular to the TOF axis and are extending out towards the observer, and fluorescence collection stack extending upwards from the ion trap region with PMT detector mounted above. The ion trap itself is located at the conjunction of the ion source, laser excitation, and detection axes.
Figure 3.4: Diagram of Ar ion laser light path. The spatial filter generates a Gaussian-shaped beam profile (TEM 00). The first polarization rotator (a) coupled with the Glan prism (b) further downstream acts as an intensity attenuator, transmitting vertically polarized light to the waveplates that control the polarization of the beam entering the trap. The 1 m focal length lens places the focal point in the center of the ion trap with a beam waist of 1 mm. The $\lambda/2$ and $\lambda/4$ waveplates set the final light polarization for studies with either linearly or circularly polarized light. Light baffle tubes minimize room light and provide additional collimation of laser light to minimize scattering off optics surfaces from entering the trap region.
focal length lens which focused the beam through a 15 μm diameter pinhole and a 5x microscope objective which re-collimated the beam. This left the beam with an approximately Gaussian-shaped transverse spatial profile. The beam was then elevated to the level of the ion trap by periscoping mirrors and the polarization was controlled by a λ/2 waveplate (linear polarization) or a λ/4 waveplate (circular polarization). A 1 m focal length lens focused the beam into the reaction region with the focal point at the center of the ion trap. The pairing of a λ/2 waveplate to rotate the vertically polarized incident light and a Glan prism allowed attenuation of the laser beam intensity for variable irradiation power studies. The beam attenuator produced linearly polarized light and was located upstream of the final polarization control optics. Finally, the beam passes through an anti-reflection (AR) coated flat window normal to the laser beam axis into the vacuum region and ion trap. Setting the windows at the Brewster angle to reduce the amount of laser light scattered off the surface is impractical in this case where multiple laser light polarizations will be used. After passing through another flat AR coated window on the opposite side of the vacuum chamber, a power meter monitored the intensity of light.

The light baffles between the vacuum chamber windows and the ion trap were designed to minimize the amount of scattered light from room lights and laser scatter off nearby optics reaching the ion trap. Each baffle consists of a 0.5 m tube with five apertures unevenly spaced along the length of the baffles. The inside of the baffles and the apertures are black anodized to absorb light. On the laser input side the apertures are 1 mm in diameter, just large enough to admit the laser beam. Those on the output side are larger (0.25 in) to ensure that all the light passing through the ion trap is allowed to reach the power meter. Section A.1.1 gives the design in detail, including adjustment pieces which allow the axes between the two baffle tubes and the ion trap to be properly aligned.
Fluorescence emitted from chromophores inside the ion trap is collected at 90° from both the irradiation and ion source axes. Looking down into the trap from above, a series of collection optics directs light originating from the ion cloud onto a photomultiplier tube (PMT) for detection as shown in Fig. 3.5. The fluorescence collection stack PMT detector housing can also be seen in the laboratory view shown in Fig. 3.3, as well as the light baffle tube through which the laser beam exists. The collection lens closest to the trap has its focal point centered so that light emanating from the ion cloud is collimated along a collection tube and re-focused by a second lens through a 1 mm pinhole. The placement of the lenses and pinhole are such that light emanating from places other than the focal point (i.e. laser light scattering off the walls of the trap chamber) is not efficiently re-focused through the pinhole and therefore is selectively blocked from the detector. A holographic notch filter (Semrock StopLine) between the two lenses blocks the wavelength of laser light with a 50% transmittance bandwidth of 16 nm, thus further discriminating against any scattered laser light from reaching the detector. The two collection lenses, holographic notch filter, and pinhole are enclosed in a single, light-tight lens tube positioned on a horizontal translation stage through a mount which allows for vertical adjustment of the collection stack as a whole. A custom designed vacuum flange window mount allows positioning of the collection lens relatively close to the ion trap. Design details of this flange are given in Sec. A.1.2. An XY translation stage is attached to the flange so that the collection lens is 100 mm above the ion trap. The collection stack moves independently from the PMT detector. Light baffles shield the junction between the collection stack and the PMT detector from room light. The refrigerated PMT (Hamamatsu R943-02 PMT with Products for Research PHOTOCOOL Housing) is coupled to a photon counter (Stanford Research SR400), and measured dark counts are typically 10-20 photons/second in the absence of laser light. Light detected from laser scatter is as
Figure 3.5: Diagram of Fluorescence Collection Optics. The confocal geometry of the two lenses and pinhole collect light emanating only from a small region near the focal point of the bottom-most lens and directs it onto the PMT detector. A holographic notch filter blocks a narrow bandwidth centered on the frequency of the exciting laser light to minimize the detection of laser scatter. The addition of light baffles around the junction between the optics stack and the detector minimizes the amount of excess room light reaching the detector.
little as 200 counts/second for 0.10 W (10^{17} photons/second at 514 nm) entering the trap region.

A rotatable polarizer can be placed between the pinhole and the detector for fluorescence polarization studies. The holographic notch filter used is normal to the detection axis for 514 nm light. When 488 nm or other wavelengths are used, the notch filter is tilted out of the plane of detection in order to effectively block the laser light. This tilt causes a s-polarized light to be blocked more efficiently than p-polarized light. The holographic notch filter is therefore rotated in conjunction with the polarizer to eliminate the effects of this polarization preference.

Efficiency of photon collection is primarily limited by a small collection angle, the detection efficiency of the PMT, and the transmittance of the collection optics. Light emanating from the ion cloud is collected through one of the 2.36 mm diameter apertures in the ion trap’s ring electrode 1.00 cm above the center of the trap, giving a solid angle of collection of \( \Omega/4\pi = 2.2 \times 10^{-3} \). The estimated transmittance though the collection optics is 0.59, and the detection efficiency of the PMT’s photocathode is approximately 0.14, giving a total estimated collection efficiency of approximately 2.7 \times 10^{-4}.^3 There is also a strong dependence on the position of the collection stack, as it is designed to collect light emanating only from the region very near the focal point of the bottom-most lens. The position dependence was calculated by Joseph Cline using a Monte-Carlo ray tracing algorithm which calculates the number of photons originating from a point source that were directed onto a detector using the fluorescence collection system described above. The results of this calculation are shown in Fig. 3.6.

These calculations show that displacement of the focal point from the center of the ion cloud by 10 mm in the vertical direction results in a signal loss of about 15%. In contrast, the same degree of signal loss is caused by the displacement of
Figure 3.6: Calculations of the spatial sensitivity of the fluorescence collection efficiency as a function of horizontal (radial) or vertical (axial) displacement away from the center of the ion cloud. Contours show the relative number of randomly emitted light rays from the point source (defined as the origin) that are successfully transmitted by the confocal optics onto the photocathode of the PMT detector calculated for a collection pinhole diameter of 1.0 mm.
Figure 3.7: Topology of light detected by the PMT as the collection stack is scanned over ion trap, showing the background-subtracted fluorescence signal and the total background scatter light detected in the absence of rhodamine dye molecules. The ion cloud as detected by the fluorescence topology is not concentric with the ion trap aperture and position of lowest background signal. The collection stack was therefore positioned for the greatest relative fluorescence signal. Only 0.5 mm in the radial direction and further displacement of the detector from the origin of the light source causes a drastic decrease in the relative number of photons. Fine adjustment using the horizontal translation stage allows location of the ion cloud with maximum fluorescence signal. Figure 3.7 shows a sample fluorescence topology map compiled from fluorescence signal detected as the collection stack was scanned over the top aperture of the ion trap. The elongated shape of the ion cloud can be seen as on the order of 1 cm in size. In comparison, the topology of background light scatter detected in a similar sweep of the collection stack position shows one of the walls of the ion trap aperture, seen as the dramatic increase in detected light scatter.
in the lower right corner of the figure. The location of the other wall of the ion trap aperture is detected in the same manner (not shown). The diameter between peaks in background signal is in agreement with the known size of the ion trap aperture. The total intensity of light scattered off the walls of the aperture is asymmetric, probably due to the directionality from which the laser light originates. Additionally, the shape of the ion cloud, as determined by the fluorescence topology, is not concentric with the center of ion trap aperture. The result is that the position of greatest fluorescence signal does not coincide with the position of lowest background laser scatter. Signal noise increases proportionately with the intensity of the total photons detected by the PMT, and therefore becomes a significant problem as the background intensity increases. The collection stack was therefore positioned for the greatest signal-to-noise ratio, rather than the largest total fluorescence detected.

3.3 Fluorescence and Photodissociation

3.3.1 Procedure

Rhodamine 575 dye molecules in solution are electrosprayed into the ion trap for a set time interval, controlled by an ion gate. During the trap fill time, the laser is blocked from the ion trap by a beam shutter (Thorlabs SH05). A 0.2 s cooling period allows the molecular cations to thermalize and form an ion cloud in the center of the trap. Once trapped, the ions are irradiated by light generated by an argon ion laser for a variable length of time up to 60 sec. Immediately following irradiation, an extraction pulse empties the trap and directs the contents to the TOF mass spectrometer. Data were collected in one of two ways: mass spectrometric ion detection by a TOF mass spectrometer or photon counting of the fluorescence emitted from the ion cloud.¹

When collecting ion TOF data, the trap was filled for 0.75 s and irradiated for
various lengths of time between 0 and 4 s. TOF mass spectrometric data was signal averaged over 60 repetitions of fill/irradiation/extraction cycles and the individual mass peaks were integrated to give irradiation-time dependence data of the ion trap contents.

Fluorescence measurements used a fill time of 5 s to increase the number of dye molecules trapped and, subsequently, the fluorescence detected. Photons detected by the PMT were counted in 0.5 or 1.0 s intervals for up to 60 s of irradiation. Fluorescence was determined by background subtraction, comparing photon counts detected during laser irradiation while the trap was empty (a measure of background scatter) to counts detected while the trap was filled with ions.

Because the mass spectrometric detection method required the destruction of the ion cloud for each measurement, collecting irradiation-time dependent data over long irradiation periods proved time-prohibitive, while fluorescence collection could monitor time-dependent behavior of a single ion cloud during irradiation. In contrast, detection efficiency for fluorescence is much lower than for the TOF mass spectrometry and requires a larger ion cloud population to be detected. For this reason, the two methods are complementary to each other.

3.3.2 Results

Figure 3.8 shows the sample mass spectra for ion data collected at various irradiation intensities and four different background gas pressures. Previous experiments using a mixed sample of rhodamine 575 and tetraoctyl amine allowed for mass calibration of the time-of-flight mass detection. The primary peak seen in Fig. 3.8 occurs at 415 m/z, corresponding to the singly-charged rhodamine 575 cation. As irradiation intensity increases, the signal strength of the parent peak diminishes while a peak at lower mass-to-charge ratios (m/z) becomes evident (most clearly seen in the 9.0 mTorr
data set. The mass difference corresponds to a loss of one ethyl group (29 amu). When laser intensity is high enough to completely deplete the parent peak, intensities above that show depletion of the product peak as well. Higher background buffer gas pressures quench the photodecomposition of the trapped rhodamine 575 cations (18 mTorr data set). Figure 3.9(a) shows the irradiation-time dependence of the population of trapped rhodamine cations in terms of the normalized ion signal $A_t/A_0$, where $A_t$ is the rhodamine ion signal for a given irradiation time, $t$, and $A_0$ is the initial ion signal for the un-irradiated rhodamine at $t = 0$. Both $A_t$ and $A_0$ ion signals are the integrated area of the rhodamine parent ion peak, averaged over 60 trap fill cycles. Under the lowest pressure condition, 0.27 $\mu$Torr, at laser power of 0.15 W and higher, the parent rhodamine signal is entirely depleted with 1 s. For irradiation intensities as low as 0.05 W, the rhodamine signal is 90% depleted within 4 s of exposure. For irradiation intensities as low as 0.05 W, the rhodamine signal is 90% depleted within 4 s of exposure. In contrast, the rhodamine parent signal suffers no depletion after 4 s of 0.05 W irradiation when the background pressure is increased to 0.95 mTorr. Fluorescence data collection under lower irradiation intensities and longer exposure times demonstrates the same qualitative behavior, as shown in Fig. 3.9(b). Fluorescence data is reported as the number of background-subtracted photon counts during a 1 s count interval, $N_t$. For comparison of fluorescence signal is normalized as $N_t/N_i$, where $N_i$ is the fluorescence signal recorded in the first counting interval, $0 < t < 1.0$ s. The longer irradiation times possible when collecting fluorescence shows that even the highest 0.95 mTorr background pressure does not entirely quench all photodecomposition, though no significant signal depletion was detected by TOF mass spectrometry after 4 s of 0.05 W irradiation.

The $\lambda_{max}$ of absorption for rhodamine 575 in solution is 518 nm, though it is expected to blue-shift in vacuum. A crude wavelength dependence of the observed
Figure 3.8: The time-of-flight mass spectra of trapped rhodamine 575 cations under 514 nm irradiation and various background He buffer gas pressures. Rhodamine parent peak shown at 4550 ns decreases over the course of irradiation and M-29 product peak evolves at approx. 3600 ns. Higher buffer gas pressure diminishes this effect.
Figure 3.9: Normalized Signal measured by a) TOF ion signal and b) fluorescence detection of the population of trapped rhodamine 575 cations over the course of irradiation with 514 nm laser light. While data shown in a) and b) were collected under different irradiation intensities and over an order of magnitude different timescales, they both show the same trend of power and pressure dependence.
Figure 3.10: Relative fluorescence intensity of trapped rhodamine 575 cations as a function of irradiation wavelength. For comparison, fluorescence counts per second have been divided by irradiation intensity in Watts and the trapped rhodamine population as measured by TOF ion signal in mV.

Fluorescence was made using three lines of Ar⁺ laser at 488, 496, and 514 nm. A dramatic increase in fluorescence was observed intensity when irradiated with shorter wavelengths as shown in Fig. 3.10). While we could also produce 476 nm from the argon ion laser, we were unable to block that wavelength due to the extreme tilt required for our holographic notch filter in use. Of the three wavelengths studied, irradiation by 488 nm light gave the greatest fluorescence intensity. As a result, the majority of the fluorescence experiments were conducted using that wavelength.
3.3.3 Photodecomposition Dynamics

The TOF mass spectra show the primary photodecomposition product is the result of a loss of one of the amine’s ethyl groups. The N-ethyl bond dissociation energy was calculated by Prof. Kent Ervin to be 3.64eV using the B3LYP/6-31G* level of theory in Gaussian03.\(^1\) It would require at least two photons of either 514 (2.41 eV) or 488 nm (2.54 eV) light to cause dissociation of this bond. The irradiation intensities used do not exceed 50 W cm\(^{-2}\), which makes simultaneous multi-photon dissociation unlikely. The pressure-dependent behavior of photodissociation corroborates the fact that this process is neither a single-photon or simultaneous multi-photon event. The power- and pressure dependence of the data shows a competition between dissociation caused by irradiation and quenching through collisions with the buffer gas. Collisions inside the trap occur nearly as often as absorption/emission events, on the order of 15-20 ms\(^{-1}\) for collisions under these buffer gas pressures and 5-10 ms\(^{-1}\) for absorptions given 0.20 W irradiation (based on solution studies).\(^1\) Therefore, the photodissociation mechanism must be such that it involves either a method of storing energy between separate absorption/emission events that is not efficiently dissipated by collisions until there is enough to break the N-ethyl bond, or some intermediate state from which single-photon dissociation is possible but is long-lived enough to allow collisions to quench this state.

Direct comparisons of experimental photodissociation data to the simulations discussed in Sec. 2.3.2 are not possible. The simulation model was a simple, two-electronic state system with a single mode of vibration. Rhodamine 575 dye molecules have many more vibrational modes available to distribute any energy stored through multiple photon absorptions. Additionally, collisions modeled in the simulation assumed strong collisional relaxation, with a single collision able to return the molecule to the ground vibrational level. In the case of the experiments conducted here, colli-
sions of Rhodamine dye molecules ($M.W.415$ amu) with helium buffer gas ($M.W.4$ amu) would be far less efficient. Calculations by Nicholas Sassin estimated that it would require approximately 150 collisions between Rhodamine 575 and helium atoms to remove the $2.41$eV of energy absorbed from a single $514$ nm photon.$^1$

The time-dependent rhodamine signal is fit to a single exponential decay curve, as shown in Fig. 3.9. Figure 3.11 shows the decay constants extracted from the fits. An attempt to fit the dissociation kinetics to a model proved difficult. After examining a wide variety of plausible kinetic models, it was determined that a multi-state system and high-order pressure dependence on relaxation was required to explain the observed data. Those same calculations indicated an effective absorption rate constant of $8$ s$^{-1}$, which would allow more than $2000$ collisions per absorption event under the buffer gas pressure conditions of the experiment.$^1$ However, rhodamine dye molecules in solution have fluorescence lifetimes that are typically on the ns timescale, and it is presumed that the fluorescence lifetime in the gas phase is not significantly different. Under this assumption, it is reasonable to deduce that many efficient absorption/emission events occur before accumulating enough energy in the molecule’s internal modes to lead to dissociation.

These results are discussed in detail in Ref. 1. In this thesis, I focus on my attempts to detect rotational orientation imparted by absorption of circularly polarized light.

As rapid photodissociation is counter-productive to our investigation of molecular rotational orientation and alignment, experimental conditions of low background pressure and high irradiation intensities were to be avoided. On the other hand, buffer gas pressures sufficient enough to effectively quench photodissociation may also be sufficient to quench any build up of rotational orientation in the chromophore population.
Figure 3.11: Decay constants from single-exponential decay fits to the experimental data as a function of laser power for various background buffer gas pressures.
3.4 Rotational Orientation

As discussed in Sec. 2.3.1, rotationally oriented molecular ions would show a polarization anisotropy for emitted light polarized parallel versus perpendicular to the light propagation axis, $\hat{k}$. Rhodamine 575 fluorescence polarized parallel to $\hat{k}$ was compared to fluorescence polarized perpendicular for both linearly (magic angle = 54° from the detection axis) and circularly (left and right) polarized 488 nm laser light as shown in Fig. 3.12. For both irradiation intensities shown, there is no difference in intensity of fluorescence polarized either parallel or perpendicular when rhodamine is irradiated with linearly polarized light (within the experimental uncertainty limits). If the rhodamine molecules had become rotationally oriented with respect to the laser beam, the fluorescence emitted should be polarized perpendicular to the laser beam axis. The majority of data in Fig. 3.12 shows higher fluorescence polarized perpendicular to the laser beam when excited with circularly polarized light, in agreement with the theory outlined in Fig. 2.2. However, the data is not conclusive as there are at least two cases of contradictory data (0.5 mTorr pressure, 0.12 W and 0.14 W RCP) and a number of cases where the difference between the two fluorescence polarizations does not exceed the uncertainty of the experiment. The greatest fluorescence polarization anisotropy is seen in the data collected under the highest He buffer gas pressures, where the previous experiments show the least amount of photodissociation.

The high background pressure (1 mTorr) which minimizes the amount of photodissociation may be destroying the rotational motion imposed by the beam of circularly polarized light. However, lower pressures which may allow a higher degree of rotational alignment are plagued with higher photodissociation rates, which, in addition to destroying the molecules that may have built up rotational orientation, decreases the ion population and fluorescence signal, making it difficult to detect any fluorescence
Figure 3.12: Polarization difference of the fluorescence emitted by trapped Rhodamine 575 cations collected over a 5 s time integral in different He buffer gas pressures irradiated by linearly (54° from detection axis), right (RCP), and left (LCP) circularly polarized 488 nm laser light, comparing fluorescence emitted parallel and perpendicular to the excitation laser beam axis. According to Fig. 2.2, perfect rotational alignment should emit fluorescence strongly polarized perpendicular to the laser beam axis.
Figure 3.13: The time-dependent fluorescence signal for light emitted perpendicular and parallel to the circularly polarized (RCP) excitation laser beam axis. The data shown here was collected under 0.18 W irradiation and 0.7 mTorr background pressure. The general trend of the data shows the greatest difference in the polarization of the fluorescence at short irradiation times. As irradiation time progresses and rhodamine molecules are lost due to dissociation, the degree of polarization difference diminishes.

anisotropy that may be present. Figure 3.13 shows the time-evolution of fluorescence polarization for data collected at 0.7 mTorr background pressure for 5 s of 0.18 W irradiation. While the data is extremely noisy, a general time-dependent trend can be observed (dotted lines in Fig. 3.13). The fluorescence polarized perpendicular to the laser beam axis is greater than parallel polarized fluorescence at the beginning of the irradiation, consistent with the generalized trend observed in Fig. 3.12. However, as irradiation continues, the difference between fluorescence polarization decreases. Moreover, the signal of perpendicularly polarized fluorescence decreases while fluorescence polarized parallel remains relatively constant over irradiation time. This
trend would suggest that as irradiation time progresses, photodissociation destroys the molecules that contribute most to the selectively polarized fluorescence. It is reasonable to propose that those molecules that have achieved the highest degree of rotational orientation relative to the laser beam axis are also the most likely to have built up vibrational energy causing photodissociation; whereas those molecules that are prevented from photodissociating by collisional relaxation have their rotational orientation destroyed by those same collisions.

Another point to consider is that the discussion in Sec 2.2 assumes a molecular shape of a symmetric prolate top. Rhodamine 575 is neither perfectly symmetric, nor an extremely prolate top. The rotational constants for rhodamine were calculated to be $A=0.0051$, $B=0.0035$, and $C=0.0023$ cm$^{-1}$, giving a symmetry parameter $\kappa = -0.14$, indicating a very slightly prolate shape. (The symmetry parameter, $\kappa$ takes on limiting values of -1 for an extremely prolate molecule and +1 for an extremely oblate molecule, with $\kappa = 0$ indicating an asymmetric molecule.) However, the fact that some amount of rotational alignment, although inconclusive, is detected in the non-ideal case of rhodamine gives promise that if a more prolate, more photosable chromophore could be found, this method may prove successful. Molecules under consideration are perylene, anthracene, and acridine orange, having symmetry parameters $\kappa = -0.42$, -0.91, and -0.96 respectively. Their structures are shown in Fig. 3.14; though these experiments will be continued by others.
Figure 3.14: Potential molecules for rotational orientation and alignment by circularly polarized light.
Bibliography


3. J. I. Cline and N. A. Sassin, private communications.


Chapter 4

Dibenzofulvene Rotor

\[ \text{E} \xrightarrow{\text{hv}} \text{Z} \]
4.1 Introduction

Currently there is significant interest in developing molecular devices that function as switches, actuators, and motors. Actuation and control of these molecular devices can be achieved by thermal,\(^1\) electrochemical,\(^2\)-\(^4\) or photochemical\(^5\)-\(^8\) processes, or some combination of these.\(^9\)-\(^15\) For example, a molecular device designed by Feringa and colleagues goes through a four-step process comprised of two light-driven and two thermally-driven steps which result in a complete 360° rotation about an intramolecular double bond.\(^11\) Another, similar molecule studied by Feringa and co-workers rotates about an internal double bond, occurring in two photo-driven and two pH-driven steps.\(^14\) Nguyen and colleagues have used electrochemical reduction-oxidation reactions to drive nanovalves.\(^2\) The coordination number of silicon in tetrafluorosilicate can be controlled via visible and near-UV irradiation.\(^8\) Wholly photoactivated devices are of particular interest because they potentially offer a high degree of temporal and positional control and extremely fast cycling rates.

The *cis-trans* photoisomerization of stilbene is a well-understood prototype for light-controlled actuators in molecular switches, sensors, and motors. Stilbene, shown in Fig. 4.1, demonstrates highly efficient photoisomerization. The quantum yields for photoisomerization, which is a measure of the probability that the absorption of any one photon will result in a photoisomerization event, are typically 0.3-0.5.\(^16\) One practical difficulty in many applications is that the *cis* and *trans* isomers of stilbene have significantly different shapes and absorption spectra. For example, to achieve fast, continuous rotary motion, two different excitation wavelengths would be required. Here we consider a family of dibenzofulvene actuators. The structure of dibenzofulvene is shown in Fig. 4.1 and the variously substituted -9-(2,2,2-triphenylethylidene)fluorene (-TEF) molecules investigated here are shown in 4.2. The symmetry of the dibenzofulvene rotor leads to photoisomers with very similar ab-
Figure 4.1: Molecular structures of fulvene, dibenzofulvene, and stilbene.
Figure 4.2: $E$ and $Z$ isomers of the variously substituted -9-(2,2,2-triphenylethylidene)fluorene (-TEF) compounds studied which are interchanged by photoisomerization about the torsional angle $\theta$

sorption spectra. The dibenzofulvene rotor moiety has $C_2$ rotational symmetry about its photoisomerizable exocyclic double bond, facilitating its incorporation as a drive unit in rotary molecular devices. One concern is that theoretical studies of the unsubstituted fulvene moiety shown in Fig. 4.1 predict an extremely low photoisomerization quantum yield. However, our previous experimental study of the photoisomerization of the dibenzofulvene TTEF, shown in Fig. 4.2, reported wavelength-dependent photoisomerization quantum yields between 0.04 and 0.09. Therefore, continuing to investigate this family of molecular rotors may give insight into the mechanisms affecting photoisomerization. By examining the effect various substituents have on the photoisomerization process, we seek to understand what affects the photostability and efficiency of light-driven molecular devices.
4.2 Experiment

4.2.1 Irradiation

Our previous photoisomerization studies of TTEF were performed in acetonitrile solvent.\textsuperscript{18} However, compounds NTEF, CTEF, and ITEF, shown in Fig. 4.2 have very poor solubility in acetonitrile and were therefore studied in a mixed solvent of 15% $p$-dioxane and 85% acetonitrile by volume. The $p$-dioxane co-solvent was used to increase the solubility of these compounds in acetonitrile to allow for comparison to our previous experiments on TTEF in a similar solvent. Figure 4.3 shows the near-UV molar absorptivity of the $E$ and $Z$ isomers of NTEF, CTEF, and ITEF in the mixed solvent obtained from a series of absorption spectra measured at concentrations between $10^{-6}$ and $10^{-5}$ M.

Thermal isomerization data was previously reported for TTEF at elevated temperatures;\textsuperscript{18} however, no thermal isomerization studies were performed here. Neither NTEF or ITEF in solution showed signs of thermal isomerization at room temperature over the course of months. Solutions of CTEF stored in darkness showed evidence of isomerization at room temperature that became detectable after 1-2 weeks. Crystalline CTEF showed no evidence of thermal isomerization at room temperature over the course of months.

Solutions were irradiated at various UV wavelengths generated either as harmonics of a pulsed Nd:YAG laser (10 Hz repetition rate) or from a Nd:YAG-pumped, frequency-doubled dye laser. Light pulses ca. 5 ns in duration of energies 0.3-0.5 mJ pulse$^{-1}$ irradiated a sample of an approximately 0.4 mM solution in a 1 cm square fused silica cuvette, giving a laser fluence of 0.4-0.6 mJ cm$^{-2}$ pulse$^{-1}$. The optical density of the solution was high enough that more than 99.5% of the laser energy was absorbed in the laser path, with the exception of CTEF and ITEF at 355 nm
Figure 4.3: Absorption spectra of $E$ (blue) and $Z$ (red) isomers of compounds NTEF, CTEF, and ITEF in a solvent mixture of 15% p-dioxane (bv) and acetonitrile.
irradiation. For these two cases, where the optical density of the sample solution was low, the energy absorbed by the solution was determined by subtraction of the measured pulse energy after sample absorption from the measured energy before passing through the sample, with the minor energy loss due to reflection at the cuvette surface taken into account. Solvent saturated nitrogen gas bubbled through the solution deoxygenated the samples prior to irradiation, and continuous stirring during irradiation ensured that all molecules were equally exposed to laser excitation. Over the course of irradiation, 40 μL aliquots of the sample were extracted at time intervals to follow the progress of photoisomerization by way of chromatographic analysis.

4.2.2 Chromatographic Analysis of Photoisomerization

The isomeric composition of NTEF as a function of irradiation time was measured using a gas chromatograph (Varian CP-3800) with a tandem mass spectrometer detector (Saturn 2200) with front injector temperature of 290 °C ramping up to 290 °C at 15 °C per minute, and a flow rate of 6 mL min⁻¹. Peak identities were verified by mass spectroscopy and by comparison with the chromatographic spectra of samples with known isomer purity.

The photoisomerization of CTEF and ITEF was measured using an HPLC (Waters 1525) with reverse-phase column (Symmetry C18 5 μm). A flow rate of 1 mL min⁻¹ of 90% methanol and 10% water was sufficient to separate the E and Z isomers of CTEF, where they were detected by absorption spectroscopy at 320 nm. ITEF was analyzed using a 100% methanol mobile phase, at a flow rate of 1 mL min⁻¹, and a detection wavelength of 298 nm. In each case, the detection wavelength was chosen such that the molar absorptivities of the E and Z isomers were equivalent. Isomer peaks were verified by comparison with the chromatographic spectra of samples with known isomer purity.
4.3 Photoisomerization

Figure 4.4 shows typical chromatograms of aliquots removed from irradiated solutions at various times. For the experiments shown in Fig. 4.4 the initial solutions contained only the Z isomer of the dibenzofulvene rotor molecule. As the UV irradiation progresses, the Z isomer peak decreases and the peak corresponding to the E isomer increases. Dividing the peak area of a given isomer by the sum of the total integrated signal gives the mole fractions $f_E$ and $f_Z$. Figure 4.5 shows the evolution of these mole fractions as a function of the average number of absorbed photons for experiments starting with both pure E and pure Z isomers. Note that $f_E$ and $f_Z$ reach the same photostationary ratios at long irradiation times regardless of the starting isomer. While the production of some photoproducts is observed for CTEF and ITEF, the photoproducts accounted for less than 1% of the total detected signal by the time $f_E$ and $f_Z$ had reached 95% of their photostationary value for the case of CTEF, and less than 5% in the case of ITEF.

Ignoring the minor photodecomposition channel, the observed photochemistry can be simply expressed as the photoisomerization reaction

$$ E \xrightleftharpoons[k_{EZ}]{k_{ZE}} Z $$

(4.1)

where $k_{EZ}$ and $k_{ZE}$ are the effective rate constants. The integrated rate equation is

$$ \frac{d[E]}{dt} = k_{ZE}[Z] - k_{EZ}[E] \quad . $$

(4.2)

The effective rate constants $k_{EZ}$ and $k_{ZE}$ depend upon the photon flux and wavelength, the absorption cross section of E and Z at that wavelength, and the photoisomerization quantum yield. To express Eq. 4.2 in a way that is more directly related to the photoisomerization quantum yields and measured mole fractions, $f_E$ and $f_Z$,
Figure 4.4: Chromatograms showing isomerization progress of compound a) NTEF for 266 nm irradiation measured by GC/MS and compounds b) CTEF and c) ITEF for 310 nm irradiation measured by HPLC at a detection wavelength where both isomers have equal absorptivity. The peaks corresponding to the $E$ and $Z$ isomers are labeled. The features appearing at shorter elution times, labeled $D$, correspond to photodecomposition products. NTEF show no noticeable decomposition over the course of the experiment.
we transform the irradiation time, $t$, into the average number of photons absorbed per molecule, $x(t)$. For an optically dense sample in which all irradiation photons are absorbed,\textsuperscript{18}

$$x(t) = \frac{\nu t E \lambda t}{hc} \frac{1}{CV N_A},$$

(4.3)

where $\lambda t$, $E_t$, and $\nu_t$ are the laser wavelength, pulse energy, and laser pulse repetition frequency and $h$ and $c$ are Planck’s constant and the speed of light, respectively. The number of rotor molecules in the sample solution is $CV N_A$, where $C$ is the solution concentration, $V$ is the volume (taking into account the volume decrease due to the removal of aliquots for chromatographic analysis), and $N_A$ is Avogadro’s number. Equation 4.2 then becomes

$$\frac{df_E}{dx} = \frac{\phi_{Z \rightarrow E} \varepsilon_Z f_Z - \phi_{E \rightarrow Z} \varepsilon_E f_E}{\varepsilon_Z f_Z + \varepsilon_E f_E},$$

(4.4)

where $\varepsilon_E$ and $\varepsilon_Z$ are the measured molar absorptivities of the $E$ and $Z$ isomers at the irradiation wavelength as shown in Table 4.1, and $\phi_{E \rightarrow Z}$ and $\phi_{Z \rightarrow E}$ are the absolute photoisomerization quantum efficiencies for $E \rightarrow Z$ and $Z \rightarrow E$, respectively, at $\lambda t$. Kinetic modeling of forward and reverse reactions of the measured $E \rightarrow Z$ photoisomerization data is accomplished by numerical integration of Eq. 4.4 to obtain $f_E(x)$ and $f_Z(x) = 1 - f_E(x)$. Optimization of $\phi_{E \rightarrow Z}$ and $\phi_{Z \rightarrow E}$ in a non-linear least-squares fit of $f_E(x)$ to the experimental data gives the curves shown in Fig. 4.5. The optimized quantum yields obtained in these fits are given in Table 4.1.

Irradiation of CTEF and ITEF give rise to photoproducts evident at shorter elution times in the chromatograms in Fig. 4.4. In the case of CTEF, the photoproducts appear as two peaks. The ratio of the product peaks areas in relation to each other shows a trend similar to that of the $E$ and $Z$ isomers of the parent CTEF. Irradiation
Figure 4.5: Photoisomerization progress measured by isomer fraction $f_E$ (●) and $f_Z$ (■) for NTEF, CTEF, and ITEF at 355 nm irradiation. The curves are obtained by least squares optimization of $\phi_{EZ}$ and $\phi_{ZE}$ in a fit to Eq. 4.4, measured starting with both $E$ (dashed) and $Z$ (solid) isomers.
Table 4.1: Molar absorptivities, photostationary isomer mole fractions, and optimized quantum efficiencies of dibenzofulvene derivatives at various irradiation wavelengths

<table>
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<tr>
<th>Substituent</th>
<th>$\lambda$ (nm)</th>
<th>$\varepsilon_E$ (L mol$^{-1}$cm$^{-1}$)</th>
<th>$\varepsilon_Z$ (L mol$^{-1}$cm$^{-1}$)</th>
<th>$f_E : f_Z$ as $t \to \infty$</th>
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<th>$\phi_{ZE}$</th>
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<tr>
<td>TTEF$^a$</td>
<td>266</td>
<td>–</td>
<td>–</td>
<td>0.59 : 0.41</td>
<td>0.07 ± 0.05</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>–</td>
<td>–</td>
<td>0.44 : 0.55</td>
<td>0.05 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>–</td>
<td>–</td>
<td>0.56 : 0.43</td>
<td>0.07 ± 0.01</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>NTEF</td>
<td>266</td>
<td>17200</td>
<td>17700</td>
<td>0.38 : 0.62</td>
<td>0.25 ± 0.05</td>
<td>0.17 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>29400</td>
<td>30500</td>
<td>0.38 : 0.62</td>
<td>0.26 ± 0.03</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>23500</td>
<td>23800</td>
<td>0.40 : 0.60</td>
<td>0.31 ± 0.03</td>
<td>0.21 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td>17700</td>
<td>18100</td>
<td>0.33 : 0.67</td>
<td>0.21 ± 0.05</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>3600</td>
<td>5400</td>
<td>0.48 : 0.52</td>
<td>0.21 ± 0.03</td>
<td>0.20 ± 0.03</td>
</tr>
<tr>
<td>CTEF</td>
<td>266</td>
<td>28100</td>
<td>28100</td>
<td>0.53 : 0.47</td>
<td>0.35 ± 0.02</td>
<td>0.42 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>16400</td>
<td>14200</td>
<td>0.47 : 0.53</td>
<td>0.34 ± 0.02</td>
<td>0.29 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td>1440</td>
<td>1550</td>
<td>0.62 : 0.38</td>
<td>0.31 ± 0.03</td>
<td>0.33 ± 0.03</td>
</tr>
<tr>
<td>ITEF</td>
<td>266</td>
<td>28200</td>
<td>28600</td>
<td>0.49 : 0.51</td>
<td>0.50 ± 0.04</td>
<td>0.46 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>15300</td>
<td>16200</td>
<td>0.52 : 0.48</td>
<td>0.49 ± 0.02</td>
<td>0.49 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td>480</td>
<td>640</td>
<td>0.52 : 0.48</td>
<td>0.55 ± 0.04</td>
<td>0.45 ± 0.04</td>
</tr>
</tbody>
</table>

$^a$ Data from Barr et al. in which isomer fractions $f_E$ and $f_Z$ were determined using NMR detection.18
of ITEF lead to the development of one major and numerous minor photodecomposition peaks. No attempt was made to isolate or characterize these photoproducts. In an attempt to quantify the amount of photodecomposition, Eq. 4.1 was modified to account for photoproducts by introduction of a photodecomposition product species, $D$.

$$
E \xrightarrow{\phi_{EZ}/\phi_{ZE}} Z 
$$

$$
E \xrightarrow{\phi_D} D 
$$

$$
Z \xrightarrow{\phi_D} D 
$$

Equation 4.4 now becomes

$$
\frac{df_E}{dx} = \frac{\phi_{ZE} \varepsilonZF - \phi_{EZ} \varepsilonFE - \phi_D \varepsilonFE}{\varepsilonFE + \varepsilonZF + \varepsilonDFD} 
$$

$$
\frac{df_Z}{dx} = \frac{-\phi_{ZE} \varepsilonZF + \phi_{EZ} \varepsilonFE - \phi_D \varepsilonFE}{\varepsilonFE + \varepsilonZF + \varepsilonDFD} 
$$

$$
\frac{df_D}{dx} = \frac{2\phi_D (\varepsilonZF + \varepsilonFE)}{\varepsilonFE + \varepsilonZF + \varepsilonDFD} 
$$

where $\phi_D$ is the photodecomposition quantum yield. The quantity $f_D$ represents the mole fraction of all product species such that $f_E + f_Z + f_D = 1$. The value of $f_D$ was measured experimentally from the area of the $E$ and $Z$ peaks in Fig. 4.4 relative to the sum of all peak areas. The detection wavelength for the HPLC analysis was chosen such that both $E$ and $Z$ isomers have the same absorptivity at that wavelength; however, the absorption spectrum of the product is unknown. Therefore, the accuracy of $f_D$ is dependent upon the difference of the molar absorptivity of the photoproducts, $\varepsilon_D$, from $\varepsilon_E$ and $\varepsilon_Z$ at the HPLC detection wavelength. The equations were integrated numerically and $\phi_{EZ}$, $\phi_{ZE}$, and $\phi_D$ were optimized in a simultaneous fit to the measured $f_E$ and $f_Z$, shown in Fig. 4.6. Here, the decomposition is manifest
Figure 4.6: Fits to the experimental data taking into account photodecomposition. The curves are obtained by least squares optimization of $\phi_{EZ}$, $\phi_{ZE}$, and $\phi_d$ in a fit to Eqs. 4.8-4.10, measured starting with both $E$ (dashed) and $Z$ (solid) isomers.
Table 4.2: Optimized photoisomerization and photodecomposition quantum yields of CTEF and ITEF.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>λ (nm)</th>
<th>$\phi_{EZ}$</th>
<th>$\phi_{ZE}$</th>
<th>$\phi_D \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTEF</td>
<td>266</td>
<td>0.40 ± 0.01</td>
<td>0.45 ± 0.01</td>
<td>0.32 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>0.31 ± 0.01</td>
<td>0.32 ± 0.01</td>
<td>0.189 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td>0.37 ± 0.04</td>
<td>0.40 ± 0.04</td>
<td>0.180 ± 0.001</td>
</tr>
<tr>
<td>ITEF</td>
<td>266</td>
<td>0.48 ± 0.06</td>
<td>0.44 ± 0.06</td>
<td>4.5 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>0.49 ± 0.01</td>
<td>0.50 ± 0.01</td>
<td>0.98 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td>0.55 ± 0.09</td>
<td>0.45 ± 0.07</td>
<td>0.13 ± 0.09</td>
</tr>
</tbody>
</table>

in the negative slope of what was previously a photostationary plateau in Fig. 4.5. This decline in both $f_E$ and $f_Z$ is most noticeable for ITEF. There was no measurable decomposition for NTEF. The same photostationary state was reached regardless of the initial isomer chosen. Table 4.2 summarizes the best-fit values of $\phi_{EZ}$, $\phi_{ZE}$, $\phi_D$, and the measured molar absorptivities of $E$ and $Z$ at each irradiation wavelength. With the exception of ITEF at 266 nm excitation, $\phi_D$ is two orders of magnitude smaller than $\phi_{EZ}$ or $\phi_{ZE}$. The additional parameter $\phi_D$ resulted in the fitted photoisomerization quantum yields $\phi_{EZ}$ and $\phi_{ZE}$ for ITEF increasing by no more than 0.02, and those for CTEF to increase an average of 0.05.

### 4.4 Discussion

Photoisomerization efficiencies for the well-studied stilbene molecule are relatively independent of substitution, varying only by about ten percent from typical values of $\phi_{\text{trans} \rightarrow \text{cis}} \sim 0.5$ and $\phi_{\text{cis} \rightarrow \text{trans}} \sim 0.3$. For the dibenzofulvene derivatives studied here, changing the substituent causes a larger change in the photoisomerization efficiency, as seen in Tables 4.1 and 4.2. The compounds show a wide range of quantum yields with TTEF having a photoisomerization quantum yield $\sim 0.07$ and increasing in the order of TTEF $<$ NTEF $<$ CTEF $<$ ITEF, where ITEF has a quantum yield of $\sim 0.50$. There is no clear wavelength dependence of the quantum yields for
Figure 4.7: Schematic of the potential energy surfaces of stilbene along the photoisomerization reaction coordinate, $\theta$, show in Fig. 4.2. Photoisomerization via the singlet mechanism occurs by vertical excitation from the ground singlet state, $S_0$, to the first excited singlet state, $S_1$. Relaxation occurs along the angle $\theta$ in $S_1$, followed by intersystem crossing to the $S_0$ surface at a conical intersection near $\theta = 90^\circ$, followed by relaxation to $\theta = 0^\circ$ or $180^\circ$ on the $S_0$ surface. Complete photoisomerization is achieved by $180^\circ$ rotation about $\theta$.

$\lambda_{ex} > 266$ nm. NTEF favors the $Z$ isomer in the photostationary state at all excitation wavelengths investigated, while the others show nearly a 1:1 photostationary isomer ratio.

A rigorous theoretical understanding of the mechanism of photoisomerization for the compounds studied here is beyond the scope of this study; here we speculate on important key processes. Figure 4.7 provides a schematic representation of the potential energy surfaces thought to be involved in the photoisomerization of stilbene. Stilbene is excited from the the ground singlet, $S_0$, to the first excited singlet $S_0$, electronic state. Torsion about the double bond angle, $\theta$, as shown in Fig. 4.1, decreases the energy of the $S_1$ state. Consequently, stilbene moves along the $S_1$ surface to $\theta = 90^\circ$ where there is a conical intersection with the $S_0$ surface allowing intersys-
tem crossing to the ground state. Relaxation on the ground $S_0$ surface from $\theta = 90^\circ$ results in either continued rotation about the double bond to $\theta = 180^\circ$, accomplishing complete isomerization, or a return to $\theta = 0^\circ$ without any net isomerization. This generic picture could be extended to the photoisomerization of fulvene, which follows a similar $S_0 \rightarrow S_1$ excitation followed by movement along the $S_1$ surface to a conical intersection where it intersystem crosses to the ground $S_0$ surface. Again, subsequent relaxation on the $S_0$ surface results in either a return to the original configuration ($\theta = 0^\circ$) or a $180^\circ$ rotation about $\theta$ resulting in isomerization. Bearpark et al.\textsuperscript{17} performed $S_1$ dynamics calculations showing a very low probability of reaching $\theta = 90^\circ$. They predicted negligible photoisomerization quantum yields, with a measurable isomerization perhaps only possible upon excitation at the $0$- vibrational origin.

Subsequent to our experimental study which showed significant quantum yields for the dibenzofulvene derivative TTEF,\textsuperscript{18} $S_1$-$S_0$ transitions in fulvene were examined in greater detail by Bearpark\textsuperscript{19} and Sumita and Saito.\textsuperscript{20} As discussed previously, Fig. 4.7 depicts the potential energy surfaces of stilbene in the single coordinate of the exocyclic double bond torsion angle $\theta$, and shows a $S_1/S_0$ conical intersection at $\theta = 90^\circ$. However, there are many more nuclear degrees of freedom; in the case of fulvene, the $S_1/S_0$ conical intersection is actually a high dimensional space in the nuclear coordinates. Theoretical studies by Bearpark examined the multi-dimensional surfaces for $S_1$ and $S_0$ in order to determine the $S_1/S_0$ surface crossing dynamics of fulvene. Figure 4.8 shows their results for the $S_1$ and $S_0$ surfaces along the nuclear coordinates of the exocyclic double bond torsion angle, $\theta$, and the “bond inversion” or “delocalization” coordinate whereby the single and double bond character in fulvene is interchanged. They show that these two coordinates are those involved in the $S_1/S_0$ conical intersection. Movement along the $S_1$ surface in the $\theta$ coordinate after
initial excitation, and keeping all other coordinates constant, leads to a local energy minimum on $S_1$ at $\theta = 90^\circ$, before reaching the location of the conical intersection. Allowing motion along the bond inversion coordinate leads to a surface crossing at $\theta < 90^\circ$. The global energy minimum on the surface crossing seam (known as the $S_1/S_0$ “degeneracy space”) for fulvene is located at $\theta = 63^\circ$.\textsuperscript{19,20} Crossing to the $S_0$ surface from this point results in a return to the original configuration at $\theta = 0^\circ$, with no net isomerization about the double bond. According to the trajectory calculations of Sumita and Saito, intersystem crossing at $80^\circ < \theta < 90^\circ$ is required in order for the relaxation trajectory on the $S_0$ surface to result in complete $180^\circ$ rotation about the double bond.\textsuperscript{20} Therefore, for fulvene the topography of the $S_1$ and $S_0$ surfaces leads to a $S_1/S_0$ curve crossing at $\theta = 63^\circ$, making photoisomerization highly improbable.

Because our previous studies TTEF showed significant photoisomerization quantum yields,\textsuperscript{18} Sumita and Saito theorized that the addition of benzene rings to fulvene may affect the $S_1/S_0$ degeneracy space in such a way as to favor a surface crossing at $\theta$ closer to $90^\circ$ before relaxing along the $S_0$ surface.\textsuperscript{20} It is reasonable to expect the highly aromatic benzene moieties to resist the formation of the single bond required for motion along the “bond inversion” coordinate of fulvene. One might suppose the surface crossing seam becomes raised in energy as it progresses along the bond inversion coordinate. In Fig. 4.8 this is theorized with the added dashed curve. Such a change in the energy of the $S_0$ and $S_1$ surfaces would cause the energetically accessible region of the conical intersection ream to be restricted to angles closer to $90^\circ$, promoting relaxation dynamics that successfully achieve isomerization.

The photoisomerization quantum yield increases in the order of TTEF $<\text{NTEF} <\text{CTEF} <\text{ITEF}$, suggesting these substituents further affect the energies of the $S_1$ and $S_0$ surfaces. The nitro and cyano functional groups are known to be strongly electron withdrawing. In contrast, the $t$-butyl functional group is strongly electron donating.\textsuperscript{21}
Potential Energy

Torsion \( \theta \)

Figure 4.8: S\(_1\) and S\(_0\) surfaces of fulvene in the nuclear coordinates of the exocyclic double bond torsion angle \( \theta \) and bond inversion. Surface crossing occurs at the conical intersection, appearing here as a two-dimensional seam (bold line). Positions CI\(_\text{plan}\) and CI\(_\text{perp}\) represent the location of the conical intersection at \( \theta = 0^\circ \) and \( 90^\circ \), respectively. Successful isomerization requires S\(_0\) \( \rightarrow \) S\(_1\) excitation at \( \theta = 0^\circ \) (blue arrow) followed by relaxation on the S\(_1\) surface to a curve crossing at \( \theta \approx TK^\circ \). The global minimum of the conical intersection space occurs at \( \theta = 63^\circ \) (Cl\(_{63}\)). The additional benzene rings in dibenzofulvene (red) may cause movement along the bond inversion coordinate to be more energetically costly, causing the accessible region of the theorized new crossing seam (dashed red line) to be restricted to angles closer to \( 90^\circ \). Image adapted from Bearpark \textit{et al.} \(^{19}\).
Given the trend in photoisomerization quantum yields, there appears to be a crude
correlation between the photoisomerization quantum yield and the electron donating
or withdrawing characteristic of the substituent. Additionally, experimental data on
the compound with the strongly electron-donating amino substituent collected by
Udaya Jayasundara in our group show very low photoisomerization quantum yields.
It may be that the strong electron withdrawing character of the substituent causes the
molecule to become even more resistant to change in the bond inversion coordinate,
further favoring relaxation dynamics that lead to surface crossings closer to $\theta = 90^\circ$,
and subsequently, complete photoisomerization. Alternatively, the substituents could
have farther-reaching effects on the $S_0$ and $S_1$ surfaces to the extent that the bond
inversion coordinate is no longer predominant in determining relaxation dynamics
and pathways more favorable to photoisomerization become available.

The compound ITEF shows photoisomerization quantum yields higher than NTEF
and CTEF, contrary to the trend mentioned above as the iodo substituent is only
mildly electron withdrawing. However, note also that the iodo substituent is sig-
nificantly larger and heavier than the other substituents investigated here. There
could be other heavy atom effects contributing to the increased photoisomerization
efficiency. Iodo substitution is well known to promote intersystem crossing, accessing
triplet isomerization mechanisms. ITEF has the highest photodecomposition quan-
tum yield.

The triplet mechanism for the photoisomerization of dibenzofulvene, or even ful-
vene, is not as well understood as the singlet mechanism, and therefore not much
can be conjectured here. However, since ITEF shows the highest photoisomeriza-
tion quantum yield of the compounds studied here, and the rationale of the singlet
mechanism for photoisomerization does not seem to apply for ITEF, it is reason-
able to suppose the iodo substituent enables access to additional triplet mechanisms.
which are more favorable to photoisomerization than pathways available in the singlet mechanism.

4.5 Conclusion

Here we have shown a series of compounds that function as actuators. The photoisomerization quantum yield, absorption spectrum, and photostability of the compound is dependent on the substituent. While ITEF shows the highest photoisomerization quantum yield, it also displays the highest photodegradation. The compound NTEF demonstrates high photostability, a broad absorption spectrum extending into the far blue of the visible region at ~400 nm, and significant photoisomerization quantum yields in the range of 0.1 to 0.3. With these qualities, it appears to be the most promising candidate we have studied for a driven molecular actuator of general utility.
Bibliography


Afterword

In conclusion, the three projects investigated here offer more insight into understanding the issues involved for detection and control of molecular rotation.

From the measurement of the preferred sense of rotation shown by the NO fragment generated from the UV photodissociation of nitrosobenzene, we have seen that detailed understanding of the electronic structure of the ground and excited states involved in the photodissociation process can help predict the preferred sense of rotation of the generated product, potentially allowing selective generation of products with a specific sense of molecular rotation.

One can envision using this information in further molecular reactions by pre-orienting the reactant species for the purposes of investigating dynamically chiral reaction processes. The information currently available on photodissociation fragment recoil trajectories gathered from a variety of parent molecules offers the potential of selectively choosing molecules which photodissociate to produce fragments having a desired specific sense of rotation. However, one is limited by the rotational preference of the photodissociation process. In some cases, the parent molecule of choice may not offer photofragments having the desired sense of rotation. Consequently, one might be required to use a different parent molecule that is either economically costly to obtain or is poorly suited to the conditions of the experiment in order to generate a photofragment having the desired sense of rotation. Additionally, if a fragment with the desired sense of rotation can be efficiently generated, the fragment recoil velocities
are not limited to a single direction in the laboratory frame. Efficient harnessing of the rotationally oriented fragments could prove to be difficult.

Alternatively, it would be advantageous if the rotational orientation of the target species is not dependent on the nature of a parent molecule. It would be an additional advantage if the directionality of rotational orientation could be tied to the laboratory frame; for example, the rotational angular momentum vector aligned with the axis of an excitation laser beam. This would offer a higher degree of selectivity and control in generating target molecules which have a desired sense of rotation. Theoretical calculations of the evolution of molecular rotational angular momentum over the course of multiple absorption events of circularly polarized photons indicate that perfect rotational orientation of an ensemble of molecules could conceivably be acquired. This provides the potential to control the directionality of rotational orientation by way of changing the chirality of the driving circularly polarized photons. However, in the same study, calculations of vibrational energy stored over multiple absorption events gave indications of some of the challenges faced in practical experiments. The photostability of the absorbing molecule may prove to be a significant limitation.

The laser dye molecule chosen to test our theory, Rhodamine 575, showed evidence of a possible small degree of rotational orientation; though, the data were inconclusive. Acknowledging that the Rhodamine 575 structure was not the ideal symmetric prolate shape modeled in the theoretical calculations, and considering the degree of photodecomposition Rhodamine 575 experienced during long irradiation times, the results of the experiment still show potential, and other molecules having structures more similar to a symmetric prolate top will be investigated in the future.

Lastly, the dibenzofulvene-based molecular motor prototype synthesized by the Bell research group showed significant photoisomerization quantum yields, demon-
strating its potential for application as a molecular device. The substituent-dependence of the absorption spectrum and photoisomerization quantum yield demonstrates the tunability of the molecule, which could be useful in customizing it as a molecular device. While two of the molecular motor prototypes demonstrated photodecomposition, the degree of decomposition was small and did not significantly affect the photoisomerization quantum yields. On-going studies by members of the Cline research group are investigating the effect of protonation on the photoisomerization quantum yields and, separately, photoisomerization detection methods after these molecules are adsorbed onto a surface.
Appendices
A.1 Vacuum Chamber Attachments

The following two sections describe the vacuum chamber attachments used for excitation and fluorescence detection discussed in Chapter 3. The conflat (CF) flanges (part G in Sec. A.1.1 and parts A,C, and G in Sec. A.1.2) were purchased from MDC Vacuum Products LLC. The in-house machinist, Walt Weaver, assembled the apparatus according to the diagrams given below.
A.1.1 Light Baffles

The mechanical drawings to follow show the light baffles designed to reduce extraneous room light and laser scatter from entering the ion trap region. The laser enters through a flat, BK-7 glass window with an anti-reflective (AR) window (part B) into the long baffle tube containing 5 unevenly spaced, black anodized aluminum aperture rings (part I), and passing through to the the ion trap. The stainless steel vacuum chamber attachment, parts E, F, and G, along with the aluminum translation stage, part D, create a vacuum seal around the baffle tube. The CF vacuum flange, part G, has a rotatable center which allows course alignment of the baffle with the ion trap. Adjustment set screws on parts D and E allow finer control of the position, yaw, and pitch of the baffle tube in order to properly align the axes of both the entrance and exit baffle tubes with the entrance and exit apertures in the ring electrode of the ion trap.

Light from scatter was of greater concern in upon entering the vacuum chamber than upon exiting. Additionally, the laser intensity was most conveniently measured after passing through the ion trap and exiting the vacuum chamber. With these two considerations in mind, the light baffle apertures were 1 mm in diameter in the entrance baffle so the laser beam diameter smaller than the aperture in the ion trap ring electrode, preventing laser light scatter so close to the ion trap. The light baffle apertures in the exit baffle tube were 1/4” in diameter to allow all of the laser beam passage through the exit baffle tube to the power meter even when the baffle tube and laser beam axes were imperfectly aligned.
A  Al Retaining Ring
   4 clear thru holes for #8-32 bolts
B  BK-7 Glass Window
C  304-Steel Intermediate Tube
   304-Steel top collar 2” od
   4 tapped blind holes for #8-32
   o ring groove for # -121
304-Steel retaining collar
D  Al Translating Stage
   interior o ring groove for -214
   4 clear thru holes 1/4” dia
   4 side tapped blind holes for #8-32
E  304-Stainless Steel Platform
   8 tapped blind holes for #8-32
   matching H
   4 tapped blind holes for #8-32
   fitting D
   o ring groove for # -118
   center clear hole 1 1/2” dia
F  304-Steel tube 1 1/2” od
G  304-Steel Rot. , CF Flange 6” od
   16 clear thru holes for
   1 clear thru hole 1 3/8” dia
H  Al set screw anchor
   2 clear thru holes for #8-32
J  Anodized Al apertures
   center hole 1/4”dia
J  Anodized Al spacing tubes
A  Al Retaining Ring
4 clear thru holes for #8-32 bolts

D  Al Translating Stage
interior o ring groove for # -214
4 clear thru holes 1/4"dia
4 side tapped blind holes for #8-32
C  304-Steel Intermediate Tube
   304-Steel top collar 2\" od
   4 tapped blind holes for #8-32
   o ring groove for # -121
   304-Steel retaining collar

I  Anodized Al apertures
   center hole 1/4\"dia

J  Anodized Al spacing tubes
E  304-Stainless Steel Platform
8 tapped blind holes for #8-32
matching H
4 tapped blind holes for #8-32
fitting D
o ring groove for # -118
center clear hole 1 1/2" dia

F  304-Steel tube 1 1/2" od

G  304-Steel Rot. CF Flange 6" od
16 clear thru holes for
1 clear thru hole 1 3/8" dia
A.1.2 Top Hat

The following two mechanical drawings show the vacuum chamber attachment designed with a drop-down window for the purposes of placing the AR-coated window directly above the ion trap aperture through which fluorescence is collected. This allows the greatest possible solid angle of collection for fluorescence detection.
A  8" 304 Stainless Steel Rot. CF Flange
B  3" 304 Stainless Steel Tube
C  4 5/8" 304 Stainless Steel non-Rot. CR Flange
D  2 1/2" Al Retaining Ring
E  1 1/2" BK-7 Glass Window
F  Viton O-ring
G  4 5/8" 304 Stainless Steel non-Rot. CF Flange
A) 8" 304 Stainless Steel Rotatable CF Flange
   20 clear thru bolt holes 0.332" dia.
B) 3" diameter 304 Stainless Steel tube
C) 4 5/8" 304 Stainless Steel Non-Rotatable CF Flange
   10 clear thru bolt holes 0.332" dia.
A.2 Morse-oscillator calculations

Calculations shown here apply to the vibrational simulations discussed in Sec. 2.3.2. The Franck-Condon probabilities were calculated using Mathematica for the transitions between the vibrational levels in the ground, \( v'' \), and excited, \( v' \), electronic states according to

\[
q_{FC}(v', v'') = |\int \Psi_{v'} \Psi_{v''} \, dr|^2 ,
\]

where the Morse oscillator wavefunctions for the ground, \( \Psi_{v''} \), and excited, \( \Psi_{v'} \), state vibrational levels are described by Rong et al.\(^1\) The waveform as a function of the vibrational quantum number, \( v \), is

\[
\Psi_v = N_v \, d^{-y/2} \, y^{\beta_v/2} \, L_{\beta_v}^v(y) ,
\]

where the normalization constant is

\[
N_v = \left[ a\beta_v \frac{\Gamma(v+1)}{\Gamma(\beta_v + v + 1)} \right]^{\frac{1}{2}}.
\]

The parameters \( \beta_v \) and \( y \) are contractions of terms dependent on the spectroscopic constants \( \omega_e \) and \( \omega_x x_e \), where

\[
\beta_v = \frac{1}{x_e} - 2v - 1 \quad \text{and} \quad y = \frac{1}{x_e} \, e^{\left[ -\alpha \frac{r - r_e}{r_e} \right]} .
\]

The Morse parameter \( \alpha \) is defined as

\[
a = \sqrt{\frac{4\pi \mu \omega_x x_e}{\hbar}} ,
\]

where \( \mu \) is the reduced mass.

Constants for the \( X \, ^1\Sigma_g^+ \rightarrow B \, ^3\Pi_{0u}^+ \, \text{Cl}_2 \) transition displayed in the following table:\(^2\)

<table>
<thead>
<tr>
<th>( T_e )</th>
<th>( \omega_e )</th>
<th>( \omega_e x_e )</th>
<th>( r_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X , ^1\Sigma_g^+ )</td>
<td>0</td>
<td>559.72</td>
<td>2.675</td>
</tr>
<tr>
<td>( B , ^3\Pi_{0u}^+ )</td>
<td>17809</td>
<td>259.57</td>
<td>5.38</td>
</tr>
</tbody>
</table>
and the reduced mass for Cl₂ is

\[ \mu = \frac{m_{Cl}m_{Cl}}{m_{Cl} + m_{Cl}} = 2.9433 \times 10^{-26} \text{ kg} \]  

(16)

The equation for the Morse potential is³

\[ V(r - r_e) = D \left( e^{-\beta(r-r_e)} - 1 \right)^2 , \]  

(17)

where D is the well depth

\[ D = \frac{1}{4} \omega_e \left( \frac{1}{x_e} - x_e \right) \]  

(18)

and

\[ \beta = \left( \frac{k}{2\hbar c D} \right)^{\frac{1}{2}} , \]  

(19)

with k being the vibrational force constant calculated by

\[ k = \mu(2\pi c \omega_e)^2 . \]  

(20)

Using the spectroscopic constants above, this gives

<table>
<thead>
<tr>
<th>constant</th>
<th>Ground</th>
<th>Excited</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>k</td>
<td>327.16</td>
<td>70.328</td>
<td>kg s⁻²</td>
</tr>
<tr>
<td>D</td>
<td>29331</td>
<td>3127.8</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>β</td>
<td>167.5</td>
<td>237.9</td>
<td>Å⁻¹</td>
</tr>
</tbody>
</table>

Plotting the potential energy curves to scale is impractical and not very useful visually, therefore, the curves shown in Fig. 2.13 were scaled as follows:

<table>
<thead>
<tr>
<th>constant</th>
<th>Ground</th>
<th>Excited</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>k</td>
<td>327.16</td>
<td>70.328</td>
<td>kg s⁻²</td>
</tr>
<tr>
<td>D</td>
<td>293.31</td>
<td>31.278</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>β</td>
<td>1.675</td>
<td>2.379</td>
<td>Å⁻¹</td>
</tr>
</tbody>
</table>

and \( T_e = 178.09 \text{ cm}^{-1} \).
The vibrational energy levels are

\[ E_{\text{vib}}(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2. \]  

(21)

Bibliography

