#### An Abstract of the Thesis of

Karen J. Castle for the degree of Doctor of Philosophy in Chemistry presented on May 5, 2000. Title: Photochemistry of Molecules Oriented with a Uniform Electric Field. Redacted for privacy Abstract approved:\_\_\_\_\_\_

Wei Kong

This thesis describes the applications of orientation with a strong, uniform electric field to studies of the photochemistry of gas phase polar molecules. Orientation of parent molecules in an external electric field induces alignment of the transition dipole. Consequently, the probability of photoexcitation by polarized light is enhanced or diminished, depending on the direction of polarization and the relative orientation of the transition dipole and the permanent dipole of the ground state. From the dependence of the yield of a photoproduct on the polarization direction of the excitation/dissociation laser, information on the transition dipole and topography of the excited state can be derived.

Based on this principle, the  $\pi^* \leftarrow n$  transitions of oriented pyridazine and pyrimidine were studied, and a theoretical treatment of asymmetric top molecules in a strong electric field was developed. The effectiveness of this new approach was shown through studies of the photodissociation dynamics of ICN, BrCN, t-butyl nitrite, nitrobenzene, and o-nitrotoluene. Advantages of this method include the ability to study large, complex systems for which traditional gas phase spectroscopic methods fail to reveal vectorial information.

### Photochemistry of Molecules Oriented with a Uniform Electric Field

by

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A Thesis Submitted to Oregon State University

In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

Presented May 5, 2000 Commencement June 2000 Doctor of Philosophy thesis of Karen J. Castle presented on May 5, 2000

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#### Acknowledgements

When I first decided to join the Kong group, I had no idea what I was getting myself into! As it turns out, I couldn't have made a better decision. Thank you, Wei, for your guidance, patience, and friendship, and for being the best role model imaginable. Also deserving mention are my doctoral committee members: Joseph Nibler, Michael Schuyler, and John Loeser from the department of chemistry, and Pui Shing Ho from the department of biochemistry and biophysics.

I would like to extend my thanks to fellow group members, past and present. Dr. Hongzhi Li taught me how to be an experimentalist, and I certainly wouldn't have learned as quickly without his continued patience and enthusiasm. Rebecca Bliesner and Catherine Norris were wonderful to work with, and are still valued friends. My current labmates, James Abbott and Xianzhao Peng, have been indispensible. Also, my deepest thanks to Ted Hinke, who in my eyes is an honorary group member.

I would especially like to thank those who have given me things to think about other than work over the past four years. I am very grateful to members of the women's and co-ed softball teams for making summers just a little bit more fun than the rest of the year. I'd also like to thank University Singers for keeping music a part of my life. Tammy Amos, what can I say? There are very few friendships in life that will last forever, and I feel very lucky to have found a friendship like that with you. I'm forever indebted to all of my family and friends for giving me so much encouragement. Finally, I would like to thank my husband, Ryan, for standing by my side through everything.

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- for my parents -

#### Photochemistry of Molecules Oriented with a Uniform Electric Field

#### 1. Introduction

#### **1.1 Background and Motivation**

Photochemistry has been a subject of fundamental as well as practical interest.<sup>1,2</sup> Measurements of product distributions through photochemical techniques can be used to study fundamental aspects of a chemical reaction. These experiments have provided information about the ground state structures of parent molecules, and have also been used to probe the nature of excited electronic states. Information thus obtained is important in many areas of chemistry, for example, in modeling of environmentally important processes such as combustion. Over the past thirty years, owing to the efforts of many researchers in this field, a large repertoire of gas phase spectroscopic techniques has been developed.<sup>3,4</sup> Studies of small molecules have advanced to an unprecedented level, and in some cases, detailed pictures of electronic and nuclear motion upon photodissociation have been obtained.

The success of studies of small molecules is partially attributed to the rapid dissociation processes associated with these species. The transition dipole moment  $(\mu_t)$  for an absorption event has a fixed direction in the molecular frame. The probability that a parent molecule will absorb a photon is proportional to  $\cos^2 \theta$ , where  $\theta$  is the angle between the electric vector of the photolysis laser and  $\mu_t$ .<sup>5</sup> Thus, when a randomly oriented sample is excited with linearly polarized light, molecules with the

proper orientation will preferentially be dissociated. If dissociation is much faster than rotation of parent molecules, most of the fragments are produced along the broken chemical bond. The result is an anisotropic distribution of photofragments. From the photofragment angular distributions and their internal and translational energy distributions, topographies of the participating potential energy surfaces and dissociation dynamics can be derived.

In probing the anisotropy and energy partitioning of the photofragments, two approaches have been developed.<sup>6-11</sup> The first was to use a mass spectrometer with time of flight (TOF) capabilities. The kinetic energy was measured through the drift time of fragments after dissociation. Using a rotating source or mass spectrometer, angular distributions can be obtained. The second method takes advantage of the fact that the Doppler profile of an emission or absorption line is directly affected by the recoil velocity, both in terms of direction and magnitude. For example, in the case of a linear molecule with  $\mu_t$  along the dissociating bond, if the molecule is dissociated with linearly polarized light, and if the dissociation is fast compared with the rotational period of the molecule, photofragments should be ejected such that their recoil velocities are preferentially parallel to polarization direction (E) of the photolysis laser. If the photofragments are probed with light propagating parallel to E, most photofragments will be moving either toward or away from the probe source. In this case, the absorption will be strong in the wings of the transition and weak at the center frequency, resulting in a dip in the middle of the Doppler profile. On the other hand, if the photofragments are probed with light propagating perpendicular to E, the majority of fragments will be moving at right angles to the probe direction. The absorption will be strongest at the center frequency, with little absorption in the wings of the transition. The shape of the Doppler profile under different pump-probe geometries can therefore be used to deduce the direction of  $\mu_t$ . In recent years, a few other related techniques have been developed, such as velocity-aided Doppler spectroscopy and velocity mapping<sup>12</sup>, but they are essentially based on the same principles as the two original approaches.

Unfortunately, the above methods often cannot be applied to complex systems. Medium to large sized molecules typically exhibit featureless absorption spectra and slow dissociation processes resulting in non-energetic fragments. When the lifetime of the dissociation is long compared to the rotational period of the molecule, the aforementioned anisotropy of photofragment distributions and recoil velocities will be lost.<sup>6-11</sup> This constraint severely limits the amount of information that can be obtained from conventional methods.

The main goal of this work has been to develop a new technique for measuring directions of transition dipole moments of medium to large sized molecules.<sup>13-23</sup> The approach uses polarization spectroscopy and steric control of reactants. When parent molecules are effectively oriented, information regarding electronic orbitals can be obtained from absorption probabilities of linearly polarized light. Although the level of detail attainable for such complex systems remains limited, fundamental information for theoretical modeling, such as the directions of transition dipole moments, is still valuable, particularly for calibration purposes of *ab initio* and semi-empirical calculations.

#### **1.2** Methods of Steric Control

In typical spectroscopic experiments, molecules freely rotate with random orientations. As discussed in section 1.1, when the rotational period of the molecule is short compared with the lifetime of a dissociation process, stereodynamical information is difficult to obtain. Spatial orientation restricts of the rotational degree of freedom, rendering the search for vectorial information possible.

In the liquid and solid phases, orientation is achieved through methods such as crystal fields or stretched films.<sup>24</sup> In combination with polarized absorption and reflection, these methods have been used to determine directions of transition dipole moments. However, environmental and crystal field effects can greatly complicate the molecular properties, and the results reflect macroscopic properties rather than properties of individual molecules. Furthermore, since theoretical calculations are based on isolated species, direct comparisons between calculations and experimental data from solid and liquid phases are inadequate due to differences in environment. Attempts to account for these differences from the theoretical side are met with only limited success.<sup>25</sup> It has been reported that crystal fields can change the order of electronic orbitals, the absorption spectrum, and even the directions of transition dipole moments.<sup>26,27</sup>

Study of gas phase molecules in a collision-free environment is necessary for direct comparison between theory and experiment. Orientation and alignment of gas phase reactants have been achieved through several methods, including hexapole field focusing,<sup>28-34</sup> collision-induced processes,<sup>35-38</sup> laser-related techniques,<sup>39-46</sup> and

uniform electric fields.<sup>47-50</sup> Hexapole field focusing has long been used to achieve orientation of symmetric top (or near-symmetric top) molecules that exhibit first-order Stark effects. However, this technique is not quite applicable when the Stark interaction is second-order, as is the usual case for diatomic, linear, and asymmetric top molecules.<sup>51</sup> In addition, orientation achieved through electric field focusing, collisions, or laser fields is experimentally challenging. The "brute force" method, i.e., orientation with a strong, uniform electric field, has the advantage of being experimentally simple and yet widely applicable. When combined with supersonic expansion, substantial orientation of linear, symmetric, or asymmetric top molecules has been reported.<sup>47-50</sup> Therefore, we have chosen this method for use in measuring directions of transition dipoles.

#### **1.3** Brute Force Orientation

The principle of brute force orientation is illustrated in figure 1.1. The technique makes use of the electrostatic interaction between the permanent dipole moment of a polar molecule and a uniform external electric field.<sup>52-54</sup> When the interaction is stronger than the rotational energy of the molecule, an insurmountable potential barrier is instituted. The molecule becomes trapped within the barrier, and thus evolves from a "free rotor" state to a "pendular" state. As a result, permanent dipole moment is preferentially oriented along the direction of the electric field. A net orientation of the ensemble is achieved when the electrostatic energy is comparable to or larger than the average rotational energy of the system.



### Conditions to Achieve Orientation:

- 1. Strong electric field
- 2. Large permanent dipole moment
- 3. Low rotational temperature

Figure 1.1 Brute force Orientation. Polar molecules from a supersonically expanded molecular beam are introduced into a strong, uniform electric field. If electrostatic interactions between the field and the permanent dipole moments are strong enough to overcome free rotation, permanent dipole moments will become preferentially oriented along the direction of the field.

In general, the ability to orient molecules with an electric field is regulated by the relative magnitudes of  $\mu$ •E and the rotational energy, BJ(J+1).<sup>55-57</sup> The combination of a large dipole moment ( $\mu$ ), a high field strength (E), and a small rotational constant (B) are favorable for orientation. Furthermore, rotational cooling can be used to restrict the population to low rotational (J) states.

In essence, this method of orientation is a direct application of the Stark effect. In an electric field, Stark effects induce splitting of energy levels.<sup>51</sup> This occurs because the field causes the angular momentum vector to precess around the direction of the field, in a cone-like pattern. The total angular momentum J is no longer conserved, but the projection of the angular momentum vector onto the direction of the field (defined by the quantum number M), remains constant for a given molecule. Thus, M is said to be a good quantum number. In an electric field, states that differ only in the sign of M have the same energy. Therefore, an electric field produces splitting of a given state into (J+1) states which are all doubly degenerate except for  $M=0,^{51}$  and the corresponding wavefunctions of the molecule are adjusted accordingly. It is this adjustment that results in net orientation of the permanent dipole.

Recently, it has been shown that orientation with a uniform electric field is possible for a wide variety of polar species including linear, symmetric, and asymmetric top molecules, due to second order Stark effects.<sup>54,55</sup> This Stark splitting is roughly proportional to the square of the strength of the electric field. It is also dependent on the magnitude of the permanent dipole, the moment of inertia, and the rotational quantum number. Very high field strengths, usually in excess of 50 kV/cm,

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are routinely used to achieve this type of orientation. Although electric fields of this magnitude have a significant effect on the rotational wavefunction, they are typically a negligible perturbation to the electronic wavefunction of the oriented molecules.

An interesting revelation on the quantum mechanical properties of molecules in strong fields can be obtained by analyzing the energy levels in infinite fields. In an infinitely strong electric field, molecules are effectively transformed from free rotors to harmonic librators.<sup>55-57</sup> This occurs because the form of the potential energy is  $V=-\mu E\cos\theta$ . As the strength of the electric field increases, the depth of the potential well increases, and in an infinitely strong field, the bottom of the well resembles that of a harmonic oscillator. However, since the field only exerts a one-dimensional constraint, molecules are in a two-dimensional harmonic field, and the energies of the pendular states are those of a two-dimensional angular oscillator or harmonic librator.<sup>56</sup>

Figure 1.2 shows a correlation diagram relating free-rotor and harmonic librator states of a linear molecule, found under field-free and infinite field conditions, respectively. At the left of the diagram are the free-rotor energy levels, designated by their rotational quantum number, J. For a free-rotor, all M states are degenerate. The right side of the diagram shows the equally spaced energy levels of a harmonic oscillator, designated by vibrational quantum number, v. The harmonic description is only valid at very high field strengths, when the bottom of the potential well is essentially harmonic. For each vibrational level, there are degenerate wavefunctions with angular momentum projections along the field (M) varying from  $v_{,}(v-2),...0$  or 1. These angular momentum projections are of the same origin as the degenerate



**Figure 1.2** Correlation diagram relating the energy levels of a linear molecule under field free conditions and in an electric field. "Free rotor" states are transformed into "harmonic librator" states in the high field limit.

vibrational mode  $v_2$  in CO<sub>2</sub>, a direct result of a two-dimensional harmonic oscillator. It can be seen from figure 1.2 that for each J,M state under field-free conditions, the vibrational quantum number of the corresponding harmonic oscillator state is v=(2J-|M|).<sup>57</sup> Figure 1.2 is meant only to show the correlation between states, and does not portray the relative energies of the free-rotor and harmonic librator states. Crossings in the figure occur only for states with different values of J and M, since these states have different symmetries.

For electric dipole transitions, selection rules require that  $\Delta M=0$  for excitation parallel to the orientation field and  $\Delta M=\pm 1$  for excitation perpendicular to the orientation field.<sup>47,55-57</sup> In the high field limit, as shown in figure 1.2, the selection rule  $\Delta M=0$  requires  $\Delta v=\pm 2$ , while  $\Delta M=\pm 1$  requires  $\Delta v=\pm 1$ . The vibrational selection rule is  $\Delta v=\pm 1$  for ideally harmonic wavefunctions, however, anharmonicity allows overtone transitions ( $\Delta v=\pm 2, \pm 3,...$ ) to occur. Thus, as the field strength is increased and the wavefunctions become more harmonic, parallel transitions should weaken while perpendicular transitions should strengthen. It is also interesting to note that from the correlation diagram in figure 1.2, Stark splittings should result in congested spectra when moderate field strengths are used. This occurs because the degenerate states under field-free conditions are split into different M states, such that each rotational transition is spread into roughly (J+1) components. Under these conditions, the number of allowed transitions appears to increase dramatically. However, as the field strength is further increased and pendular behavior is adopted, some degeneracy of states is recovered, and the resulting spectra should be simplified.<sup>47</sup>

The feasibility and applications of orientation with a uniform electric field have been explored recently. This method has been used to investigate steric effects in bimolecular collisions by Stolte's and Loesch's groups.<sup>58,59</sup> In unimolecular reactions, dissociation of oriented species leads to information regarding the anisotropy of dissociative surfaces. Miller's group, for instance, has used orientation achieved via a uniform electric field to study the dissociation of van der Waals clusters.<sup>60,61</sup> Vigue's group has characterized the alignment of molecular axes in oriented ICl by studying the iodine fragment following photolysis.<sup>62</sup> We have applied this technique for achieving selective dissociation when more than one potential surface is simultaneously accessible in a single-photon process.<sup>14</sup> This is possible because alignment of parent molecules allows polarization control of excitation. Brute force orientation can thus simplify a complex dissociation process, lending itself to investigations of the photoexcitation of large systems.

#### 1.4 Research Goals

The emphasis of this thesis is the application of brute force orientation for measuring directions of transition dipole moments, and for investigating dissociation dynamics. Chapter 2 will detail the experimental design and approach.<sup>13,15</sup> In chapter 3, the  $\pi^* \leftarrow$  n transitions of pyridazine and pyrimidine will be examined through polarization spectroscopy of oriented molecules.<sup>13,18</sup> Quantitative measurements of orientation of molecular axes will be developed. Theoretical treatment of asymmetric tops in a uniform electric field will also be discussed. Chapter 4 will present our first

effort to use this technique in photodissociation studies.<sup>14,16,17,19</sup> The dissociation of ICN and BrCN under field-free conditions as well as in a strong electric field will be examined. A general methodology for measuring directions of transition dipole moments will be presented. In an effort to refine the technique for study of larger molecules, chapter 5 presents measurements of the first two excited singlet states of t-butyl nitrite.<sup>20,21</sup> Photodissociation of the nitroaromatic molecules nitrobenzene and o-nitrotoluene will be documented in chapter 6.<sup>22,23</sup> This represents our first attempt to study large molecules that exhibit slow dissociation. Previous studies of nitroaromatic compounds using conventional methods were not able to reveal information on the transition dipoles. New information on the potential energy surfaces, obtained through brute force orientation of parent molecules prior to dissociation, will be presented.

#### 2. Experimental

#### 2.1 General Description

The experimental apparatus was designed for studying the photoexciation or photodissociation of oriented molecules. A schematic diagram of the experimental setup is given in figure 2.1, and a close-up view of the apparatus found inside the vacuum chamber is given in figure 2.2. A standard molecular beam machine with a pulsed valve and skimmer were used for supersonic cooling and collimation. The orientation field was generated by two 5.5 x 3.0 cm stainless steel plates, separated by 0.6 cm, and connected to voltage supplies of opposite polarity. Field strengths up to 66.7 kV/cm were generated.

Two Nd:YAG-pumped dye laser systems were available for photoexciation/ photodissociation and for detection of photoproducts. In combination with frequency doubling crystals, tunable light ranging from 220 to 360 nm in wavelength was attainable. In addition, light at fixed wavelengths of 532, 355, 266, and 213 nm could be produced directly from the Nd:YAG lasers through harmonic generation or sum frequency generation. The detection methods employed, laser-induced fluorescence (LIF) and resonantly enhanced multiphoton ionization (REMPI), will be discussed in section 2.4.



**Figure 2.1** Schematic diagram of the experimental setup. Two counterpropagating laser beams were used for photoexcitation and detection. Signal collected by either a photomultiplier tube (PMT) or multichannel plate (MCP) was processed by a boxcar integrator and recorded by a computer.



**Figure 2.2** Schematic diagram of the experimental apparatus within the high vacuum chamber. The sample was supersonically cooled and collimated using a pulsed valve and skimmer. The orientation electrodes were stainless steel plates separated by 0.6 cm. The bottom electrode had a mesh-covered hole to allow ion transmission for TOF-REMPI detection. A set of collection lenses and a photomultiplier tube (PMT) were used for LIF detection. The excitation and ionization lasers were generated using Nd:YAG-pumped dye laser systems.

#### 2.2 Laser Systems

Counterpropagating Nd:YAG (Spectra Physics, GCR 230 and GCR 190) pumped dye laser (LAS, LDL 2051 and LDL 20505) systems were used as dissociation/probe or excitation/ionization sources. In some cases, a single laser was used for photodissociation and detection of photofragments. Visible output from the dye lasers were frequency doubled using non-linear crystals. A beta-barium borate (BBO) crystal ( $\beta$ -BaB<sub>2</sub>O<sub>4</sub>) was used to obtain wavelengths in the 220-266 nm region, while a potassium dihydrogen phosphate (KDP) crystal (KH<sub>2</sub>PO<sub>4</sub>) was used for the longer wavelengths. The BBO crystal was positioned in an Inrad Autotracker III system, which adjusted the position of the crystal when scanning to ensure the proper phase matching conditions. Table 2.1 lists the various laser dyes used to obtain the tunable, wavelength ranges given. Pellin-Broca prisms were used to separate the second harmonic from the fundamental frequencies. Typical output powers were between 0.2 and 2.0 mJ.

Uniformity and stability of the laser beams was crucial in these experiments. To avoid partial saturation in the excitation step of the diazine experiments (chapter 3), a series of pinholes and collimating lenses was used to improve the beam profile.<sup>13,18</sup> Slight focusing of the dissociation beam (~ 1.0 mm diameter) was necessary in the BrCN and nitroaromatic experiments due to the low absorption crosssections. However, caution was taken to avoid saturation effects. When scanning over a large wavelength region, shifts in beam path due to rotation of the doubling

**Table 2.1** Summary of laser dyes. A Nd:YAG laser was used for pumping in all cases, and all dyes were prepared in methanol. The tuning range and wavelengths of maximum intensity before frequency doubling are given.

Dye	Pump Wavelength (nm)	Maximum (nm)	Tuning Range (nm)
Stilbene 3	355	425	414-445
Coumarin 2	355	448	435-463
Coumarin 47	355	460	446-478
Coumarin 102	355	481	460-495
Coumarin 307	355	508	488-540
Coumarin 153	355	540	515-570
DCM	532	640	607-663
Pyridine 1	532	698	665-725
Pyridine 2	532	722	695-745

crystal are sometimes troublesome. For particularly long scans, two Pellin-Broca prisms, arranged as mirror images of each other, were used. The resulting light path was stable for scans of a few nanometers. In some cases, a complete spectrum was obtained by connecting several discrete segments and correcting for the shifting beam path.<sup>21-23</sup>

In most cases, the polarization directions of the laser beams were parallel to each other, in the plane determined by the molecular beam and the propagation directions of the lasers (termed "horizontal polarization"). Rotating the polarization direction of the resonant or dissociation beam for polarization spectroscopy experiments was accomplished by using a double Fresnel rhomb (CVI lasers), a Pockels cell (Cleveland Crystals), or a half-wave plate (CVI lasers), depending on the wavelength. Early experiments (chapters 3 and 4) used the double Fresnel rhomb,<sup>13-17</sup> which caused a slight shift in the position and direction of the output beam. This phenomenon resulted in an instability of experimental conditions, and contributed to a large error bar associated with the experimental data. In an effort to improve the stability, a Pockels cell was used to rotation the polarization of the resonant laser in the pyrimidine experiments.<sup>18</sup> No change in the light path was observed when the voltage to the Pockels cell was toggled from 0 V (horizontal polarization) to 800 V (vertical polarization). The optics in the Pockels cell absorb ultraviolet radiation, and therefore could not be used for wavelengths less than about 300 nm. For the remaining experiments, half-wave plates were used to rotate the polarization direction of the dissociation beam.<sup>19-23</sup>

#### 2.3 Molecular Beam

#### 2.3.1 Background

The technique of supersonic expansion has been around for decades, however, its application to orientation and alignment of polar molecules is relatively new. The theory of supersonic molecular beams is well documented,<sup>63,64</sup> and will only be discussed briefly here. Advantages of the technique include extreme internal cooling and production of a collision-free environment. The former property results in a very low rotational temperature, which is a necessary condition for brute force orientation (chapter 1).

The basic principle underlying the generation of a supersonic molecular beam is the expansion of molecules from a region of high pressure (~1400 torr) into a vacuum (~10<sup>-5</sup> torr) through a small orifice or nozzle. In a thermal sample, molecular velocities are randomly distributed. However, at the beginning of the gas expansion, molecular velocities will become aligned along the expansion axis through intermolecular collisions. The initial thermal energy of the molecules is transferred into translational energy in the direction of the molecular beam. When the thermal energy of the molecules is lower than the internal energy, intermolecular collisions further redistribute the internal energy to the various internal degrees of freedom, resulting in low rotational and vibrational temperatures. As the expansion continues, and more molecules are moving with a similar speed in the same direction, the supersonic molecular beam becomes essentially collision-free.

A skimmer is introduced in the collision-free region to further collimate the molecular beam. This allows only a small central portion of the beam to pass through to the reaction chamber. The central region of the molecular beam, along the expansion axis, achieves the best degree of cooling. Thus, molecules reach lower effective temperatures in a collimated beam than in a free expansion molecular beam.

The pressure inside the vacuum chamber rapidly increases upon introduction of a sample. The chamber must be pumped at a very high rate to prevent a high background pressure, which would depreciate the molecular beam. The use of a pulsed valve to introduce the sample into the vacuum chamber reduces the work load of the diffusion pumps, keeps the supersonic molecular beam pristine, and reduces the amount of sample consumed in an experiment.

#### 2.3.2 Apparatus

The molecular beam source and apparatus found within the reaction chamber are depicted in figure 2.2. A piezo-electric pulsed valve was used to release the sample upon application of an appropriate pulsed voltage. The pulse width was used to control the amount of sample introduced. The skimmer, located approximately 2 cm downstream from the pulsed valve, had an aperture with a diameter of 0.5 mm. The skimmer was mounted in a stainless steel beaker, and the nozzle-skimmer distance could be adjusted by pulling back the pulsed valve. The pulsed valve and skimmer were aligned coaxially, and the molecular beam was aligned through the center of the orientation electrodes. The source chamber was pumped by a diffusion pump (Varian 0173), resulting in a pressure of approximately 8 x  $10^{-6}$  torr when the pulsed valve was off. The reaction chamber was pumped by an Edwards Diffstak 160/700M diffusion pump, resulting in a pressure of ~8 x  $10^{-6}$  torr. When the pulsed valve was turned on, the pressure in the source chamber increased to ~ $10^{-4}$  torr, while the pressure in the reaction chamber remained unchanged.

#### 2.3.3 Rotational Temperature Measurements

The rotational temperature of the molecular beam is affected by the nozzleskimmer distance, delay time between the valve opening and the laser pulse, width of the pulse used to open the valve, stagnation pressure, and identity of the sample.<sup>64</sup> The optimum experimental conditions were obtained by trial and error. As mentioned in section 2.3.2, the nozzle-skimmer distance was about 2 cm. The delay time between the valve opening and the laser pulse varied between experiments, ranging between 10 and 300  $\mu$ s. The pulsed valve width was generally set at 200  $\mu$ s. Stagnation pressures below 1000 torr often resulted in higher rotational temperatures, and thus were not used.

The rotational temperature of the molecular beam can be measured from the rotationally resolved laser-induced fluorescence (LIF) or resonantly enhanced multiphoton ionization (REMPI) spectrum of a species seeded in the molecular beam (see section 2.4 for detection methods). Molecular iodine, NO, pyridazine, and pyrimidine were used to measure rotational temperatures in the work presented in this

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thesis, depending on the identity of the sample under study (see chapters 3-6 for discussion). Precise rotational temperatures were determined by fitting the observed spectra to simulations. Figures 2.3 and 2.4 show the LIF spectra (see section 2.4) of supersonically cooled molecular iodine and nitric oxide from our apparatus. The solid lines indicate experimental data, and the dashed lines represent simulations at the appropriate rotational temperatures. The data imply that the rotational temperature of I<sub>2</sub> in this particular scan was 1.0 K, and the temperature of a 2% mixture of NO in helium was 2.0 K. Variation of the concentration of the NO mixture between 2 and 6.5% resulted in a slight increase in the rotational temperature of the molecular beam, however, below 2% the rotational temperature was independent of concentration.

#### 2.4 Methods of Detection

Most of the photoexcitation/photodissociation experiments presented in this thesis required the use of two laser beams: one laser for the initial excitation/dissociation step, and a second laser for probing the products. Detection was generally accomplished through either laser-induced fluorescence or resonantly enhanced multiphoton ionization. The experimental apparatus for detection by LIF and REMPI is given in figure 2.2.



Figure 2.3 Rotational temperature measurement of  $I_2$ . The dashed line, which agrees well with experiment, indicates simulation assuming a rotational temperature of 1.0 K.


**Figure 2.4** Rotational temperature measurement of 2% NO in helium. The dashed line indicates simulation assuming a rotational temperature of 2.0 K.

## 2.4.1 LIF

LIF is one of the most extensively used methods of detection for rotational and vibrational energy distributions. This technique was developed nearly 30 years ago by Zare *et al.*,<sup>65</sup> who used it to analyze fragments produced from reactive collisions. The fluorescence intensity depends on the details of the angular momentum distribution and the detection geometry. Zare also developed a theoretical treatment for deriving internal state populations from the intensity of the fluorescence spectrum.<sup>66,67</sup> Since then, LIF techniques have been used extensively to determine population, orientation, and alignment terms of angular momentum.

One reason for the popularity of LIF detection is its experimental simplicity. Figure 2.5 outlines the basic principle of this technique.<sup>64</sup> The product of interest from the initial photoexcitation/photodissociation is generally formed in the ground state. A photon from the probe laser is used to excite the product to a higher energy electronic state, which fluoresces back to the initial state. During undispersed detection, fluorescence at all wavelengths is collected with a lens system and imaged onto a photomultiplier tube (PMT). In general, the fluorescence signal is of longer wavelengths than the probe beam due to internal conversion and Franck-Condon factors. Thus, filters can be inserted in front of the detector to prevent background signal due to stray photons from the probe beam.

LIF spectra can be used to map the vibrational and rotational populations of the photoproducts from the initial excitation/dissociation. The intensity of each

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**Figure 2.5** Energy level diagram illustrating laser-induced fluorescence. A molecule in the ground state is promoted to an excited electronic state with a photon from the probe laser beam. A photon is released as the molecule fluoresces back to the ground state.

rovibrational transition is proportional to the population of the initial state, the Hönl-London factor, the Franck-Condon factor, and alignment and orientation factors. When alignment effects are ignored, the LIFBASE spectral simulation program can be used to simulate spectral intensities and determine populations.

Advantages of LIF include ease of implementation, high resolution, and high sensitivity. The resolution attainable with this technique is usually only limited by Doppler broadening and the linewidth of the detection laser. On the other hand, using a narrow bandwidth laser, the Doppler effect has been exploited extensively to derive translational velocities of photofragments. Another advantage to LIF detection is the high sensitivity achieved by collection lenses. An important disadvantage is the lack of mass selection, therefore analysis of LIF spectra relies on prior knowledge of the spectra of the detected species. Furthermore, the collection efficiency of LIF is much lower than REMPI. In the latter case, almost 100% collection efficiency can be expected in ideal cases.

### 2.4.2 REMPI

Figure 2.4 illustrates the concept of REMPI detection.<sup>64</sup> As the name implies at least two photons are needed for REMPI. In the simplest type of experiment, the two photons come from a single laser. The first photon has an energy that is resonant with an intermediate state of the molecule or atom of interest, while the second photon is used to achieve ionization. The resulting cations can be collected with a simple



**Figure 2.6** Energy level diagram illustrating (1+1) resonantly enhanced multiphoton ionization. A molecule in the ground state is promoted to an excited electronic state with the first photon. A second photon is used to ionize the molecule for detection.

electrode, or a time of flight tube for mass analysis. We have adopted the latter approach, which allows separation of the ion signal from that of oil contamination. In our experiment, ions are collected with a multichannel plate (MCP). Signal intensities are very sensitive to the experimental conditions, particularly to the voltages applied on the electrodes, flight tube, and MCP. Optimal conditions for an orientation field strength of 50 kV/cm include +25 kV on the top electrode, -5 kV on the bottom electrode, -1700 V on the flight tube, and 2.3 kV on the MCP (see figure 2.2).

More generally, REMPI detection schemes may involve one, two, or more light sources, and each step (excitation and ionization) may involve one or more photons.<sup>64</sup> A one-color experiment is denoted as an (m+n) REMPI experiment, where there are m photons absorbed in the excitation step and n photons needed for ionization. If two colors are used, the process is denoted an (m+n') REMPI experiment, where the prime denotes the use of a second wavelength for ionization.

There are certain advantages and disadvantages to the REMPI detection scheme. As mentioned above, mass selection is an important advantage. Compared with LIF, a much broader range of species can be studied with REMPI since there is no requirement of fluorescence. In addition, REMPI offers a higher collection efficiency than LIF. A disadvantage to the REMPI method of detection is that pump oil contamination can result in a constant background signal. Furthermore, in REMPI experiments, the possibility of saturation in detection must always be considered. Finally, the REMPI method is not always applicable since it is limited to a judicious choice of resonant states, which may not be available for an arbitrary species.

## 2.5 Data Acquisition

The entire experiment was run in a pulsed mode with a repetition rate of 10 Hz. The internal clock of a computer was used to trigger a delay generator (Stanford Research, DG535). The delay generator was used to trigger the Nd:YAG lasers, dye lasers, pulsed valve, and boxcar integrators with appropriate delay times. The delay time between the photoexcitation and probe laser beams was between 2 and 200 ns, and varied between experiments.

The fluorescence or ion signal (measured with a PMT or MCP, respectively) was sent to a boxcar integrator. The boxcar was used to average the pulsed signal over 3-30 laser shots, and to convert the signal to a DC voltage before sending it to the computer. When scanning a full spectrum, the laser power was recorded for normalization purposes. In this case, a photodiode was placed near the reaction chamber window for detection of scattered laser light. The photodiode signal was processed with a second boxcar integrator. In some cases, both fluorescence and ion signals were collected simultaneously using two boxcars.

The experiment is controlled by two Visual Basic programs running on the personal computer. One program is used to control the operation of the pulsed valve. This program can be used to change the delay time between the laser and the pulsed valve as well as the width of the pulse. The second program is used to scan the probe dye laser, receive data from the boxcars, and save data files. Using this program, the scanning range and step size of the dye laser can easily be adjusted.

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# 2.6 Summary

The experimental apparatus allows study of the photoexcitation or photodissociation of polar molecules. Using supersonic expansion, rotational temperatures between 1 and 3 K were achieved, making orientation with a strong, uniform electric field of up to 67 kV/cm feasible. All laser wavelengths used were generated by Nd:YAG or frequency doubled Nd:YAG-pumped dye laser systems. Products from photoexcitation or photodissociation of the molecules of interest were detected by either LIF or REMPI. This apparatus is versatile and may be used for future studies of the dissociation of monomers and clusters. In most regards, the entire experiment is automated and controlled by a personal computer. Timing is initiated by the internal clock of the computer, and appropriate delay times are controlled by a delay generator.

Experimental aspects that are unique to the molecule under study will be discussed in the "experimental details" sections of chapters 3-6.

# 3. Diazines

# 3.1 Introduction

The ability to achieve orientation of reactants with a uniform electric field offers an opportunity to investigate vectorial properties of electronic transitions, such as directions of transition dipole moments.<sup>3,4</sup> However, quantitative interpretation of the experimental results requires a detailed knowledge of the distribution of molecular axes achieved with the uniform electric field. On the other hand, for a transition with a well-determined transition dipole, variation of the transition probability of oriented molecules with the polarization direction of excitation reveals the distribution of molecular axes. The goal of this chapter is to characterize the orientation of molecular axes of pyridazine (1,2-diazine) and pyrimidine (1,3-diazine) in a uniform electric field by studying the well-characterized  $\pi^* \leftarrow n$  transitions.<sup>13,18</sup> These molecules are ideal for this type of investigation because of their large permanent dipole moments (4 and 2.3 D, respectively<sup>68,69</sup>) and rotationally resolved ultraviolet absorption spectra.<sup>70</sup> The former property makes orientation with a uniform electric field easily achieved, while the latter allows accurate determination of the rotational temperature of the supersonic molecular beam.<sup>71</sup> Together with theoretical modeling of the Stark effect in the strong electric field, a detailed description of molecular orientation can be determined.

A unique property of pyrimidine is its quick internal conversion upon excitation to the  $S_1$  state.<sup>72-76</sup> It demonstrates rotational dependent intersystem

crossing (ISC), and its complex mechanism has been the subject of many studies in the past.<sup>77-82</sup> Fluorescence from the S<sub>1</sub> state has been reported as bi-exponential for  $J' \ge 4$  levels<sup>80</sup> (J' is the rotational angular momentum quantum number.) The lifetime of the fast component is on the order of nanoseconds or even shorter, and the lifetime of the slow component is approximately 800 ns.<sup>80</sup> The fluorescence yield decreases with the increase of rotational angular momentum due to K'-scrambling and possible Coriolis coupling<sup>72</sup> (K' is the projection of J' along the symmetry axis.) High-resolution photoexcitation spectroscopy has been used to identify molecular eigenstates resulting from interaction with a nearby triplet state.<sup>77</sup> Coupling between rotational levels of the singlet and triplet states is enhanced in a magnetic field due to spin-decoupling, field-enhanced coupling with other triplet states, and nuclear hyperfine mixing.<sup>82</sup> The yield of the slow fluorescence component was quenched by 60-75% in a field of 200 Gauss. In an electric field of 1 kV/cm, the quenching effect amounted to 6%.<sup>83</sup>

This work presents measurements of the  $\pi^* \leftarrow n$  transitions of pyridazine and pyrimidine for characterization of the alignment of molecular axes in a strong, uniform electric field.<sup>13,18</sup> Ion and fluorescence yields will be used to identify the excitation probabilities in these systems. Using a quantum mechanical approach, experimental observations will be explained, and a general theory for determining directions of transition dipoles through this type of experiment will be developed. In addition, observations of the complex relaxation dynamics of pyrimidine in an electric field will be presented.

# **3.2 Experimental Details**

The experimental apparatus has been described in chapter 2. Room temperature pyridazine vapor (Aldrich, 99%) was carried into the reaction chamber by helium with a stagnation pressure of 1270 torr. The  $\pi^* \leftarrow$  n transition of pyridazine was probed by (1+1') REMPI.<sup>13,71</sup> The first laser beam, at energies around 27,192 cm<sup>-1</sup>, was resonant with a vibronic transition of pyridazine (16b<sup>2</sup><sub>0</sub> band), and its polarization direction was rotated with a double Fresnel rhomb. The ionization beam was kept at 45,454 cm<sup>-1</sup>. During the experiment, neither laser beam was focused, and no single laser signal from either laser was observable.

Room temperature pyrimidine vapor (Aldrich, 99%) was co-expanded with helium at a stagnation pressure of 1400 torr. Reactions between pyrimidine and the Oring of the piezo-electric valve caused some instability in the rotational temperature of the molecular beam over a period of several hours. Precautions were taken to maintain the consistency of measurements. Cluster formation was only noticeable after an extended period of experimentation. All results presented here were confirmed to be from monomers based on their mass spectra. The  $\pi^* \leftarrow$  n transition of pyrimidine was detected by both LIF and REMPI.<sup>18</sup> In the REMPI experiment, the resonant laser was around 31,073 cm<sup>-1</sup> while the ionization laser was kept at 45,454 cm<sup>-1</sup>. The polarization direction of the resonant laser was rotated with a Pockels cell.

# 3.3 Theoretical Treatment

Detailed treatment of the energy levels and orientation of molecular axes of symmetric top and linear molecules in a uniform electric field has been given in the Orientation of asymmetric top molecules was investigated by literature.<sup>56,57,62</sup> Bulthuis et al.<sup>84</sup> The authors pointed out that the energy levels of asymmetric top molecules exhibited avoided crossings as the orientation field was increased, while for symmetric top molecules, these crossing were allowed for symmetry reasons. Depending on the time scale of molecular rotation and the rate of change of the Stark field exerted on the molecular beam, the probability of curve crossing, the final state distribution, and therefore the extent of molecular orientation would be different. Based on the work of Bulthuis et al.<sup>84</sup>, our group has further developed a general methodology for determining properties of electronic transitions of asymmetric top molecules in a strong Stark field.<sup>13,18,85</sup> Electronic transitions are treated with a full quantum mechanical approach, and neither the asymmetry nor the electric field is treated as a perturbation. Effects of alignment of molecular axes on the spectral intensity distribution and overall transition probability have been obtained.

In our approach, the rotational wavefunctions of asymmetric top molecules are expressed as linear combinations of symmetric top wavefunctions. In an electric field, the magnetic quantum number M is the only good quantum number, and the total rotational angular momentum J is no longer conserved. States with  $\pm$ M values are degenerate, so only positive M values must be considered. Under field-free conditions, basis functions with the same J but different K quantum numbers will be

mixed due to the asymmetry of the molecular system.<sup>13</sup> The orientation field further results in mixing of basis functions with the same K but different J values. Under low fields, terms related to the occupied low-energy levels and a few higher levels are sufficient for an accurate calculation. However, as the field strength increases, more high-energy basis functions must be included for convergence.

Figure 3.1 shows the coordinate system and principal axes of pyridazine. The rotational constants and permanent dipole are also given.<sup>70</sup> Using the values listed in figure 3.1, calculated energies of the J=1 levels are shown in figure 3.2. The labeling has the format  $J_{KaKc}(M)$ . Each  $J_{KaKc}$  state is split into two sublevels with M=0 and 1. Different  $1_{KaKc}$  states have different symmetries, thus, crossings between these curves are allowed even for this asymmetric top. Avoided crossings are uncommon in pyridazine due to the similarity of its rotational constants to those of an oblate symmetric top. Some of the sublevels have elevated energies as the field is initially increased. However, all energy levels of the J=1 manifold have decreased energies at high fields. For levels with higher J values, similar behavior can be observed, although to achieve the same Stark shift in energy, higher field strengths are required.

Figure 3.3 shows the calculated distributions of the permanent dipole under three different orientation fields. This calculation assumes a thermal (Boltzmann) distribution of states in the electric field. Normalization was achieved by setting the area beneath the distribution function to unity. This treatment ignored any anisotropy in the plane perpendicular to the orientation axis, since the orientation field should not have any direct impact on this plane. As the field strength increases, more molecules



**Figure 3.1** Coordinate system of pyridazine. The rotational constants are given in  $cm^{-1}$ , and the permanent dipole moment is given in Debye. The transition dipole is along the C axis, perpendicular to the molecular plane. The permanent dipole moment is along the A axis, which is the symmetry axis of this  $C_{2v}$  molecule.



**Figure 3.2** Effect of an electric field on the energies of the J=1 states. The labeling follows  $J_{KaKc}(M)$ . Crossings shown in the figure are allowed for symmetry reasons.



Figure 3.3 Distributions of the permanent dipole moment of pyridazine in three different orientation fields. The variable  $\Theta$  refers to the angle between the orientation field and the permanent dipole moment. The populations were normalized by setting the overall population (integrated areas under the curves) to unity.

are oriented with their permanent dipoles along the orientation field. Consequently, the molecular plane becomes parallel with the orientation field. At 60 kV/cm, twice as many molecules are aligned with the orientation field as are perpendicular to it. This corresponds to 70% of the pyridazine molecules having their nitrogen ends preferentially pointing to the positive electrode, and about 50% restricted within a cone of  $60^{\circ}$  around the electric field.

#### **3.4** Experimental Results: Pyridazine

Figure 3.4 shows a REMPI spectrum of pyridazine recorded under field-free conditions from a free jet (no skimmer was used).<sup>13</sup> Calculation results are overlaid on the experimental data. The diatomic-like appearance of this spectrum is due to small changes in the C constant between the upper and lower states of this vibronic transition. Each peak is therefore an overlapping of transitions with the same J but different K values. Comparison between theory and experiment allows determination of the rotational temperature of the molecular beam. At 1.0 K, the agreement between theory and experiment is remarkable. During the experiment, however, a skimmer was used, and insufficient pumping of the pulsed valve region resulted in an increased rotational temperature of  $\sim$ 2.0 K.

Figure 3.5 shows the REMPI spectra of pyridazine recorded when the orientation field was increased from 0 to 16 kV/cm. Both the resonant and ionization lasers were polarized perpendicular to the orientation field. As the field



Figure 3.4 REMPI spectrum of pyridazine. The rotational temperature of the free jet expansion was 1.0 K.



Figure 3.5 REMPI spectra of pyridazine showing the effect of orientation fields.

strength was increased to 8.5 kV/cm, transition from lower rotational levels (J'' $\leq$ 2) became broad. At 16 kV/cm, the spectrum became nearly featureless. With the increase of the orientation field, Stark shifts in energy levels of both the ground and excited states result in splitting of each rovibronic transition. A single transition under field free conditions is thus split into several transitions, resulting in a broadening of peaks as the field strength is increased. The selection rule is  $\Delta$ M=0 (or ±1) when the polarization direction of the resonant laser is parallel (or perpendicular) to the orientation field. The permanent dipole moment of the upper electronic state (2.8 D) is smaller than that of the ground state.<sup>70</sup> Consequently, the vibronic band was shifted to a higher energy.

Figure 3.6 shows REMPI spectra recorded when the resonant laser was polarized parallel and perpendicular to the orientation field.<sup>13</sup> The two spectra show dramatic differences not only in their intensity distributions, but also in overall transition strength. To confirm that these differences are solely related to the orientation and alignment effect of the electric field, the same comparison was made under field-free conditions. No differences between the spectra were observable without the orientation field, implying that the ionization step is independent of the alignment of pyridazine caused by the linearly polarized resonant laser. This is because the ionization step is a bound-to-continuum transition, and the transition dipole moment to the continuum has both parallel and perpendicular components. The ejected electrons in a photoionization step can carry excess angular momentum, resulting in near equal contributions from both the parallel and perpendicular



Figure 3.6 Polarization dependence of the REMPI spectra of pyridazine in an orientation field of 56 kV/cm. The two spectra were recorded when the polarization direction of the resonant laser was parallel or perpendicular to the orientation field.

transition. Variations of the REMPI spectra under different polarization directions of the resonant laser were thus solely related to the efficiency of the first excitation step, which is directly affected by the alignment of ground state molecules.

In a strong uniform electric field, the permanent dipole is preferentially parallel to the orientation field. The dependence of the overall transition intensity on the polarization direction of excitation reveals the direction of the transition dipole. When the resonant laser was polarized perpendicular to the orientation field, its electric field was perpendicular to the permanent dipole and parallel to the transition dipole. Excitation in this case should have a favorable efficiency, and the overall transition probability should be increased. Effects of the polarization direction of the resonant laser will be quantified by defining the polarization ratio,  $\rho$ , as the ratio of overall transition intensities when the laser was polarized perpendicular/parallel to the orientation field. Figure 3.7 displays the dependence of the polarization ratio on the strength of the orientation field. The polarization ratio is unity under field-free conditions, confirming that the ionization laser was not probing the alignment effect induced by the resonant laser. At 56 kV/cm, a 40% enhancement in the overall transition probability was observed when the laser was changed from parallel to perpendicular to the field. The solid line in figure 3.7 represents calculation of the expected trend. The uncertainty in experimental data is partially caused by variations in the overlap between the two laser beams in this (1+1') REMPI experiment. The Fresnel-Rhomb that was used to rotate the polarization direction of the resonant laser would change both the position and direction of the output beam. Other factors, such



Figure 3.7 Effect of the orientation field on the polarization dependence of the overall transition probabilities of pyridazine. The vertical axis shows the polarization ratio – the ratio of transition intensity when the polarization direction of the resonant laser was perpendicular/parallel to the orientation field.

as instability of the pulsed valve and fluctuations in laser power, also contributed to the experimental uncertainty.

# 3.5 Experimental Results: Pyrimidine

#### 3.5.1 LIF and REMPI under Field-Free Conditions

Figure 3.8 shows the REMPI and LIF spectra of pyrimidine under field-free conditions.<sup>18</sup> The REMPI spectrum showed no significant dependence on the delay time between the two lasers, and the LIF spectrum showed no dependence on the delay of the boxcar. The origin band of this  $\pi^* \leftarrow n$  transition is at 31,072.5 cm<sup>-1</sup>. The selection rule for this transition is  $\Delta K_c=0$ . Small changes in values of rotational constants result in a strong Q branch and evenly spaced P and R branches, similar to pyridazine (section 3.4). In figure 3.8, the REMPI and LIF spectra are essentially identical, and the calculation successfully reproduces both experimental spectra assuming a rotational temperature of 1.8 K.

The observation in figure 3.8 agrees with previous reports on fluorescence properties of pyrimidine.<sup>80</sup> In the supersonic molecular beam with a rotational temperature of 1.8 K, only levels with  $J'' \leq 4$  are occupied appreciably. The fluorescence yield ( $\Phi_f$ ) of these levels is believed to be more or less independent of the rotational quantum number, although for transitions involving higher J' values,  $\Phi_f$  is proportional to  $(2J'+1)^{-1}$ .<sup>82</sup> The fluorescence signal in figure 3.8, therefore, reflects the population of the S<sub>1</sub> level, consistent with the measurement of the REMPI experiment.



**Figure 3.8** REMPI and LIF spectra of pyrimidine. The calculation reproduces the experimental data assuming a rotational temperature of 1.8 K.

The agreement between the REMPI and LIF spectra confirms the literature report that the observed slow fluorescence signal is from the initially prepared singlet state, not phosphorescence from a triplet state.<sup>72</sup>

This property of pyrimidine falls in between the two other diazine isomers.<sup>70</sup> In pyrazine (1,4-diazine),  $\Phi_f$  is a function of J' even for low rotational levels.<sup>86-88</sup> The fluorescence spectrum dramatically deviates from a regular Boltzmann-type distribution. Pyridazine, on the other hand, has no phosphorescence, and a negligible  $\Phi_f$ . The N=N bond in pyridazine is a strong enough perturbation to alter the aromaticity of the molecular frame, resulting in a fundamentally different behavior.<sup>89-92</sup> The triplet level of pyridazine is believed to couple to the ground state through quick intersystem crossing.<sup>92</sup>

## 3.5.2 REMPI in a Field of 50 kV/cm

The REMPI spectra in an orientation field of 50 kV/cm are shown in figure 3.9.<sup>13</sup> The top panel was obtained when the polarization direction of the resonant laser was parallel to the orientation field, and the bottom panel was obtained when the resonant laser was polarized perpendicular to the orientation field. The two spectra were plotted on the same vertical scale. Each spectrum was an average of 50 laser shots per point. The time delay between the resonant laser and the ionization laser was set at 50 ns.



Figure 3.9 REMPI spectra of pyrimidine in an orientation field of 50 kV/cm. The calculation assumed a permanent dipole of +0.6 D for the excited electronic state.

The permanent dipole moment of pyrimidine is in the molecular plane bisecting the N-C-N bond angle, while the transition dipole ( $\pi^* \leftarrow n$ ) is perpendicular to the molecular plane.<sup>70</sup> It is, therefore, expected that if sufficient orientation is achieved via the electric field, the overall intensity of the bottom panel should be stronger than that of the top panel. Figure 3.9 shows the correct intensity difference.

Calculations in figure 3.9 for the two different polarization directions used the same intensity factor, and the agreement between theory and experiment is remarkable.<sup>18</sup> Almost all of the fine structure in the spectra has been reproduced. In an electric field, the selection rule is  $\Delta M=\pm 1$  for perpendicular excitation and  $\Delta M=0$ for parallel excitation. Although only levels with  $J'' \leq 4$  are appreciably occupied at a rotational temperature of 1.8 K, Stark effects have mixed levels as high as J=10 in the wavefunction of the original J $\leq$ 4 levels. For M=0 and J ranges from 0 to 10, there are 121 energy levels; and in a field of 66.7 kV/cm, there are in total over 12,000 allowed transitions for all the M values under perpendicular excitation.<sup>51</sup> Stark splitting of each rotational level results in extensive overlapping among these transitions, which makes assignment of figure 3.9 a difficult task. In the bottom panel of the figure, transitions on the low-energy side are still primarily the P branch, with  $\Delta M$ =-1, and those on the high-energy side are the R branch, with  $\Delta M=1$ . The Q branch dominates the middle section, overlapping with transitions from the P and R branches. The two strongest central features are dominated by  $P_1/Q_1/R_0$  transitions with the left corresponding  $M=0 \leftarrow 1$ corresponding  $M=1 \leftarrow 0$ . to and the right to

Overlaid on the experimental data in figure 3.9 are calculations assuming a permanent dipole of 0.6 D. This kind of comparison between theory and experiment allows determination of the permanent dipole moment of the excited electronic state. The permanent dipole for the ground state of pyrimidine is known to be 2.334  $D^{69}$ , but two different values (-0.6 and 1.5 D) have been reported for the excited state.<sup>93-95</sup> In the calculation of figure 3.9, the energy axis is uniquely defined based on spectra under field free conditions. The excellent agreement between calculation and experiment indicates that the permanent dipole is +0.6 D, rather than either of the reported values. Calculations using -0.6 and 1.5 D are shown in figure 3.10. Discrepancies with experimental data are obvious. Ohta and Tanaka reported an absolute value of 0.6 D for the  $S_1$  state based on measurements of quantum beats induced by an electric field.<sup>96</sup> The authors deduced the direction based on a theoretical calculation.<sup>97</sup> Figures 3.9 and 3.10 unequivocally demonstrate that the permanent dipole moment of the S<sub>1</sub> state is of the same direction as that of the ground state, with a value of 0.6 D.

Orientation of molecular axes can be represented by the polarization ratio,  $\rho$ , which is the ratio of overall transition probabilities when the resonant laser was polarized perpendicular/parallel to the orientation field. The diamonds and squares in figure 3.11 show values of  $\rho$  obtained from the REMPI and LIF spectra of pyrimidine, respectively. As in the case of pyridazine,  $\rho$  is unity under field-free conditions, signifying an isotropic distribution in the supersonic molecular beam, and that no alignment effect from the resonant laser is observed. As the field strength is



**Figure 3.10** Calculation results assuming +1.5 and -0.6 D for the permanent dipole of the excited state. The disagreement with experimental data from both calculations supports the value of +0.6 D, as shown in figure 3.9 and discussed in the text.



Figure 3.11 Dependence of the polarization ratios of pyrimidine on the strength of the orientation field. These ratios were obtained from integrations of spectra under perpendicular/parallel excitation. The REMPI data were shifted by -1 kV/cm for clarity.

increased, the overall excitation probability shows a preference for perpendicular excitation. In a field of 50 kV/cm, the preference amounts to 20%.

As discussed in chapter 1, the rotational temperature of the molecular beam plays a crucial role in molecular orientation. It was noticed during the experiment that due to reactions between pyrimidine and an O-ring in the pulsed valve, the rotational temperature of the molecular beam increased gradually.<sup>18</sup> Results presented in figures 3.8-3.11 were obtained within a few hours of each replacement of the O-ring. Spectra taken afterwards demonstrated a higher rotational temperature up to 2.5 K. Figure 3.12 shows the temperature dependence of the polarization ratios for both REMPI and LIF studies. As the temperature increased, orientation by the electric field was less effective, and the preference for perpendicular excitation deteriorated, resulting in a decreased value of  $\rho$ .

### 3.5.3 Lifetime of the $S_1$ State in an Electric Field

In an electric field, the spectral intensity distributions of both REMPI and LIF experiments showed dependence on the delay time, although under field-free conditions, no such dependence was observed. In the latter case, rotational intensity distributions of both spectra remained the same even under delays as long as 1 ms, although the overall intensity was dramatically decreased. The REMPI spectra in an orientation field of 50 kV/cm recorded under two different delay times are shown in the top panel of figure 3.13. The polarization direction of the resonant laser was



**Figure 3.12** Dependence of the polarization ratio on the rotational temperature of the molecular beam. The REMPI results were obtained in an orientation field of 50 kV/cm, while the LIF data were obtained in a field of 66.7 kV/cm.



Figure 3.13 REMPI spectra under different delay times. The polarization direction of the resonant laser was perpendicular to the orientation field. The top panel shows variation of spectral intensity distributions with the delay time of the ionization laser relative to the resonant excitation laser. The bottom panel shows two calculation results: one with a Boltzmann distribution of 1.8 K, and one upon elimination of contributions from M' $\geq$ 3 levels.

perpendicular to the orientation field. At a delay of 200 ns, adjustment of the spatial position of the ionization laser was necessary to compensate for the group velocity of the supersonic molecular beam. The two experimental spectra in figure 3.13 were not plotted on the same vertical scale, so no comparison between the absolute signal intensities should be made. The relative intensity distributions illustrate that transitions at both wings of the intense block showed decreased intensity as the delay time was increased. Spectra from the LIF experiment also showed a similar trend, although the wings in the LIF spectra were all weaker than those in the corresponding REMPI spectra.

One possible origin of this variation with delay time in high fields is fieldinduced decay for high rotational levels of the S<sub>1</sub> state. In a magnetic field, these levels have proven to be more effectively quenched.<sup>82</sup> The wings of this vibronic transition are composed of transitions originating from these levels. It is therefore reasonable to assume that the intensity loss in the wings of figure 3.13 is caused by effective quenching of high rotational levels by the orientation field. Two calculation results are given in the bottom panel of figure 3.13. The dashed line was the result assuming a Boltzmann distribution at 1.8 K, while the solid line was obtained by a modified calculation ignoring contributions from levels with  $M' \ge 3$ . In the latter case, observable narrowing effects are reproduced. In fact, the agreement of this calculation with the REMPI spectra at a 200 ns delay is quite satisfactory.

Figure 3.14 shows the LIF spectra under two different polarization directions of the excitation laser in an orientation field of 66.7 kV/cm. The delay time between

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Figure 3.14 LIF spectra of pyrimidine in an orientation field of 66.7 kV/cm. The solid lines were calculation results assuming a Boltzmann distribution of 1.8 K, and the dashed line in the bottom panel was obtained by eliminating contributions from  $M' \ge 3$  levels.
excitation and detection was 100 ns, and the width for the gate of the boxcar was 200 ns, enclosing most of the intense segment of the fluorescence signal. The solid lines are calculation results assuming a permanent dipole of 0.6 D for the S<sub>1</sub> state. Dependence of  $\rho$  on the orientation field was given in figure 3.11. Values from the LIF spectra were so close to those from the REMPI experiment that for clarity, the horizontal axis was shifted by -1 kV/cm for the LIF data. Polarization ratios for two different rotational temperatures in a field of 66.7 kV/cm are given in figure 3.12. Similar dependence of orientation effect on the rotational temperature was seen for LIF and REMPI data.

The solid lines in figure 3.14 were calculated in the same manner as those given in figure 3.9, however, agreement between theory and experiment is not as good as in figure 3.9. The primary discrepancy is in the high-energy wing of the spectra, where the experimental data show much weaker intensities than the calculation. Comparisons between the LIF and REMPI spectra at 50 kV/cm (not shown) under the same delay time also showed that the LIF spectra had weaker transitions in the high and low-energy wings than the REMPI spectra. This phenomenon suggests the possibility that the fluorescence levels in the LIF experiment may not be exactly the same as those probed in the REMPI experiment.

The dashed line in the bottom panel of figure 3.14 was obtained by ignoring contributions from M' $\geq$ 3 levels. The LIF spectra represent an average effect with delays between 100 and 300 ns. It is, therefore, not surprising that the modified calculation shows better agreement with the experimental data. However, a similar calculation for the top panel of figure 3.14 did not result in an equally satisfactory

result, and the intensity of the peak at 31,072.9 cm<sup>-1</sup> was not attenuated. Based on the calculation, this peak is composed of three transitions: 40% of the strength has the character of an R<sub>2</sub> transition with M''=1 and 2, and 60% has the character of an R<sub>1</sub> transition with M''=1. The modified calculation cannot decrease the strength of this feature by filtering out transitions with M'≥3.

The reason for the failure of the calculation of parallel excitation and the success in perpendicular excitation can be qualitatively understood from analysis of the selection rule. For the case of perpendicular excitation (bottom panel of figure 3.14), half of the contributions from M''=2 and 3 levels are accounted for in the calculation, since the other half have  $M' \ge 3$ . However, for the case of parallel polarization, contributions from the M"=2 levels are fully taken into account because M'=2. The calculation for parallel excitation, therefore, contains more contributions from the M''=2 levels and less from the M''=3 levels than those from perpendicular excitation. This difference should be prominent for the transition with R<sub>2</sub> character, resulting in an unattenuated transition intensity at 31,072.9 cm<sup>-1</sup> under parallel excitation. It is worth noting that the present approach is only a simple-minded calculation method, and only qualitative results can be obtained. Contributions from high rotational levels with M' < 3 are still included in the modified calculation. A quantitative description of the decay process in an electric field awaits studies of ultrahigh resolution spectroscopy and a more detailed calculation. Furthermore, even under the same delay, the LIF spectra showed lower intensities in the wings than the REMPI spectra. This difference cannot be explained based on the present model.

Significant quenching of the overall fluorescence intensity was observed as the orientation field was increased. In a field of 50 kV/cm, the intensity of the LIF signal was only <sup>1</sup>/<sub>4</sub> that under field-free conditions. The amount of quenching by the electric field agreed with that caused by magnetic fields. According to Ohta<sup>82</sup>, in magnetic fields above 200 Gauss, the fluorescence intensity dropped to 20-33% of its original value. The origin of the effect could be traced to spin decoupling of the triplet state in an external field. Under field-free conditions, the interaction between  $S_1$  and  $T_1$  is limited to  $\Delta J'=0$  states. In the triplet manifold, J'=N'+S', where N' is the nuclear rotational quantum number, and S'=1 with three values of projection. Spin decoupling in a strong external field results in a selection rule of J'=N', so three times as many levels can participate with the same J' level of the singlet state. Since only singlet levels carry oscillator strength, this enhanced coupling with  $T_1$  effectively decreases the transition intensity to 1/3 of its field-free value. Other effects caused by the field, such as enhanced coupling between  $T_1$  and another nearby triplet state  $T_2$ , or nuclear hyperfine decoupling, contribute to further dilution of the singlet transition.

The data in figure 3.14 were obtained by sampling only the slow component of the fluorescence decay profile. It was reported that in a magnetic field, the fluorescence decay could be transformed from a single exponential to a biexponential function.<sup>82</sup> We were unable to quantitatively determine this effect due to a technical difficulty: the low fluorescence intensity in an orientation field naturally enhanced the relative intensity of scattered light, so the decay profile became biexponential regardless of the decay property of the fluorescence.

## **3.6** General Methodology for Measuring Directions of Transition Dipoles

The polarization ratio,  $\rho$ , is reliant on the angle between the permanent dipole and the transition dipole. Orientation of the permanent dipole along the electric field results in alignment of the transition dipole. Polarized excitation of such an anisotropic system reveals the direction of the transition dipole relative to the permanent dipole. For the  $\pi^* \leftarrow$  n transition of pyrimidine, an enhanced absorption was detected when the resonant laser was polarized perpendicular to the orientation field. The transition dipole can thus be deduced to be perpendicular to the orientation field, therefore, perpendicular to the permanent dipole. In cases when the permanent dipole is parallel to the orientation field, a reversed polarization preference should be observed.

Determination of transition dipole moment directions using this method relies on knowledge of the distribution function of the permanent dipole and modeling of the transition intensity under polarized excitation.<sup>98,99</sup> For a given rotational temperature, the distribution function can be determined from theoretical modeling of Stark levels. The excitation probability of a molecule is determined by the projection of the transition dipole on the polarization direction of the laser.<sup>5</sup> Figure 3.15 shows directions of the permanent dipole  $\mu_p$  and the transition dipole  $\mu_t$  in a general scenario. The direction of the permanent dipole is set to be the z axis in the molecular frame and the transition dipole is chosen to be within the x-z plane forming a polar angle a with the permanent dipole. The angles  $\phi$  and  $\chi$  are azimuthal angles in the laboratory and



# Coordinate system

**Figure 3.15** Coordinate system illustrating the laboratory frame and the molecular frame. In the molecular frame, the permanent dipole  $(\mu_p)$  is chosen to be the z-axis, and the azimuthal angle of the transition dipole  $(\mu_t)$  is set to 0°. In the laboratory frame, the orientation electric field is chosen to be the Z-axis, and the two perpendicular polarizations of the laser beam are used to define the XZ plane.

the molecular frame. The transition dipole traces a uniform cone surrounding the permanent dipole, while the permanent dipole traces a uniform cone of angle  $\theta$  in the laboratory frame. The laser beam can be polarized along two perpendicular directions Z (II) and X( $\perp$ ). The projection of the transition dipole on the polarization direction of the laser beam (Z or X axis) can thus be calculated using the rotation matrix<sup>5</sup>

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} C\phi C\theta C\chi - S\phi S\chi & -C\phi C\theta S\chi - S\phi C\chi & C\phi S\theta \\ S\phi C\theta C\chi + C\phi S\chi & -S\phi C\theta S\chi + C\phi C\chi & S\phi S\theta \\ -S\theta C\chi & S\theta S\chi & C\theta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix},$$
(3.1)

where  $C \equiv \cos$ , and  $S \equiv \sin$ .

In the molecular frame,

$$\mu_{\mathbf{t}} = \mu_{\mathbf{t}} \begin{bmatrix} \sin \alpha \\ 0 \\ \cos \alpha \end{bmatrix}.$$
(3.2)

If the final state is continuous, the transition intensity is independent of the angular momentum quantum number of the ground state. Absorption of a linearly polarized laser follows:

$$A_{\mathbb{W}}(\alpha) \propto \int_{0}^{2\pi} d\phi \int_{0}^{2\pi} d\chi \int_{0}^{\pi} P(C\theta) [S\theta C\chi S\alpha - C\theta C\alpha]^{2} S\theta d\theta, \quad and$$

$$A_{\perp}(\alpha) \propto \int_{0}^{2\pi} d\phi \int_{0}^{2\pi} d\chi \int_{0}^{\pi} P(C\theta) [C\phi C\theta C\chi S\alpha - S\phi S\chi S\alpha - C\phi S\theta C\alpha]^{2} S\theta d\theta,$$
(3.3)

given a distribution function  $P(\cos \theta)$  of the permanent dipole. The polarization ratio,  $\rho$  is given by:

$$\rho(\alpha) = \frac{A_{\perp}(\alpha)}{A_{\parallel}(\alpha)}.$$
(3.4)

If the transition intensity is dependent on the angular momentum quantum number, such as in the case of pyrimidine<sup>72-76</sup>, the intensity of a single photon transition can be calculated for each eigenstate, and the overall intensity can be obtained assuming  $\alpha$ =0 (A<sub>1</sub>(0)) or 90°. The polarization ratio for an arbitrary value of  $\alpha$  can thus be expressed as:

$$\rho(\alpha) = \frac{[1 - A_{\rm H}(0)] - (1/2)\sin^2\alpha(1 - 3A_{\rm H}(0))}{2A_{\rm H}(0) + \sin^2\alpha[1 - 3A_{\rm H}(0)]} .$$
(3.5)

The polarization ratios assuming  $\alpha = 0^{\circ}$  and  $\alpha = 90^{\circ}$  are:

$$\rho(0) = \frac{1 - A_{ll}(0)}{2A_{ll}(0)} \quad \text{and} \quad \rho(90) = \frac{1 + A_{ll}(0)}{2[1 - A_{ll}(0)]}.$$
(3.6)

Substituting equation 3.6 into equation 3.5,

$$\rho(\alpha) = \frac{\rho(0) + 1/2 \sin^2 \alpha [1 - \rho(0)]}{1 - \sin^2 \alpha [1 - \rho(0)]} \text{ or } \rho(\alpha) = \frac{1 - \sin^2 \alpha [1 - \rho(90)]}{2\rho(90) - 1 + 2 \sin^2 \alpha [1 - \rho(90)]}.$$
(3.7)

Based on experimental values of  $\rho$  and theoretical calculation of  $\rho(0)$  or  $\rho(90)$ , the angle  $\alpha$  can be determined following equation 3.7.<sup>18</sup> For example, in the case of pyrimidine with an orientation field of 50 kV/cm, the theoretical value of  $\rho(90)$  is 1.2, the same as the experimental value, so the angle between the transition dipole and the permanent dipole is  $90^{\circ}$ . It is worth noting that in cases when more than one transition is simultaneously accessed, this approach determines the direction of the vector sum of the transition dipoles (see chapter 4).

This approach for determination of directions of transition dipoles is direct and universal. It does not depend on rotational profile analysis or photofragment translational spectroscopy.<sup>3,4</sup> As demonstrated from the LIF experiment on pyrimidine,  $\rho$  is independent of the dynamics of the upper state.<sup>18</sup> Furthermore, the distribution function of the molecular axes can be easily controlled by the strength of the orientation field. Fitting  $\rho$  to a variety of distribution functions will result in an improved experimental uncertainty.

## 3.7 Conclusions

This work demonstrated the feasibility and characterized the degree of molecular alignment achieved with a uniform electric field. From dependence of the overall transition probability on the polarization direction of a linearly polarized laser, distributions of molecular axes were obtained. At a field strength of 56 kV/cm, the ionization efficiency from (1+1') REMPI of pyridazine was enhanced by 40% as the polarization direction of the resonant laser was changed from parallel to perpendicular to the orientation field. This corresponds to approximately 50% of molecules having the proper orientation within a  $60^{\circ}$  cone surrounding the direction of the orientation field. Theoretical modeling of the Stark levels, transition intensity distributions, and

overall transition probability resulted in good agreement with experimental observations.

Orientation of pyrimidine, an asymmetric top molecule with a moderate sized permanent dipole (2.3 D) demonstrates the universality of this orientation technique.<sup>18</sup> From the polarization ratios obtained under two different polarization directions of the resonant excitation beam, the relationship between the permanent dipole and the transition dipole can be confirmed. Furthermore, the complex mechanism of rotational dependent relaxation of the upper state did not seem to affect  $\rho$ , nor did the value of the permanent dipole moment of the upper state. The polarization ratio is, therefore, only a function of the orientation effect on the ground state. Since the rotational temperature of the molecular beam has a dramatic effect on the degree of molecular orientation, achieving a low rotational temperature is the key to the success of this type of experiment.

The orientation field results in mixing of wavefunctions of different rotational states. For pyrimidine, the effect of this mixing was manifested in two aspects: the overall fluorescence yield was substantially reduced, and the intensity distribution of the REMPI and LIF spectra showed dependence on the delay time. Elimination of contributions from levels with  $M' \ge 3$  resulted in qualitative agreement between theory and the experimental observation under a prolonged delay time, thereby confirming the J-dependent decay mechanism in pyrimidine.

## 4. Cyanogen Halides

#### 4.1 Introduction

The cyanogen halides are good prototypes for studies of dissociation dynamics,<sup>100-123</sup> and thus represent our first attempt at using brute force orientation for photodissociation experiments. Both ICN and BrCN are readily dissociated to halogen and CN fragments upon UV absorption, and the CN fragments are easy to detect by laser-induced fluorescence. The halogen fragments exhibit spin-orbit splitting, and may be formed in either of two spin-orbit states ( ${}^{2}P_{1/2}$  or  ${}^{2}P_{3/2}$ ).<sup>51</sup> In either case, the halide atoms can be detected using REMPI. Branching ratios, which measure the preferential production of one spin-orbit state over the other, can also be used to probe dissociation mechanisms. Furthermore, the cyanogen halides are ideal for study via orientation with a uniform electric field due to their large permanent dipole moments.<sup>124,125</sup>

The photodissociation of ICN has been studied extensively,<sup>100-114</sup> and satisfactory agreement between theory and experiment has been achieved. Five potential surfaces resulting from the  $(2\pi)^3(5\sigma)^1$  configuration are thought to be involved in the absorption feature centered around 260 nm. Among these, the parallel  ${}^3\Pi_{0+}$  transition is the major component, while the perpendicular  ${}^1\Pi_1$  and  ${}^3\Pi_1$ transitions are thought to contribute more in the blue and red wings of the absorption curve. The resulting CN fragments primarily populate the v=0 level with multiple rotational temperatures. The  ${}^3\Pi_{0+}$  surface adiabatically correlates to the I<sup>\*</sup> ( ${}^2P_{1/2}$ ) product and has only a slight preference for bending along the dissociation coordinate. This pathway is responsible for most CN fragments of low rotation and for small amounts of rotationally excited fragments. The  ${}^{1}\Pi_{1}$  and  ${}^{3}\Pi_{1}$  surfaces adiabatically correlate to the I ( ${}^{2}P_{3/2}$ ) product and have a strong preference for bending, leading to mainly rotationally excited CN fragments. A conical intersection between the  ${}^{3}\Pi_{0+}$  and  ${}^{1}\Pi_{1}$  surfaces causes non-adiabatic coupling, and as a result, both of these surfaces may lead to the I <sup>\*</sup> product.

In contrast to ICN, few studies of the dissociation dynamics of BrCN have been performed. The absorption curve is shifted towards higher energies than ICN, and the main absorption feature exhibits a maximum at approximately 205 nm.<sup>115</sup> Most work on BrCN has concentrated on vibrational and rotational population distributions.<sup>115-120</sup> The CN fragments are reported to have high rotational excitation. At a dissociation wavelength of 193 nm, less than 6% of CN fragments are formed in vibrationally excited states.<sup>118</sup> The rotational distribution shifts toward higher energies with increasing photolysis energy, while the vibrational distribution shows the opposite trend. Similar to ICN, there are two sets of potential energy surfaces involved in the photodissociation of BrCN; one leading to CN + Br (<sup>2</sup>P<sub>3/2</sub>) (denoted Br) and another leading to CN + Br (<sup>2</sup>P<sub>1/2</sub>) (denoted Br<sup>\*</sup>).<sup>120</sup> In the wavelength region between 193 and 222 nm, the CN rotational distribution is described by an impulsive model assuming sole production of CN + Br (<sup>\*</sup>).<sup>122</sup> At longer wavelengths, the model only fits experimental data when production of CN + Br is assumed, thus suggesting a change in dissociation pathway. Halpern and Jackson concluded from analysis of population measurements that the upper electronic state of BrCN is bent.<sup>118</sup>

Wannenmacher *et al.* performed vector correlation experiments using Doppler spectroscopy on BrCN between 206 and 260 nm.<sup>116</sup> The authors determined the branching ratio for producing  $Br^*$  over Br at several wavelengths in this region. For the J"=40 rotational level, the branching ratio was 100% Br<sup>\*</sup> at a photolysis wavelength of 206.1 nm, 90% Br<sup>\*</sup> at 222 nm, and 0% Br<sup>\*</sup> at 260 nm. These results give further evidence of a shifting dissociation pathway with dissociation wavelengths longer than 222 nm. This group also found that the dissociation of BrCN between 209 and 248 nm was predominantly a parallel transition with some mixing of perpendicular character. The Br<sup>\*</sup> channel showed 6% perpendicular character while the Br channel showed 13% perpendicular character.

In this work, the dissociation dynamics of ICN at 250 and 266 nm, and BrCN at 213 and 230 nm will be reported.<sup>14,16,17,19</sup> For ICN, both the heavy (I<sup>\*</sup>) and light (CN) fragments will be measured, while only results on the CN fragments from BrCN will be presented. Through orientation of parent molecules and polarization control of excitation, the directions of the effective transition dipoles will be determined. Data on ICN will be used to confirm previous conclusions in the literature regarding the nature of the potential energy surfaces. By comparing our results on BrCN with the more established model of ICN, some insight into the dissociation dynamics of this molecule will be gained.

## 4.2 **Experimental Details**

Cyanogen iodide (Aldrich, 93%) and cyanogen bromide (Aldrich, 97%) were used without further purification. Room temperature ICN vapor was carried into the chamber by helium. Due to the high vapor pressure of BrCN, a 2% mixture of the sample in helium was prepared. The stagnation pressure in either case was kept at 1300 torr. Precautions were taken when switching from one sample to the other to prevent cross-contamination.

CN fragments were detected by laser-induced fluorescence through the B  ${}^{2}\Sigma^{+}$   $\leftarrow X {}^{2}\Sigma^{+}$  transition.<sup>51</sup> For I<sup>\*</sup> fragments, the probe laser was tuned to the  ${}^{2}D_{3/2} \leftarrow {}^{2}P_{1/2}$ transition of iodine, and resonantly enhanced multiphoton ionization (REMPI) was used for detection. The I product had a strong single laser signal from the  ${}^{2}D_{5/2} \leftarrow {}^{2}P_{3/2}$  transition, so no investigation of this channel was conducted. The power of the dissociation laser beam at 213, 230, 250, or 266 nm was kept between 300 and 500 µJ. The delay between the dissociation and probe lasers was approximately 200 ns.

## 4.3 CN product from ICN

#### 4.3.1 Dissociation at 266 nm

The complete spectrum of CN from dissociation of ICN at 266 nm is given in figure 4.1, and transitions of the R branch have been identified by their rotational quantum numbers, J". The spectrum is similar to that observed by Marinelli *et al.*,<sup>103</sup>



Figure 4.1 LIF spectrum of the CN fragment from dissociation of ICN at 266 nm.

who described the rotational distribution as a superposition of low, moderate, and high-temperature Boltzmann distributions. The first three rotational levels comprise the low-temperature component, and this was found to be the major contributor. The levels of high rotational excitation were less extensively populated.

The present experiment on orientation of parent molecules was restricted to the first 12 rotational levels of the CN fragment due to signal/noise ratio limitations. This portion of the spectrum is given in figure 4.2 under three different experimental conditions. The horizontal axes of the spectra obtained in high fields have been shifted for clarity. The P branch of the B  ${}^{2}\Sigma$  (v'=1)  $\leftarrow X {}^{2}\Sigma$  (v''=0) transition of CN formed a bandhead, so in the polarization measurements, only the well-resolved R branch was used. Spin-rotation interaction causes splitting of the high J levels, while in an orientation field of 50 kV/cm, Stark effects result in a slight broadening in the low J levels (less than 0.11 cm<sup>-1</sup> for J=1). The strength of each transition was therefore best described by the integrated peak area.

Among the three spectra in figure 4.2, the rotational distribution of CN fragments from perpendicular dissociation resembles that obtained under field-free conditions, i.e., from dissociation of a randomly oriented system. This observation is not difficult to understand given that the distribution from a randomly distributed system should be the sum of the parallel excitation (the z direction) and twice the perpendicular excitation (the x and y directions).

The dependence of the yield of CN on the polarization direction of the dissociation laser reveals the nature of the transition dipole of the molecule. To



**Figure 4.2** Effect of brute force orientation on the yield of CN from photolysis of ICN at 266 nm. Only the intense segment of the LIF spectrum is shown. The horizontal axes of the spectra in a field of 50 kV/cm have been shifted for comparison. The label J" denotes the rotational quantum number of the CN fragment.

quantify the effects of the orientation field, the polarization ratio,  $\rho$ , is the ratio of the yield of CN when the dissociation laser is polarized perpendicular/parallel to the orientation field. Figure 4.3 outlines the results of the study from dissociation of ICN at 266 nm, obtained in an orientation field of 50 kV/cm. The polarization ratios are less than unity for all rotational levels studied, thus the parallel polarization direction of the dissociation laser is favored. The polarization direction of the probe laser remained constant throughout the measurements, so variations in the polarization ratio should only be a result of the polarization direction of the dissociation laser.

It is worth noting that fragment alignment under field-free conditions can also result in a polarization ratio that deviates from unity, but in the case of ICN, this natural trend is the opposite of our observed preference in high fields. Alignment of the rotational angular momentum vector is determined by the dynamics of dissociation.<sup>67</sup> In ICN, this effect results in preference for the perpendicular polarization direction of the dissociation beam, as reported by Houston's group.<sup>110</sup> When using extremely low laser intensities and removing the skimmer, we were also successful in seeing similar effects under field-free conditions, with a polarization ratio larger than unity. These conditions, however, are not conducive to brute force orientation studies and thus were not used in this experiment. To avoid effects of fragment rotational alignment and to emphasize effects of the orientation field, all polarization ratios were normalized with respect to the ratio under field-free conditions. In this experiment, the deviation of  $\rho$  from unity is only an effect of the orientation field. The large experimental error bar was primarily caused by the

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**Figure 4.3** Polarization ratios of the CN fragment from dissociation of ICN at 266 nm. The values represent the ratio of signal when the dissociation laser was polarized perpendicular/parallel to the orientation field of 50 kV/cm. The horizontal lines correspond to the lower limits of the ratio assuming a pure parallel transition for rotational temperatures of 1.2 and 1.5 K.

Fresnel Rhomb as the position of the dissociation laser was adversely shifted during the rotation of the polarization direction. Instability of the pulsed valve and fluctuation of the laser power also contributed to the uncertainty.

The preference for the parallel polarization of the dissociation beam is related to the direction of the transition dipole moment in the absorption process. Quantitative interpretation of the experimental results relies on knowledge of the axis distribution.<sup>13</sup> Using the approach of Loesch and Remsheid<sup>54</sup>, this distribution was calculated for ICN assuming a rotational temperature of 1.5 K, a permanent dipole moment of 3.8 D, and a rotational constant of 0.1 cm<sup>-1</sup>. The resulting distribution of the molecular axis of ICN is given in figure 4.4, and the vertical axis was chosen such that the total population (the area under each curve) is unity. At 50 kV/cm, 84% of ICN molecules have their iodine end preferentially pointing to the negative electrode, and 40 % of the molecules are trapped within a cone of 45°.

A lower limit of the polarization ratio can be calculated assuming a pure parallel transition (i.e., only the  ${}^{3}\Pi_{0+}$  surface is directly accessed). The signal intensity is proportional to P( $\theta$ )(cos  $\theta$ )<sup>2</sup> when the dissociation laser is polarized parallel to the orientation field, and  ${}^{1}_{2}P(\theta)(\sin \theta)^{2}$  when the laser is polarized perpendicular to the field. The factor of  ${}^{1}_{2}$  in the latter calculation is due to the fact that when the laser is polarized perpendicular to the orientation field, only half of the projected population in the plane perpendicular to the electric field is accessible.<sup>13</sup> The calculated lower limit is 0.67 at 1.5 K and 0.77 at 2 K. Contribution from a perpendicular transition will increase the ratio due to preference for the perpendicular polarization. The two



**Figure 4.4** Distribution of the molecular axis of ICN in an orientation field of 50 kV/cm. The angle  $\Theta$  was defined by the orientation field and the molecular axis of ICN. The population was normalized by setting the integration of the distribution function to unity.

horizontal lines shown in figure 4.3 represent the calculated lower limits at rotational temperatures of 1.2 and 1.5 K.

As stated in chapter 1, rotational temperature plays a key role in the ability to achieve molecular orientation. Figure 4.5 shows the calculated temperature dependence of p for ICN at 50 kV/cm and BrCN at 58 kV/cm. As seen in the figure, the ratio expected for ICN is 0.77 at a rotational temperature of 2 K, and 0.68 at 1.5 K, both of which are larger than most of the observed experimental ratios. This observation can be explained from the following considerations. First, we are most likely dealing with a rotational temperature of < 1.5 K, since our ratios are smaller than the corresponding theoretical lower limit. From measurements of the rotational temperature using  $I_2$  and 2% NO in helium (chapter 2), we arrived at the conclusion that our molecular beam was between 1 and 2 K. The rotational temperature measured with  $I_2$  (1 K) should be closer to that of the ICN sample since these two compounds are similar in structure and composition. A second important observation is that our ratio is very near the lower limit, even if the rotational temperature is taken to be as low as 1.2 K. Therefore, the dissociation of ICN at 266 nm seems to correspond to a nearly pure parallel transition.

#### 4.3.2 Dissociation at 250 nm

The CN spectrum from dissociation of ICN at 250 nm is given in figure 4.6. Unlike at 266 nm, the rotational distribution at 250 nm shows a significant population.



**Figure 4.5** Calculated rotational temperature dependence of the polarization ratios for ICN at 50 kV/cm and BrCN at 58 kV/cm. The horizontal lines indicate the ratio at a rotational temperature of 1.5 K.



Figure 4.6 LIF spectrum of the CN fragment from dissociation of ICN at 250 nm.

in highly rotationally excited states, and a reduction in the relative population of the low J component. This suggests a change in dissociation mechanism, since more of the available energy is distributed to rotation of the CN fragment

Figure 4.7 shows the polarization ratios of the LIF signal of CN from dissociation of ICN at 250 nm in an orientation field of 50 kV/cm. For low J states, experimentally measured values of  $\rho$  are significantly less than unity, indicating a preference for the parallel polarization direction of the dissociation laser. For the J = 0 fragment, a 70% enhancement in the yield of CN fragments was observed when the dissociation laser was polarized parallel, rather than perpendicular, to the orientation field. Values of  $\rho$  approach unity as J approaches 30, and a slight increase in polarization ratio is observable as J further increases. The horizontal lines in figure 4.7 indicate calculations for pure parallel transitions at rotational temperatures of 1.5 and 2.0 K. As explained earlier, these values are lower limits for the polarization ratio. The low J states are in fairly good agreement with the calculations, indicating a nearly pure parallel transition. However, high J states do not display a marked preference for the parallel polarization of the dissociation beam, indicating contributions from both parallel and perpendicular transitions.

The variation of  $\rho$  with J agrees with the model given in the literature.<sup>100</sup> As discussed in section 4.1, the  ${}^{3}\Pi_{0+}$  potential surface is responsible for most CN fragments formed in low J states, since it is correlated to a linear dissociation geometry. Therefore, it is not surprising that low J states have polarization ratios resembling a pure parallel transition. However, the  ${}^{1}\Pi_{1}$  and  ${}^{3}\Pi_{1}$  surfaces are



**Figure 4.7** Polarization ratios of the CN product from photodissociation of ICN at 250 nm in an orientation field of 50 kV/cm. The horizontal lines are calculated lower limits at rotational temperatures of 1.5 and 2.0 K.

associated with CN fragments of high rotational excitation, and these surfaces are both accessed through perpendicular transition. The increased polarization ratios for the high J states confirm participation of one of both of these potential surfaces at 250 nm.

The experimental value of  $\rho$  for the J=0 state is less than the lower limit, and this is probably related to the angular momentum constraints during dissociation. A correlation might exist between the J=0 fragment and the angular momentum of the parent molecules, and the J=0 fragment might mainly come from low rotational states. Molecules in these states are most effectively oriented in the electric field. Since only the parallel transition is likely to produce J=0 fragments, it is possible that  $\rho$  for J=0 represents dissociation of the most oriented molecules. The lower limit calculation represents the average effect for a system at 1.5 K, which includes contribution from less oriented molecules than those related to the J=0 fragments. For fragments with J  $\geq$  1, on the other hand, the angular momentum of the fragment could originate from either the parent rotation or the slight bending motion during dissociation. Less strict angular momentum constraints should result in a smaller enhancement effect due to less effective orientation. In this case, the thermal average of 1.5 K is more appropriate to describe the polarization ratios of the fragments.

#### 4.3.3 Summary of Results on the CN Product from ICN

Our experimental observations of the CN fragment from dissociation of ICN at 266 and 250 nm support previous conclusions concerning the participating potential energy surfaces.<sup>100</sup> At 266 nm, the LIF signal from the CN fragment was 60%

stronger when the dissociation laser was polarized parallel, rather than perpendicular, to the orientation field. These results are in excellent agreement with calculation of a pure parallel transition at a rotational temperature between 1.2 and 1.5 K.<sup>17</sup> The low J states of the CN fragment from dissociation of ICN at 250 nm are also in agreement with calculation of a pure parallel transition. This is expected, since the low J sates are thought to come from the  ${}^{3}\Pi_{0+}$  surface. However, the near unity polarization ratios of the rotationally excited fragments offer direct evidence of the participation of one or more potential surfaces accessed through perpendicular transitions.

## 4.4 **I**<sup>\*</sup> Product from ICN

In the past, studies of the heavy fragments from photodissociation have been challenging. These products are generally produced with low velocities, resulting in only small Doppler effects and low collection efficiencies when using mass spectrometry for detection. Furthermore, heavy fragments are less sensitive than light fragments to the dynamics of dissociation, and often cannot be used to determine vectorial information with high precision. The brute force method does not depend on the translational energy of photofragments, nor does it require Doppler profile analysis. Thus, it can be used to study both heavy and light fragments with equally reliable results. To demonstrate this ability, measurements of the I\* (heavy) product from dissociation of ICN will be presented.

Figure 4.8 shows the REMPI signal of  $I^*$  from dissociation of ICN at 250 nm in an orientation field of 56 kV/cm. When the polarization direction of the



**Figure 4.8** REMPI spectra of  $I^*$  from photodissociation of ICN at 250 nm. The orientation field strength was 56 kV/cm, and the polarization direction of the dissociation laser relative to the orientation field is given. The overall enhancement in the signal strength under parallel polarization was 30%. The doublet was due to nuclear hyperfine splitting.

dissociation laser was parallel to the orientation field, a stronger I<sup>\*</sup> signal was observed. The overall enhancement in the yield of I<sup>\*</sup>, determined from integrated peak areas, was 30%. The splitting in the spectra was 0.47 cm<sup>-1</sup>, so the doublet feature should not be the Doppler profile of the iodine fragment. The available energy from dissociation at 250 nm is 6130 cm<sup>-1</sup>, and the maximum Doppler width of the iodine component is only 0.1 cm<sup>-1</sup>, which is much smaller than the observed separation in the spectra. The hyperfine splitting of the <sup>2</sup>P<sub>1/2</sub> state is 0.66 cm<sup>-1</sup>, so the observed spectra should be convolutions of the nuclear hyperfine structure with the Doppler lineshape of I<sup>\*</sup> and the laser lineshape.<sup>126</sup>

The polarization ratio is the yield of  $I^*$  when the dissociation laser was polarized perpendicular/parallel to the orientation field. As mentioned above, the  $I^*$ yield from the parallel polarization of the dissociation laser at 250 nm was enhanced by 30% in an orientation field of 56 kV/cm. This corresponds to a polarization ratio of 0.77. Figure 4.9 shows the polarization ratio as a function of the strength of the orientation field for the  $I^*$  fragment from dissociation of ICN at 266 nm. At 50 kV/cm, the polarization ratio at 266 nm was 0.67 (50% enhancement in  $I^*$  yield for the parallel polarization direction). Polarization ratios were normalized with respect to field-free conditions, as discussed in section 4.3.1.

The results from study of the  $I^*$  fragment further confirm conclusions drawn from observations of the CN fragment.<sup>14,16,17</sup> The preference for the parallel polarization direction of the dissociation beam is related to the direction of the transition dipole moment in the absorption process, and the probability of



**Figure 4.9** Dependence of the polarization ratio of  $I^*$  from ICN on the strength of the orientation field. The dissociation wavelength was 266 nm, and the solid line is the calculated lower limit assuming a rotational temperature of 1.5 K.

non-adiabatic coupling. At 266 nm, the experimental values of  $\rho$  are in agreement with the lower limit calculation, confirming the nearly pure parallel nature of this transition. In contrast, the polarization ratio at 250 nm is 0.77, above the lower limit. Caution must be exercised in quantitative interpretation of this number because the conical intersection between the  ${}^{3}\Pi_{0+}$  and  ${}^{1}\Pi_{1}$  surfaces of ICN causes non-adiabatic coupling, and as a result, both of these surfaces may lead to the I<sup>\*</sup> product. Furthermore, it should be noted that the polarization ratio of the I\* fragment represents an average over all rotational levels. Since the rotational averaging and conical intersection can increase the value of  $\rho$ , the polarization ratio for the I\* product should be larger than the low J component of the CN fragment (0.67), but still less than the high J component (1.00).

#### 4.5 CN Product from BrCN

While ICN has been studied extensively through both experimental and theoretical efforts, many aspects of the dissociative potential surfaces of BrCN remain uncertain. As outlined in section 4.1, previous studies of the dissociation of BrCN between 209 and 248 nm have implied a mixing of potential surfaces accessed through parallel and perpendicular transitions.<sup>115-120</sup> However, a detailed theoretical study of these potential surfaces, analogous to the study on ICN by Qian *et al.*<sup>100</sup>, has not been documented. Our experiments on BrCN using a uniform electric field were designed to further probe the dissociation dynamics in this region, and to identify similarities and differences between the cyanogen halide molecules.<sup>17,19</sup>

#### 4.5.1 Population distributions of the CN fragment at 213 nm

The CN fragment from dissociation of BrCN at 213 nm was formed with high rotational excitation. The complete LIF spectrum is given in figure 4.10. The rotational level of greatest intensity, J'' = 42, corresponds to a rotational energy of 3500 cm<sup>-1</sup>. The CN fragment was not formed with significant vibrational excitation. These observations are in agreement with the work done by Halpern's group.<sup>115</sup>

Following the method of Simons and Tasker,<sup>127</sup> the rotational distribution of the CN fragment may be used to estimate the distribution of impact parameters during dissociation. In accordance with the work summarized in the introduction section, we will assume that all Br fragments are formed in the excited  ${}^{2}P_{1/2}$  state. The impact parameter can be calculated according to:

$$b = \left[ \left( \frac{m_{CN}}{m_{BrCN}} \right) \left( \frac{E_{rot}}{E_{avail}} \right) \right]^{1/2} r_e$$

where  $E_{rot}$  represents the rotation energy,  $E_{avail}$  is the available energy of the system, m<sub>x</sub> is the reduced mass of molecule x, and r<sub>e</sub> is the distance between the bromine atom and the center of mass of the CN fragment.<sup>115</sup> In the present experiment, the impact parameter for the most populated rotational level (J''=42) is 0.053 nm. This corresponds to a Br-C-N bond angle of approximately 68°. The maximum rotation level with a significant population yields and impact parameter of 0.065 nm and a bond angle slightly greater than 90°. Although they did not publish the CN spectrum



Figure 4.10 LIF spectrum of the CN fragment from BrCN at 213 nm.

from photolysis at 213 nm, Halpern's group found that the distributions of impact parameters, and ultimately the dissociation bond angles, were identical for wavelengths between 193 and 242 nm.<sup>115</sup> They reported impact parameters of 0.042 nm for the most populated rotational level and 0.061 nm for the maximum rotational level, in good agreement with our results.

#### 4.5.2 Orientation Effects at 213 nm

Figure 4.11 shows the results from the dissociation of BrCN at 213 nm in a field strength of 58 kV/cm. Rotational levels were chosen to include lines from both the P and R branches and levels of both high and low rotational excitation. As in the analysis of ICN, quantitative interpretation of these results on BrCN requires comparison with theoretical calculations, which depends critically on the rotational temperature of the molecular beam. Again, we would expect the rotational temperature of BrCN to be more like that of I<sub>2</sub> (1 K) than NO (2 K) because of the similarities between these halogen-containing compounds. Since we are confident that our ICN molecular beam was < 1.5 K, it is likely that the BrCN sample was also < 1.5 K. In figure 4.5, calculation of the rotational temperature dependence of  $\rho$  assumes a permanent dipole moment of 2.94 D and a rotational constant of 0.137 cm<sup>-1</sup>.<sup>125</sup> The horizontal line in figure 4.11 represents calculation of a pure parallel transition at a rotational temperature of 1.5 K. The average experimental polarization ratio was approximately 0.83  $\pm$  0.03, or 20% enhancement when the laser was polarized



**Figure 4.11** Polarization ratios for various rotational levels of the CN fragment from photodissociation of BrCN at 213 nm. The long dashed horizontal line indicates the calculated value of  $\rho$  for a pure parallel transition at a rotational temperature of 1.5 K. The short dashed line indicates the calculation when 33% contribution from a perpendicular transition is assumed.

parallel to the orientation field. This is significantly higher than the calculation of a pure parallel transition. This result indicates that contribution from a perpendicular transition is not negligible in BrCN. Furthermore, unlike our observation of ICN at 250 nm, the polarization ratio is virtually independent of rotational quantum number. The uniform value of  $\rho$  throughout the rotational distribution implies that the surfaces involved in the dissociation of BrCN have similar topography and bending angle.

Figure 4.12 outlines the dependence of  $\rho$  on the strength of the electric field obtained using the P(17) transition of CN. At zero field strength,  $\rho$  is unity. Since all polarization ratios were normalized with respect to field-free conditions, these measurements contain no information on fragment alignment. As the strength of the field is increased, more molecules become oriented. Since the parallel transition is dominant, the value of  $\rho$  is expected to decrease with increasing field strengths. The solid line in the figure represents calculation of a pure parallel transition. Once again, the experimental values of  $\rho$  are well above this calculation, which further confirms the presence of a perpendicular component.

#### 4.5.3 Orientation Effects at 230 nm

The rotational distribution of CN from BrCN at 230 nm is highly rotationally excited, similar to the observations at 213 nm. However, at 230 nm, the CN fragment was observed in vibrationally excited states, while at 213 nm, almost all fragments were formed in the ground vibrational state. For the v''=0 level, the rotational


Figure 4.12 Dependence of the polarization ratio of BrCN on the strength of the orientation field. The experimental values were obtained using the P(17) transition of CN. The solid line represents the calculated trend for a pure parallel transition while the dashed line factors in one-third perpendicular contribution.

transition of greatest intensity is found at J''= 44. Limited by signal/noise ratios due to the relatively low absorption cross-section of BrCN at this wavelength, only this rotational level was investigated in detail.

The LIF signal of the J" = 44 rotational level is given in figure 4.13. The two spectra were obtained when the dissociation laser was polarized parallel (solid line) and perpendicular (dashed line) to the orientation field of 58 kV/cm. Each point represents an average of 4500 laser shots, and each spectrum contains 22 data points. Comparison of integrated peak areas implies a polarization ratio of  $0.80 \pm 0.03$ . Stark effects on the energy level of the J" = 44 state are expected to be negligible. Calculation assuming a rotational constant of  $1.8994 \text{ cm}^{-1}$  yields an energy deviation of only 0.002% for the J" = 10 rotational level. Therefore, the observed enhancement in signal strength under parallel excitation should be attributed solely to orientation effects of the parent molecules.

#### 4.5.4 Direction of the Effective Transition Dipole

From the experimental values of the polarization ratio, the direction of the effective transition dipole moment can be derived. In the case of BrCN, when two transitions are simultaneously accessible, the direction of the effective transition dipole can help determine the relative contribution from each transition. A coordinate system illustrating the laboratory and molecular frames associated with this experiment was given in chapter 3, figure 3.15. For the dissociation of BrCN, the two



**Figure 4.13** Polarization dependence of the LIF signal of the J'' = 44 rotational level from photolysis of BrCN at 230 nm in a field strength of 58 kV/cm. When the dissociation beam was kept parallel to the orientation field, there was a 25 % enhancement in the signal strength compared with that of the perpendicular polarization.

types of transition dipoles involved are parallel and perpendicular to the z-axis of the molecular frame. The vector sum of these transitions defines an effective transition dipole vector,  $\mu_t$ , which is defined by an angle  $\alpha$  with respect to the molecular z-axis.

Using equations 3.3 and 3.4, the dependence of  $\rho$  on the angle  $\alpha$  can be calculated, and the results are given in figure 4.14. The average experimental value of  $\rho$  is 0.83, which from the plot corresponds to an angle  $\alpha$  of approximately 35°. The fraction of perpendicular contribution is given by  $\sin^2 \alpha$ . Thus, we arrive at the conclusion that this transition has approximately 33% perpendicular character. The short dashed lines in figures 4.11 and 4.12 represent calculations assuming that the transition is one-third perpendicular in nature. The experimental data are in very good agreement with these calculations. Similarly, at 230 nm, the transition at 230 nm was found to possess approximately 20% perpendicular character.

### 4.6 Comparison of BrCN and ICN

Rotational distributions of the CN fragments from dissociation of BrCN and ICN under field-free conditions imply dramatically different dissociation dynamics. The CN fragments from ICN at 266 nm have a strong low J component, with a large population in J''=0,1,and 2 rotational levels. On the other hand, CN fragments from BrCN at 213 and 230 nm have almost no low J component. This implies the absence of the "linear" dissociation mechanism in BrCN at these wavelengths.



Figure 4.14 Dependence of the polarization ratio on the direction of the transition dipole moment.  $\alpha$  is the angle between the effective transition dipole and the molecular z-axis. The amount of perpendicular character present in the dissociation is given by  $\sin^2 \alpha$ .

A summary of our results on the dissociation of the cyanogen halides in a strong, uniform electric field is given in table 4.1.<sup>14,16,17,19</sup> One similarity between the two compounds is that parallel transitions are dominant for all of the dissociation wavelengths studied. The most striking difference is that photodissociation of BrCN shows significant perpendicular character. At a dissociation wavelength of 213 nm, we have seen that nearly a third of the absorption originated from a perpendicular transition. At 230 nm, toward the red wing of the absorption curve, a smaller, yet significant, perpendicular contribution was found. In contrast to BrCN, dissociation of ICN at 266 nm yielded values of  $\rho$  very near the theoretical lower limit, indicating that the transition is almost purely parallel in nature. This assessment on ICN at 266 nm agrees with the theoretical absorption cross sections proposed by Qian *et al.*<sup>100</sup> At 250 nm, the dramatic change in polarization ratio with rotational quantum number signifies both the pure parallel nature of the low J states and the presence of a perpendicular surface contributing to the high J states.

It is interesting to note that both 266 nm for ICN and 213 nm for BrCN lie near the center, but slightly towards the lower energy half of their respective absorption curves. However, the potential surfaces involved in the dissociation of the two appear to be quite different. One possible explanation of this difference is spin-orbit coupling. In ICN, strong coupling between the  ${}^{3}\Pi_{0+}$  and  ${}^{1}\Pi_{1}$  surfaces accounts for the dominance of the parallel transition. BrCN has a smaller spin-orbit coupling, therefore it is not surprising to see a larger perpendicular contribution in BrCN.

Another significant difference between BrCN and ICN lies in the dependence of  $\rho$  on rotational quantum number. For ICN at 250 nm, the polarization ratio shows a

**Table 4.1** Summary of experimental polarization ratios from studies of jet-cooled BrCN and ICN. The orientation field strengths were a) 58 kV/cm, b) 50 kV/cm, and c) 56 kV/cm.

	Low J"	High J″	Upper Limit 1.5 K	Upper Limit 1.2 K
CN from BrCN (213 nm) <sup>a</sup>	$0.83 \pm 0.03$	$0.83 \pm 0.03$	0.71	0.65
CN from BrCN (230 nm) <sup>a</sup>		$0.80 \pm 0.03$	0.71	0.65
CN from ICN (249 nm) <sup>b</sup>	$0.67 \pm 0.05$	$1.00 \pm 0.05$	0.68	0.63
CN from ICN (266 nm) <sup>b</sup>	$0.65 \pm 0.05$		0.68	0.63
I* from ICN (250 nm) <sup>c</sup>	$0.77 \pm 0.08$		0.66	0.60
I* from ICN (266 nm) <sup>c</sup>	$0.67 \pm 0.08$		0.66	0.60

large dependence on rotational quantum number, arising from the fact that production of CN in low rotational states is thought to originate solely from a parallel transition. The CN fragment formed in higher rotational states may come from either parallel or perpendicular transitions. Therefore, the decreased polarization ratio for high rotational levels indicates the presence of a perpendicular transition. Data from studies of the I<sup>\*</sup> fragment from ICN at 250 nm also support these conclusions, since the polarization ratio represents an average over all rotational levels. In contrast to ICN, there is a uniform polarization ratio over levels of high and low rotational excitation of the CN fragment from BrCN. This shows that the potential surface accessed through a parallel transition does not have the same topography as in ICN. In BrCN, surfaces accessed through both parallel and perpendicular transitions must posses a bent geometry, and they are likely to have similar bending angles.

## 4.7 Conclusions

Orientation of parent molecules prior to dissociation revealed the directions of transition dipole moments, and lead to information regarding the potential energy surfaces of ICN and BrCN. <sup>14,16,17,19</sup> Dissociation of ICN at 266 nm is accomplished through a pure parallel transition, while some perpendicular character is involved at 250 nm. Evidence of a perpendicular component in the dissociation of BrCN at both 230 and 213 nm was observed, and was found to contribute 20 and 33 %, respectively, to the overall oscillator strength.

This work demonstrated the possibility of selective excitation through brute force orientation and polarized excitation. For example, for ICN with a permanent dipole of 3.8 D and a rotational temperature of 1.5 K, enhancement of ~50% in the CN fragments of low rotational energies was observed when the excitation laser of 250 nm was polarized parallel to the orientation field. This is caused by a preferential excitation of the parallel, rather than the perpendicular, transition in ICN. Preferential excitation to one set of potential surfaces is particularly advantageous for simplification of complex dissociation processes from large molecular systems.

It is also worth mentioning that using brute force orientation, we were able to obtain steric information from both the heavy  $(I^*)$  and light (CN) fragments of ICN, and arrive at the same conclusion. This is a unique advantage of brute force orientation for studies of photodissociation processes. With initial orientation of parent molecules, the kinematic constraint on heavy fragments in photofragment translational spectroscopy and Doppler spectroscopy can be lifted.

# **5.** Aliphatic Nitrites

### 5.1 Introduction

As stated in chapter one, the goal of this work is to develop a methodology for studies of medium to large sized molecular spectroscopy. As our first step in this direction, we investigated the photochemistry of aliphatic nitrites. The spectroscopy and photodissociation dynamics of small aliphatic nitrites (R–O–N=O) have been intensively studied in the past.<sup>3,128-147</sup> The absorption spectrum of t-butyl nitrite is shown in figure 5.1, and two regions of interest have been identified. The first, and more thoroughly studied, is a structured band between 310 and 430 nm. A magnified view of this region is shown in the insert. Absorption in this region has been identified as an [S<sub>1</sub>( $n\pi^*$ )  $\leftarrow$  S<sub>0</sub>] transition. The vibrational progression visible in the absorption spectrum has been assigned to the N=O stretching mode v<sub>3</sub>. Vibrational predissociation limits the lifetime, resulting in the partially resolved spectrum. Due to this nonadiabatic process, excitation of the v'=n overtone of this mode in the parent molecule yields NO fragments preferentially in the v''=(n-1) level.

The dissociation of t-butyl nitrite between 310 and 430 nm has been explored by several groups.<sup>128-131,142-144</sup> From measurements of the Q branch of NO (v''=1) fragments, Schwartz-Lavi and Rosenwaks found that the value of the alignment parameter,  $A_0^{(2)}$ , was 0.38 ± 0.19 at a photolysis wavelength of 365.8 nm and 0.42 ± 0.10 at 351.8 nm.<sup>141</sup> Furthermore, sub-Doppler profiles of the NO fragment from



Figure 5.1 Gas phase absorption spectrum of t-butyl nitrite. The insert shows a magnified view of the  $S_1$  region. The arrows mark wavelengths explored in this study.

dissociation at 363.9 nm were used to determine the anisotropy parameter,  $\beta$ , which was approximately  $-0.68 \pm 0.06$ .<sup>145</sup> These measurements implied that excitation of t-butyl nitrite in this region results in predominantly planar fragmentation, and that the transition dipole is perpendicular to the dissociation axis.<sup>143</sup> Calculations using an impulsive model successfully reproduced some of the main features of the final state distribution. The A'' symmetry of the S<sub>1</sub> state was further confirmed from measurements of the preferential population of the NO fragment with its unpaired  $\pi$ orbital parallel to the rotation axis.<sup>143</sup> The preference for the lower component of the spin-orbit doublet, <sup>2</sup> $\Pi_{1/2}$ , remains unexplained.

The second region of interest in the absorption spectrum is a diffuse band centered around 220 nm, corresponding to an  $[S_2(\pi\pi^*) \leftarrow S_0]$  transition.<sup>131,132,141,146,147</sup> This region is believed to exhibit fast, direct dissociation attributed to charge transfer from the (CH<sub>3</sub>)<sub>3</sub>CO group to the NO group. Little vibrational excitation was observed in NO, and the rotational distribution shifted to higher energies compared with that from the S<sub>1</sub> state. Schwartz-Lavi and Rosenwaks reported that the direction of the unpaired  $\pi$  orbital of NO was preferentially parallel to the rotational angular momentum, but the preference for the lower spin-orbit component in the S<sub>2</sub> state was not as obvious as that in the S<sub>1</sub> state.<sup>141</sup> The alignment and anisotropy parameters were found to be -0.30 ± 0.06 and 1.06 ± 0.04 respectively at a photolysis wavelength of 250 nm. It was therefore concluded that the transition dipole is parallel to the dissociation axis and that the fragment angular momentum vector is preferentially perpendicular to the transition dipole (cartwheel motion). Measurements by Andreson's group at 193 nm yielded a value of  $\beta$  of 0.57 ± 0.05, and no evidence of alignment of the NO fragment was observed.<sup>140</sup> The authors suggested the presence of a second potential energy surface at higher photolysis wavelengths in this region of the absorption band.

Despite the previous work on this molecule, no study of the wavelength dependence of the photodissociation dynamics has been carried out. We performed a detailed study between 224 and 250 nm.<sup>21</sup> Internal energy distributions of the NO fragment throughout this region were be characterized. Measurements of the  $S_1 \leftarrow S_0$  transition at photolysis wavelengths of 365.8 and 351.8 nm (the second and third overtones of the N=O stretching mode), and the  $S_2 \leftarrow S_0$  transition at photolysis wavelengths of 250 and 224 nm, will be presented. Directions of transition dipole moments at these dissociation wavelengths will be determined from measurements of the NO fragment using a linearly polarized dissociation laser and orientation of parent molecules.<sup>20</sup> These results will be compared with literature data on t-butyl nitrite and methyl nitrite whenever possible.

### 5.2 **Experimental Details**

The molecular beam was produced using 1-4% mixtures of t-butyl nitrite (Aldrich, 96%) in helium, and stagnation pressures between 1200 torr and 1300 torr were used. These conditions were proven to be efficient in simultaneously preventing cluster formation and achieving a low rotational temperature (less than 3 K). Variation of the stagnation pressure above 1400 torr was found to change the

rotational distribution of the NO fragment from photodissociation, and this can most likely be attributed to the formation of clusters. Huber's group studied homogeneous clusters of t-butyl nitrite produced by adiabatic jet expansion of a 5% mixture in helium.<sup>142</sup> They found that the onset of cluster formation was rather abrupt at a stagnation pressure of approximately 1400 torr, which is in good agreement with our observations. Below 1300 torr no dependence of the rotational distribution on the stagnation pressure was observed, thus cluster formation was unlikely.

Detection of NO was achieved using (1+1) REMPI through the A  ${}^{2}\Sigma^{+}$  state. The delay time between the dissociation and probe lasers was maintained at 5 ns. Polarization ratios were independent of the polarization direction of the probe beam, and no product alignment was detectable under our experimental conditions. Experiments on oriented parent molecules at a photolysis wavelength of 224 nm were performed using a single laser that served as both the dissociation and probe beam sources. Therefore, the actual dissociation wavelength varied between 223.5 and 224.5 nm in these measurements. However, no additional complications are expected from rotating the polarization directions of the dissociation and probe beams simultaneously.

# 5.3 Photodissociation between 224 and 250 nm under Feld-Free Conditions

The electronic transition of NO used for detection in this experiment is an  $A^2\Sigma^+$   $\leftarrow X^2\Pi$  transition. Spin-doublet and  $\Lambda$ -doublet splittings lead to 12 possible branches: Q<sub>1</sub> (or Q<sub>11</sub>), P<sub>1</sub>, R<sub>1</sub>, Q<sub>2</sub> (or Q<sub>22</sub>), P<sub>2</sub>, R<sub>2</sub>, Q<sub>12</sub>, P<sub>12</sub>, R<sub>12</sub>, Q<sub>21</sub>, P<sub>21</sub>, and R<sub>21</sub>.<sup>51</sup> If the spin splitting of the <sup>2</sup> $\Sigma$  state is small, the Q<sub>12</sub>, R<sub>12</sub>, P<sub>21</sub> and Q<sub>21</sub> branches become redundant. Closely spaced rotational transitions result in spectral congestion, especially near the bandheads of several branches. Throughout this experiment, rotational transitions of NO were assigned based on the spectral simulation program LIFBASE.<sup>148</sup>

Figure 5.2 shows the  $A^2\Sigma^+$  (v'=0)  $\leftarrow X^2\Pi$  (v''=1) band (denoted as  $0 \leftarrow 1$  in the following) of NO under an excitation wavelength of 224 nm. Rotational levels of the  $Q_2$  and  $Q_1$  branches are labeled in the figure. A clear bimodal distribution is observable, and the separation between the low J and high J components is large. As the dissociation energy increased from 250 to 224 nm, more fragments were produced in vibrationally excited states. Within each vibrational state, the rotational distribution maintained a similar bimodal distribution. At 250 nm, NO fragments were predominantly produced in the ground vibrational state with  $J''_{max}=52.5$ . This observation is in good agreement with Schwartz-Lavi and Rosenwaks, who reported that 92% of the NO fragments were formed in the v''=0 state with  $J''_{max}=53.5$ .<sup>141</sup> Due to contamination caused by pure NO in the gas line (possibly from thermally dissociated t-butyl nitrite), we were unable to characterize the low J component for the v''=0 state. However, the  $0 \leftarrow 1$  transition at 250 nm was successfully recorded, and the results confirmed the bimodal distribution. It is worth noting that the low J component of the  $0 \leftarrow 1$  transition in figure 5.2 cannot be attributed to NO contamination in the molecular beam, because even at room temperature, the population of pure NO with v''=1 is negligible.



Figure 5.2 REMPI spectrum of NO (v''=1) from photodissociation of t-butyl nitrite at 224 nm. The bimodal distribution is not caused by cluster formation in the molecular beam or by contamination.

The overall intensity of the low J component is only about one tenth that of the high J component, so the low J component is only a minor channel in the dissociation of t-butyl nitrite on the  $S_2$  surface. Nevertheless, this result is a manifestation that the dissociation dynamics are not as simple as initially believed,<sup>3</sup> and that at least two dissociation pathways coexist. Although the high J component has been fit to an impulsive model for a transition state with an ONO bending angle of  $114^{\circ}$ ,<sup>132,146</sup> the low J component should be related to a near linear transition state for the O-N=O moiety.

With increasing dissociation energy, the relative population in high vibrational states of NO increased dramatically. Figure 5.3 shows a segment of the spectrum of NO under four dissociation wavelengths. The high energy side of the spectrum is the high J component of the  $0 \leftarrow 0$  band, and the low energy region is the low J component from the  $1 \leftarrow 1$  band. The high J component of the  $1 \leftarrow 1$  band is in a higher energy region outside the range of the abscissa in the figure. For clarity, only a few spectral features are identified. The vertical axes of the spectra are not normalized relative to the energies of the dissociation laser and the probe laser, so figure 5.3 is only intended for a relative measurement of the populations at v''= 0 and 1. A dramatic variation in the vibrational population can be seen from the figure. Transitions from fragments with v''=0 dominate the spectrum at 250 nm, while at 236 nm, transitions from v''=0 and 1 states are comparable in intensity. At 232 nm, the spectrum shows stronger intensity from the v''=1 fragments. It is worth noting that in



Figure 5.3 REMPI spectra of NO from photodissociation of t-butyl nitrite at different photolysis wavelengths. The range of the abscissa includes the high J component of the v''=0 level and the low J component of the v''=1 level.

figure 5.3, the comparison is between the major component of the v''=0 channel (the high J component) and the minor component of the v''=1 channel (the low J component). The actual variation in population distribution should be even more prevalent.

Figure 5.4 shows the population distribution of NO from dissociation at four different wavelengths. Due to a technical difficulty, alignment parameters were not obtained, so the population for the low J component cannot be obtained with credibility. In figure 5.4, only the high J components are shown, and the population was obtained by dividing the intensity of the spectrum by the Hönl-London factor and the Franck-Condon factor.<sup>51,149</sup> The change in the vibrational distribution of NO with dissociation wavelength is staggering, while the change in the rotational population distribution is almost unnoticeable within each vibrational band. For an energy range of 500 cm<sup>-1</sup> of the dissociation laser, the population of the v''=0 state varies from 92% of the overall population at 250 nm to an undetectable level.<sup>141</sup> Given a vibrational frequency of 1900 cm<sup>-1</sup>, almost 40% of the additional available energy is channeled into the vibrational freedom of NO. During dissociation, the -N=O bond length must change significantly from that of the ground state or the final free NO. The rotational population for each vibrational level, however, only demonstrates a minor dependence on the dissociation wavelength. The most populated level shifts to a slightly higher J value as the dissociation energy increases. At least for the high J component of the NO fragment, the bending angle of ONO in the transition state remains unchanged with dissociation wavelength.



**Figure 5.4** Population distributions of NO from photodissociation of t-butyl nitrite. Only the high J component of each vibrational state is shown.

Variations in the spin-orbit and A-doublet distributions with dissociation energy are also observed. Figure 5.5 shows the average population ratios at four dissociation wavelengths. At 250 nm, these results agree with previous reports by Lavi *et al.*<sup>141</sup> The NO fragment is preferentially produced in the low spin-orbit component with its  $\pi$  lobe anti-symmetric with respect to the rotation plane. However, these preferences are inverted at wavelength shorter than 236 nm: the F<sub>2</sub> component becomes more populated than F<sub>1</sub>, and the  $\pi$  lobe of NO lies in the rotation plane. Winniczek *et al.* reported the ratios for the S<sub>2</sub> state of methyl nitrite between 223 and 227 nm.<sup>147</sup> Their results showed a complex relationship between these ratios: the F<sub>1</sub> component was favored for  $\Pi_{\infty}$ , while the F<sub>2</sub> component was favored for  $\Pi_8$ . Similarly, the  $\Pi_{\infty}$  component was favored for F<sub>1</sub>, while the  $\Pi_8$  component was favored for F<sub>2</sub>. In contrast, the values we observed do not exhibit such an alternation. Within our error limit of  $\pm$  0.1, similar ratios for F<sub>1</sub>/F<sub>2</sub> were obtained for both A-doublets, and similar ratios of  $\Pi_{\infty}/\Pi_8$  were obtained for both spin-orbit components.

A comparison can be made between the present observation and that of methyl nitrite.<sup>150</sup> Based on the work by Huber's group at 250 nm,<sup>151</sup> dissociation of methyl nitrite on the S<sub>2</sub> surface yields predominant production of NO (v''=0) and almost equal population for the symmetric and anti-symmetric  $\Lambda$  states and the spin-orbit states. The strong repulsive O-N bond results in dissociation within 10 fs, and the similarity between the –N=O bond length and the NO product determines little vibrational excitation in the NO fragment. Within our knowledge, no systematic study of the





dissociation dynamics of methyl nitrite has been conducted between 220 and 248 nm. For t-butyl nitrite, the present study shows bimodal rotational distributions and increasing vibrational excitation with increasing dissociation energy. It is unclear whether similar variations in vibrational and rotational distributions exist in methyl nitrite under similar excitation energies. Nevertheless, our results demonstrate that a complex surface topography and strong exit channel effects may play an important role in t-butyl nitrite. Using a rigid impulsive model for the NO moiety, Huber's group has calculated the final state distribution of t-butyl nitrite following excitation at 248 nm.<sup>146</sup> The rigid NO bond in this model results in little excitation of NO vibration, but extensive butoxy excitation which leads to secondary dissociation. Clearly this model does not describe the physics at higher excitation energies. Relaxation in the rigidity of the -N=O bond in the impulsive model (the "soft" impulsive model) partially solves the problem of vibrational excitation in the NO fragment, as illustrated in the calculation at 248 nm,<sup>132,152</sup> but this simple modification sacrifices the agreement in other degrees of freedom.

# 5.4 Photodissociation of Oriented Parent Molecules: $S_2 \leftarrow S_0$ Transition

#### 5.4.1 250 nm

As discussed in chapter 4, when parent molecules are effectively oriented by a strong, uniform electric field prior to photodissociation, the dependence of the yield of photofragments on the polarization direction of the dissociation laser gives information regarding the direction of the transition dipole moment. For t-butyl nitrite, if the transition dipole is parallel to the permanent dipole (and thus preferentially parallel to the orientation field), an enhanced yield of NO fragments will be seen when the dissociation laser is polarized parallel to the field. Conversely, if the transition dipole is perpendicular in nature, the NO yield will be greater when the dissociation laser is polarized perpendicular to the orientation field. The polarization ratio,  $\rho$ , is defined as the ratio of REMPI signal of the NO fragment when the dissociation laser is polarized perpendicular/parallel to the orientation field.

Table 5.1 lists the experimental values of  $\rho$  for each measured rotational level at different photolysis wavelengths in an orientation field of 50 kV/cm. Examples of the normalized spectra under two different polarization directions of the dissociation laser in an orientation field of 50 kV/cm are shown in figure 5.6. The  $Q_1(58.5)/Q_2(58.5)/P_2(65.5)$  line from the  $A(v'=0) \leftarrow X(v''=0)$  transition was used because of its high intensity relative to the  $A(v'=0) \leftarrow X(v''=1)$  band. Each point in this figure represents an average of 80 laser shots. By comparing integrated peak areas, the polarization ratio for this line was found to be  $0.69 \pm 0.06$ . Data for both the  $Q_1(58.5)/Q_2(58.5)/P_2(65.5)$  and  $P_2(51.5)$  transitions of the  $A(v'=0) \leftarrow X(v''=0)$ vibrational band are given in table 1. The data at 250 nm show a 46% enhancement in the NO signal from the parallel polarization of the dissociation laser compared with the perpendicular polarization. The transition dipole is thus parallel to the permanent dipole of the molecule, consistent with literature reports that the transition is accomplished through unlocalized  $\pi^* \leftarrow \pi$  charge transfer.<sup>141</sup> **Table 5.1** Polarization ratios for various rotational levels at the photolysis wavelengths explored in this study. The polarization ratio is the ratio of the yield of NO when the dissociation laser is polarized parallel/perpendicular to the orientation field of 50 kV/cm. The results indicate that photolysis of t-butyl nitrite at 365.8 nm and 351.8 nm is accomplished through a perpendicular transition while photolysis at 250 nm and 224 nm is parallel in nature.

Polarization Ratios, p							
	365.8 nm	351.8 nm	224 nm	250 nm			
R <sub>1</sub> (4.5)/P <sub>1</sub> (20.5)			$0.69 \pm 0.03$				
<b>R</b> <sub>1</sub> (6.5)	$1.46 \pm 0.05$		$0.68 \pm 0.03$				
<b>R</b> <sub>1</sub> (8.5)	$1.48 \pm 0.05$		$0.69 \pm 0.03$				
$R_1(9.5)/P_1(24.5)$	$1.49 \pm 0.05$	$1.47 \pm 0.06$	$0.68 \pm 0.03$				
$P_1(27.5)/Q_2(23.5)$	$1.45 \pm 0.05$						
$Q_1(58.5)/Q_2(58.5)/P_2(65.5)$				$0.69 \pm 0.03$			
P <sub>2</sub> (51.5)				$0.68 \pm 0.03$			



**Figure 5.6** Normalized spectra when the dissociation laser at 250 nm is polarized parallel and perpendicular to the orientation field of 50 kV/cm. The  $Q_1(58.5)/Q_2(58.5)/P_2(65.5)$  peak is depicted here, and each point is an average of 80 laser shots. The value of  $\rho$  was found to be 0.69 ± 0.03.

The dependence of  $\rho$  on the strength of the orientation field for photolysis at 250 and 224 nm is given in figure 5.7. The squares show experimental data obtained for the  $Q_1(58.5)/Q_2(58.5)/P_2(65.5)$  peak of the A(v'=0)  $\leftarrow$  X(v''=0) transition at 250 nm. Since polarization ratios were all normalized with respect to field-free conditions,  $\rho$  has a value of 1 at zero field, and these measurements contain no information on rotational alignment. As the field strength was increased, more molecules became oriented, and the preference for the parallel polarization direction of the dissociation laser became more apparent. The solid line in the figure represents a calculation of this trend assuming a permanent dipole moment of 2.77 D<sup>153</sup> and rotational constants taken from reference 154. The rotational temperature was assumed to be 2.08 K, and this assignment was based on the following observations. Decomposition of the sample resulted in supersonically cooled, pure NO in the molecular beam. Measurements of this impurity implied rotational temperatures between 2 and 3 K. The choice of 2.08 K is consistent with the present observations and previous measurements of the molecular beam from our studies of pyridazine and pyrimidine (chapter 3), and ICN and BrCN (chapter 4). Excellent agreement between calculation and experiment is achieved.

#### 5.4.2 224 nm

The results from the polarization experiment at 224 nm are also given in table 5.1. The rotational transitions listed are from the  $A(v'=1) \leftarrow X(v''=1)$  vibrational



**Figure 5.7.** Dependence of the polarization ratio from the  $S_2 \leftarrow S_0$  transition on the strength of the orientation field. The data were collected on the  $Q_1(58.5)/Q_2(58.5)/P_2(65.5)$  peak at a photolysis wavelength of 250 nm and the  $R_1(9.5)/P_1(24.5)$  peak at a photolysis wavelength of 224 nm. The horizontal axis of the data at 250 nm is shifted by 1 kV/cm for clarity. The solid line represents calculation of the expected trend for a pure parallel transition.

band. The polarization ratios are all less than unity, and the average value is approximately 0.69, thus the transition at this photolysis wavelength is still parallel in nature. Once again, the value of  $\rho$  was found to be independent of the rotational excitation of the NO fragment. The degree of enhancement in NO signal from the parallel polarization direction of the dissociation laser at 224 nm is the same as that at 250 nm. In addition, the dependence of  $\rho$  on the strength of the electric field (shown by the diamonds in figure 5.7) is almost identical to the trend at 250 nm. Both sets of data are in fairly good agreement with the calculation. This is not surprising given the smooth, unresolved absorption peak between 250 and 220 nm (see figure 5.1). It seems that only one type of potential energy surface is involved in this region, and the transition dipoles accessing these surfaces are parallel to the permanent dipole. The dissociative pathways on these surfaces, however, must be different, resulting in a bimodal distribution.

# 5.5 Photodissociation of Oriented Parent Molecules: $S_1 \leftarrow S_0$ Transition

The first excited singlet state of t-butyl nitrite was studied by exciting molecules at 365.8 or 351.8 nm. Our observations of the vibrational and rotational energy distributions are in qualitative agreement with Schwartz-Lavi and Rosenwaks.<sup>141</sup> Only a very small fraction of NO fragments were formed in the lowest vibrational level following photolysis at these wavelengths, thus the  $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$  vibrational band was used for the polarization measurements. The

maximum rotational population at these photolysis wavelengths was found at approximately  $J''_{max}=27.5$ .

Both low J and high J lines of different branches were studied, and the results are given in table 5.1. As in all of these experiments (chapters 4-6), the transitions chosen for this study were based on the symmetry of their lineshapes. Two of the peaks studied at 365.8 nm, the R<sub>1</sub>(8.5) and the R<sub>1</sub>(9.5)/P<sub>1</sub>(24.5), overlap with the Q<sub>1</sub>(43.5) and P<sub>2</sub>(51.5) transitions of the A(v'=0)  $\leftarrow$  X(v''=0) vibrational band respectively. However, since the population of this vibrational band is very small compared to the A(v'=1)  $\leftarrow$  X(v''=1) band, its contribution will be neglected.

All polarization ratios were normalized by comparison to their respective ratios under field-free conditions. At 365.8 nm, the average value of  $\rho$  among all the transitions is approximately 1.47. A value of  $\rho$  greater than unity implies that the perpendicular polarization direction of the dissociation laser was favored at high field strengths. Thus, the transition dipole must have a perpendicular relationship with the permanent dipole. At a dissociation wavelength of 351.8 nm, the R<sub>1</sub>(9.5)/P<sub>1</sub>(24.5) peak also had a polarization ratio of 1.47, which further supports the above conclusion. In this study,  $\rho$  was found to be independent of rotational quantum number throughout the region studied. Our observations are consistent with literature reports that dissociation at these wavelengths occurs through promotion of a nonbonding electron from the N=O group to an antibonding  $\pi$  orbital,<sup>141</sup> i.e., the transition dipole is perpendicular to the O-N=O plane. Figure 5.8 shows the dependence of  $\rho$  on the strength of the orientation field at a dissociation wavelength of 365.8 nm. The diamonds represent experimental data from the R<sub>1</sub>(9.5)/P<sub>1</sub>(24.5) transition. In contrast to figure 5.7, as the field strength was increased, the preference for the perpendicular polarization direction of the dissociation laser became more apparent. The solid line in the figure represents a calculation of this trend for a pure perpendicular transition assuming a permanent dipole moment of 2.77 D<sup>153</sup> and a rotational temperature of 2.08 K. Experimental results are in excellent agreement with this calculation.

## 5.6 Conclusions

Comparison of the vibrational and rotational energy partitioning of the NO fragment upon photodissociation of t-butyl nitrite at various wavelengths reveals a dramatic difference in the dissociation mechanisms and potential surfaces of the  $S_1$  and  $S_2$  states. Photolysis at 365.8 and 351.8 nm ( $S_1$  state) yielded NO fragments with a vibrational propensity rule of  $\Delta v$ =-1 and intermediate rotational excitation. Dissociation at 250 and 224 nm ( $S_2$  state) both yielded highly rotationally excited NO fragments with almost identical rotational distributions. The product vibrational distribution in this region shows a dramatic dependence on the excitation energy, with the v''=0 fragment of NO changing from the major channel at 250 nm to a minor channel at 220 nm. Throughout the region, product rotational distributions are



**Figure 5.8** Dependence of the polarization ratio of NO from the  $S_1 \leftarrow S_0$  transition on the strength of the orientation field. The diamonds show experimental ratios of the  $R_1(9.5)/P_1(24.5)$  peak at a dissociation wavelength of 365.8 nm. The solid line represents calculation of the expected trend.

bimodal, with low J and high J components separated by more than 30 rotational states. Although only a minor channel, the low J component implies a curve crossing to a state with a linear -O-N=O configuration. These results demonstrate disagreements with those obtained from photodissociation of methyl nitrite, so a more detailed look at the potential surface of the S<sub>2</sub> state and the dissociation dynamics of this complex nitrite is needed.<sup>151</sup>

Orientation via a uniform electric field was used to study the polarization directions of the dissociative electronic transitions of t-butyl nitrite at 365.8, 351.8, 250, and 224 nm. The ratio of the REMPI signal of NO from perpendicular/parallel polarization of the photolysis beam was found to be approximately 1.47 for the  $S_1 \leftarrow S_0$  transition, while  $\rho$  was approximately 0.69 for the  $S_2 \leftarrow S_0$  transition. Thus, the former transition is perpendicular while the latter is parallel to the direction of the permanent dipole, which lies in the O–N=O plane along the pseudo C<sub>3</sub> symmetry axis of the tertiary butyl group.<sup>154</sup>

# 6. Nitroaromatics

### 6.1 Introduction

Understanding the electronic potential energy surfaces and dissociation pathways of organic nitro compounds can offer insight into the detonation mechanisms of nitroexplosives. Since small nitroalkyl and nitroaromatic molecules possess many of the same properties as larger members of this class of compounds, their dissociation has been studied extensively.<sup>155-173</sup> Upon UV absorption, these compounds typically produce NO<sub>2</sub> and NO fragments. For example, the major channel in dissociation of nitromethane at 193 nm is the production of CH<sub>3</sub> and NO<sub>2</sub> fragments.<sup>155-157</sup> Secondary dissociation of the NO<sub>2</sub> is responsible for most of the observed NO ( $X^2\Pi$ ) and O ( ${}^3\Pi$ ) fragments.<sup>155</sup> Another mechanism leading to the NO product, suggested by Wodtke *et al.*, involves the isomerization of nitromethane to methyl nitrite prior to dissociation.<sup>158</sup> A minor channel resulting in electronically excited NO ( $A^2\Sigma^+$ ) fragments has also been reported.<sup>155</sup>

The dissociation of nitrobenzene between 226 and 280 nm is similar to that of nitromethane at 193 nm: there are two primary channels, which lead to the production of either NO<sub>2</sub> or O fragments, and two minor channels, which both produce NO.<sup>167</sup> Only one channel produces energetic NO, and two possible dissociation mechanisms for this channel have been proposed: 1) a two-step mechanism first producing nitrogen dioxide and subsequently NO; and 2) rearrangement of nitrobenzene to a phenylnitrite intermediate before dissociation to NO and C<sub>6</sub>H<sub>5</sub>O.<sup>167</sup> A theoretical

study by Glenewinkel-Meyer and  $\operatorname{Crim}^{174}$  has shown that the phenyl nitrite intermediate is a metastable state which leads to production of NO and phenoxy radicals. Although the phenylnitrite intermediate has not been consistently observed, Marshall *et al.*<sup>167</sup> found that the distribution of NO fragments from dissociation of nitrobenzene is different from that of NO fragments from nitrogen dioxide. This observation undermines the probability of the sequential dissociation pathway.

Dissociation of the nitrotoluene isomers has not been studied extensively. In a femtosecond mass spectroscopic experiment at 375 nm, NO<sub>2</sub> and NO loss channels were observed for all three nitrotoluene isomers.<sup>166</sup> The p-nitrotoluene isomer also exhibited a small peak corresponding to the loss of O fragments. In the dissociation of o-nitrotoluene, OH is a significant product that can be attributed to the so-called "ortho effect."<sup>166,175,176</sup> The proximity of the methyl and nitro groups leads to steric interactions. Consequently, the ground state geometry of o-nitrotoluene is unlike that of its isomers, characterized by a twisting of the NO<sub>2</sub> group from the plane of the aromatic ring.<sup>177</sup> A dissociation mechanism involving bicyclic intermediates, and possibly, rearrangement to the nitrite form prior to fragmentation was suggested to explain the OH channel.<sup>175</sup> The hydrogen atom in the OH product was shown to come exclusively from the methyl group.<sup>175</sup> Marshall et al. observed the NO fragment from dissociation of o-nitrotoluene between 224 and 238.<sup>169</sup> In this study, it was noted that the product internal energy distributions were unlike those of NO fragments from dissociation of nitrobenzene or NO<sub>2</sub>. However, it is unclear whether this conclusion is supportive of the isomerization pathway. To our knowledge, there has been no theoretical study of the molecular rearrangement pathway for the nitrotoluene isomers, analogous to the work on nitrobenzene by Glenewinkel-Meyer and Crim.<sup>174</sup>

Measurements of symmetry properties of excited electronic states of small nitroalkyl compounds have been performed.<sup>155-157,161-163</sup> In a photofragment translational spectroscopic study of nitromethane at 193 nm, Butler *et al.* found that the transition dipole was perpendicular to the C<sub>2v</sub> symmetry axis of the NO<sub>2</sub> moiety.<sup>157</sup> However, the anisotropy parameter ( $\beta$ ) deviated from a pure perpendicular transition. It was suggested that a change in symmetry from the C<sub>2v</sub> ground state to C<sub>s</sub> resulted in configuration interaction between a <sup>1</sup>B<sub>2</sub> and a <sup>1</sup>A<sub>1</sub> state, thus tilting the direction of the effective transition dipole. Kwok *et al.*<sup>161</sup> measured gas phase absorption spectra and resonance Raman intensities of nitroethane and 1-nitropropane, and reported a predissociative mechanism. Although the direction of the transition dipole moment was not specifically pursued in their experiment, the results indicated a mixing of states.

Symmetry properties of the excited states of nitroaromatic compounds have proven difficult to obtain. Experiments are limited by the broad, featureless absorption spectra and the slow dissociation of these compounds, resulting in an isotropic distribution of photofragments and low translational energy release.<sup>167</sup> These properties are typical of large molecules, and often hinder investigations using conventional gas phase techniques such as Doppler or other photofragment translational spectroscopic methods. On the other hand, several theoretical efforts have been made to describe the excited singlet states of nitrobenzene,<sup>174,178-182</sup> and a
Table 6.1 Theoretical calculations on nitrobenzene. Energies are given in eV. In some cases, the symmetry group changes from  $C_{2\nu}$  to  $C_s$ .

Reference:	21	26	24	25	23	22
Method:	MP2/ 6-31G*	PPP	SINDO/ CI	CNDO/ S	AM1	CAS- SCF
S <sub>1</sub> Energy	4.91	4.59	3.87	4.06	4.30	3.00
S <sub>1</sub> Symmetry	<sup>1</sup> A <sub>2</sub>	<sup>1</sup> B <sub>1</sub>	$^{1}B_{2}$	<sup>1</sup> B <sub>2</sub>	$^{1}B_{1}$	<sup>1</sup> A <sub>2</sub>
S <sub>2</sub> Energy	5.19	4.76	4.95	4.64	4.35	3.45
S <sub>2</sub> Symmetry	<sup>1</sup> B <sub>1</sub>	<sup>1</sup> A <sub>1</sub>	<sup>1</sup> A <sub>1</sub>	<sup>1</sup> B <sub>1</sub>	$^{1}B_{2}$	<sup>1</sup> A'
S <sub>3</sub> Energy	5.80	5.84	5.70	4.90	4.66	4.61
S <sub>3</sub> Symmetry	<sup>1</sup> B <sub>2</sub>	${}^{1}\mathbf{B}_{1}$	<sup>1</sup> A'	<sup>1</sup> A <sub>1</sub>	<sup>1</sup> A <sub>1</sub>	<sup>1</sup> A <sub>2</sub>

summary of these results is given in table 6.1. The discrepancies between these calculations, including symmetries and energies, are disturbingly dramatic.

In the current work, measurements of the NO fragment from dissociation of nitrobenzene and o-nitrotoluene between 220 and 250 nm will be presented.<sup>22,23</sup> Directions of transition dipole moments of both compounds will be determined from measurements of the polarization spectroscopy of oriented parent molecules. For o-nitrotoluene, internal energy distributions will also be characterized. The results will be compared with studies of related organic nitro compounds, such as nitromethane.<sup>155-157,161-163</sup> These observations provided an understanding of the photodissociation dynamics and relevant potential energy surfaces of organic nitro compounds.

### 6.2 Experimental Details

Nitrobenzene (Aldrich, 99+%) and o-nitrotoluene (Aldrich, 99+%) were used without further purification. Room temperature vapor was seeded in helium prior to expansion through the pulsed nozzle. A stagnation pressure between 1300 and 1350 torr was used throughout the experiment in order to simultaneously keep a low rotational temperature and to prevent cluster formation. Variation of the stagnation pressure below 1400 torr resulted in no significant change in the rotational distribution of the NO fragments, supportive of a negligible cluster concentration. Galloway *et al.* reported NO distributions upon dissociation of nitrobenzene at 226 and 280 nm.<sup>167</sup> They used a much lower stagnation pressure (295 torr) and a heated nozzle (100  $^{\circ}$ C).

Our rotational distribution of NO is essentially identical to that of Galloway *et al.*, which further confirms negligible cluster concentration in our molecular beam. The rotational temperature of the molecular beam was measured by replacing nitroaromatic sample with pyrimidine (see chapter 3). From the rotationally resolved REMPI spectrum of the  $\pi^* \leftarrow$  n transition in pyrimidine, the rotational temperature was found to be between 2.0 and 2.5 K.<sup>18</sup>

# 6.3 Dissociation under Field-Free Conditions

The gas phase absorption spectra of nitromethane, nitrobenzene and onitrotoluene between 200 and 350 nm are given in figure 6.1. The weak absorption feature of nitromethane at 270 nm was assigned as a  $\pi \leftarrow n$  transition. The strong feature, centered around 200 nm, was assigned as a  $\pi^* \leftarrow \pi$  transition localized on the NO<sub>2</sub> moiety.<sup>155,157</sup> The absorption curves of nitrobenzene and o-nitrotoluene are very similar, with features centered at 240 nm and tails at longer wavelengths. Calculations of nitrobenzene by Gonzalez-Lafont *et al.* have indicated that with the exception of the S<sub>1</sub> state, which is probably seen at the tail of the 240 nm absorption feature, all higher excited singlet states are predominantly accessed through  $\pi^* \leftarrow \pi$  transitions.<sup>179</sup>

The laser-induced fluorescence (LIF) spectra of the NO fragment from dissociation of nitrobenzene at 226 and 280 nm have been reported by Galloway *et al.*<sup>167</sup> The authors found that the rotational state population of the vibrational ground state could be described by a Boltzmann distribution with a rotational temperature of



Figure 6.1 Gas phase absorption spectra of nitromethane, nitrobenzene, and onitrotoluene.

(3700 ± 350) K. The REMPI spectrum of the ground vibrational state from photolysis between 230 and 250 nm in the present experiment showed a similar, highly rotationally excited distribution. Galloway *et al.* observed no vibrationally excited NO fragments, and concluded that no more than 10% of NO fragments were formed in excited vibrational states.<sup>167</sup> In a one-laser experiment on nitrobenzene, *Daugey et al.* observed NO fragments in v''=0,1,2, and 3 vibrational states with intensity ratios of 1:0.3:0.1:0.02.<sup>164</sup> Due to the need for high signal to noise ratios, our measurements on nitrobenzene in the present work are limited to the ground vibrational state.

Figure 6.2 shows the (1+1) REMPI spectra of three vibrational bands of the NO fragment following dissociation of o-nitrotoluene. Since a single laser was used for dissociation of parent molecules and detection of products, the actual dissociation wavelength varied between 220 and 250 nm. The dissociation dynamics are not expected to change much throughout this wavelength region, so problems due to the varying dissociation wavelength are not anticipated. This assessment is based on our experience with nitrobenzene. Two-laser experiments were performed on nitrobenzene, in which the dissociation wavelength was fixed at 230, 240, or 250 nm. These results were almost identical to those obtained when a single laser was used for dissociation and detection. Furthermore, Crim's group studied the NO fragment from nitrobenzene in a single laser experiment between 220 and 227 nm.<sup>167</sup> The observed NO internal energy distributions were very similar to the results of our two-laser experiments. Rotational levels in figure 6.2 were assigned based on the spectral simulation program LIFBASE,<sup>148</sup> and the Q<sub>1</sub> branch has been identified. The v''=1



**Figure 6.2** REMPI spectra of three vibrational bands of the NO fragment from photodissociation of o-nitrotoluene between 220 and 250 nm. Rotational transitions of the  $Q_1$  branch are identified. The range of the abscissa for the v''=2 band is smaller than that of the v''=0 and 1 bands.

spectrum has a better signal to noise ratio than the v''=0 band due to a greater NO signal intensity. This is attributed to the larger Franck-Condon factor of the  ${}^{2}\Sigma^{+}$  (v'=0)  $\leftarrow {}^{2}\Pi$  (v''=1) transition and the availability of a higher laser power for this wavelength region.<sup>149</sup>

The vibrational and rotational population distributions from the Q1 branch are outlined in figure 6.3. For visual guidance, trendlines are overlaid on the experimental data. The relative intensity was calculated by dividing the experimental intensity by the Hönl-London factor<sup>51</sup>, the Franck-Condon factor<sup>149</sup>, and the laser power. Since alignment parameters were not obtained in this experiment, populations in low J levels cannot be calculated with credibility and were not included in the figure. Furthermore, rotational transitions with quantum number less than 10.5 were generally not resolvable with the current laser system. The NO fragments were formed in v''=0, 1, and 2 vibrational states with relative populations of 1:0.6:0.06. The average vibrational energy was  $1760 \text{ cm}^{-1}$ , or approximately 4.6% of the available energy. All of the rotational distributions are non-Boltzmann, and fragments in the first two vibrational levels are highly rotationally excited. The average rotational energies are approximately 2050 cm<sup>-1</sup> for the lowest vibrational band and 1900 cm<sup>-1</sup> for the first excited vibrational band. The v''=2 level is considerably colder with an average rotational energy of 460 cm<sup>-1</sup>.

Table 6.2 lists the average rotational  $(E_r)$  and vibrational  $(E_v)$  energies of the NO fragment from o-nitrotoluene as determined in this experiment. The rotational



**Figure 6.3** Vibrational and rotational populations of the NO fragment. Hönl-London factors, Franck-Condon factors, and laser power were factored into the calculations of the relative population.

**Table 6.2** Average rotational ( $E_r$ ) and vibrational ( $E_v$ ) energies for the NO fragments from o-nitrotoluene (o-NT) and nitrobenzene (NB). The available energies ( $E_{av}$ ) are approximately 37900, 36300, and 34700 cm<sup>-1</sup> for v''=0, 1, and 2 respectively. The calculated energies for the impulsive and statistical models of energy release for nitrobenzene are also given.<sup>18</sup>

	o-NT 226 nm	NB 226 nm <sup>18</sup>	Impulsive model (NB) <sup>18</sup>	Statistical model (NB) <sup>18</sup>
$E_r (cm^{-1}), v''=0$	$2050 \pm 110$	$2580 \pm 242$	9680	1610
% of E <sub>av</sub>	$5.4 \pm 0.3$	$6.8 \pm 0.6$	25.5	4.3
$E_r (cm^{-1}), v''=1$	1900 ± 100			
% of E <sub>av</sub>	$5.2 \pm 0.3$			
$E_r (cm^{-1}), v''=2$	$460 \pm 25$			
% of E <sub>av</sub>	$1.3 \pm 0.1$			
E <sub>r</sub> (cm <sup>-1</sup> ), avg.	1940 ± 110	$2580\pm242$		
% of E <sub>av</sub>	$5.3 \pm 0.3$	$6.8 \pm 0.6$		
E <sub>v</sub> (cm <sup>-1</sup> )	$1760 \pm 90$	< 810	1130	810
% of E <sub>av</sub>	$4.6 \pm 0.2$	< 2.1	3.0	2.1

energy for each vibrational level is listed individually, and the average rotational energy was obtained by taking into account the relative populations of the contributing vibrational states. Based on an estimated energy of the C-NO<sub>2</sub> bond of o-nitrotoluene, the available energy for the system is between 34,700 and 37,900 cm<sup>-1</sup>, depending on photolysis wavelength.<sup>167</sup> Experimental and calculated energies for nitrobenzene, as obtained by Galloway et al., are also given in table 6.2.<sup>167</sup> For nitrobenzene, the impulsive model of energy release predicts that a large fraction of the available energy will be found in rotation of the NO fragment, which doesn't agree with experimental observations.<sup>167</sup> The statistical model provides a better approximation to experiments on nitrobenzene, but still fails to describe the photodissociation completely. In the present experiment on o-nitrotoluene, the NO fragment is formed with less rotational energy, but nearly twice as much vibrational energy as that from nitrobenzene. Quantitative comparisons between our observations of o-nitrotoluene and statistical calculations cannot be performed due to a lack of information regarding the rovibronic density of states and vibrational frequencies. It is clear, however, that the statistical model is better suited for o-nitrotoluene.

Figure 6.4 shows the preference of the NO fragment for spin-orbit doublet and  $\Lambda$ -doublet states. For all three vibrational bands, the NO product from o-nitrotoluene was preferentially produced in the low spin-orbit component (F<sub>1</sub>) with an F<sub>1</sub>/F<sub>2</sub> ratio of approximately 1.4. A preferential population of the P and R branches relative to Q branches was also observed. The  $\Lambda$  doublet ratio,  $\Lambda'/\Lambda''$ , for each of the three vibrational bands was approximately 1.7. Thus, the unpaired  $\pi$  orbital of the NO





fragment lies in the plane of rotation, and A' symmetry of the excited electronic state of o-nitrotoluene is implied.

To our knowledge, a complete study of the dissociation dynamics of onitrotoluene between 220 and 250 nm has not been pursued, so a comparison with studies of nitrobenzene and nitromethane will be informative. In the present experiment, a significant fraction of NO fragments from o-nitrotoluene was formed in the first excited vibrational state. Galloway et al. placed an upper limit of 10% on the fraction of NO fragments from dissociation of nitrobenzene that could be produced in vibrationally excited states.<sup>167</sup> However, Daugev et al. reported that 21% of NO fragments from nitrobenzene were formed in vibrationally excited states.<sup>164</sup> For nitromethane, Moss et al. found that at least 90% of the NO fragments from nitromethane were formed in the ground vibrational state.<sup>155</sup> Thus, our observations indicate that the NO fragment from o-nitrotoluene is produced with a significantly higher vibrational energy than that from nitrobenzene or nitromethane. This difference could be related to a more dramatic change in geometry during dissociation of o-nitrotoluene, which might be a manifestation of the perturbation caused by the nearby methyl group. The relative population between spin-orbit states of NO in the current work shows the same trend as that from nitromethane, in which the  ${}^{2}\Pi_{1/2}$ component was preferentially populated by a factor of 2:1.<sup>155</sup>

# 6.4 Orientation Effect on the yield of NO from nitrobenzene

Table 6.3 lists the experimental values of  $\rho$  for the NO fragment from nitrobenzene. All rotational levels are from the v''=0 band, and three different photolysis wavelengths were used. The strength of the orientation field was 50 kV/cm. The polarization ratios in table 2 are consistently larger than unity, indicating the preference for the perpendicular polarization direction of the photolysis beam. The values of  $\rho$  are almost identical for the three dissociation wavelengths, and are virtually independent of rotational quantum number.

A few of these NO transitions were measured in a one-laser experiment, where a single laser was used to dissociate nitrobenzene and induce REMPI of the NO fragment. As in our study of the NO fragment from dissociation of t-butyl nitrite at 351.8 nm (chapter 5),  $\rho$  was found to be independent of the polarization direction of the probe beam, and no product alignment was detectable under our experimental conditions. Thus, in the present experiment, no additional complications are expected from rotating the polarization directions of the dissociation and probe beams simultaneously. This conclusion provides the basis of the one-laser experiment in section 6.4.

Figure 6.5 plots  $\rho$  vs. rotational quantum number for the NO fragment from dissociation of nitrobenzene at 230 nm in an orientation field of 50 kV/cm. The solid horizontal line represents calculation of  $\rho$  for a pure perpendicular transition. The calculation assumes a permanent dipole moment of 3.9 D<sup>183</sup> and a rotational

Table 6.3 Polarization ratios for a few rotational levels of the NO fragment from photodissociation of nitrobenzene at three photolysis wavelengths. The ratio represents the NO fragment yield when the dissociation laser was polarized perpendicular/parallel to the orientation field of 50 kV/cm.

	<u>230 nm</u>	<u>240 nm</u>	<u>250 nm</u>
Q <sub>2</sub> (54.5)/P <sub>1</sub> (61.5)	$1.44 \pm 0.05$	$1.45 \pm 0.05$	$1.42 \pm 0.06$
P <sub>2</sub> (37.5)	$1.45 \pm 0.05$	$1.43 \pm 0.05$	$1.41 \pm 0.06$
Q <sub>1</sub> (63.5)/P <sub>1</sub> (70.5)	$1.44 \pm 0.05$	$1.42 \pm 0.05$	$1.44 \pm 0.06$



**Figure 6.5** Polarization ratios for a few rotational levels of NO following dissociation of nitrobenzene at 230 nm in an orientation field of 50 kV/cm. The solid line indicates the expected ratio for a pure perpendicular transition. The dashed line factors in 20% parallel character.

temperature of 2.5 K. Rotational constants are taken from reference 184. The calculated polarization ratio may be taken as an upper limit of the expected experimental ratio. Contribution from a parallel transition will decrease the ratio due to increased preference for the parallel polarization direction of the photolysis beam. As shown in section 4.5.4, the experimental polarization ratio can be used to determine the amount of parallel character involved in the transition. This result implies 20% contribution from a parallel transition, as shown by the dashed line in figure 6.5.

The dependence of  $\rho$  on the strength of the orientation field is given in figure 6.6. The experimental points represent the P<sub>2</sub>(37.5) transition of NO following dissociation at 240 nm. Since polarization ratios are all normalized with respect to field-free conditions,  $\rho$  has a value of unity at zero field strength, and the measurement contains no information on rotational alignment. As the field strength was increased, more molecules became oriented, and the preference for a perpendicularly polarized dissociation beam increased. The solid line in the figure shows the calculated polarization ratio for a pure perpendicular transition, while the dashed line factors in 20% contribution from a parallel transition. The experimental data agrees well with the latter calculation. These results are indicative of the presence of a second potential energy surface in the dissociation process.

Our data on nitrobenzene agrees with observations of the dissociation of nitromethane by Butler *et al.*<sup>157</sup> The parallel component in the dissociative transition of nitrobenzene can arise from curve crossing facilitated by the change in symmetry of



**Figure 6.6** Dependence of the polarization ratio of the  $P_2(37.5)$  transition of the NO fragment on the strength of the orientation field. The photolysis wavelength was 240 nm. The solid line represents calculation of a pure perpendicular transition, while the dashed line assumes 20% contribution from a parallel transition.

the NO<sub>2</sub> group. These results can be compared with the theoretical work listed in table 6.1. The most recent *ab initio* calculations by the Crim group indicate that the first transition is forbidden while the second and third transitions are both allowed through perpendicularly polarized excitation.<sup>174</sup> No higher energy orbitals were reported. Our measurements cannot distinguish between the two types of perpendicular transitions (to states of B<sub>1</sub> and B<sub>2</sub> symmetries), but the presence of a surface with A<sub>1</sub> symmetry is necessary to explain our results. Perhaps higher energy orbitals need to be considered in these calculations to complete the physical picture. The rest of the calculations in table 6.1, however, were performed using semi-empirical methods, and they all predicted some mixing of perpendicular and parallel transitions.<sup>178-182</sup>

# 6.5 Orientation Effect on the Yield of NO from o-Nitrotoluene

To compare the electronic states of nitrobenzene and o-nitrotoluene and to determine the localization properties of the NO<sub>2</sub> moiety, the symmetry of the excited electronic state of o-nitrotoluene was probed. A few rotational transitions from the v''=0, 1, and 2 vibrational bands were used to measure effects of the polarization direction of the dissociation laser. Table 6.4 lists experimentally determined values of  $\rho$  for the NO fragment from o-nitrotoluene in an orientation field of 50 kV/cm. Rotational transitions listed with a slash between them were too close in wavelength to be resolved with the current laser system. The average value of  $\rho$  was 1.46, indicating a predominantly perpendicular relationship between the permanent dipole moment and

Table 6.4 Polarization ratios of the NO fragment from photodissociation of onitrotoluene between 220 and 250 nm. The ratio represents the yield of NO when the dissociation laser was polarized perpendicular/parallel to the orientation field of 50 kV/cm.

	v''=0	v''=1	v''=2
$Q_2(54.5)/P_1(61.5)$	$1.47 \pm 0.06$		
$P_2(37.5)/R_{21}(16.5)$	$1.47 \pm 0.05$		
P <sub>2</sub> (47.5)/Q <sub>1</sub> (39.5)	1.45 ± 0.06		
$P_1(18.5)/R_2(24.5)/R_2(12.5)/R_2(12.5)/R_2(0.5)$		$1.45 \pm 0.05$	
$\frac{P_1(17.5)/Q_1(8.5)}{R_1(2.5)/R_{21}(0.5)}$			1.46 ± 0.06

the transition dipole moment. The polarization ratio was virtually independent of rotational and vibrational quantum numbers, implying that the potential energy surface(s) involved have similar topography.

Figure 6.7 illustrates the relationship between  $\rho$  and rotational quantum number for the v''=0 vibrational band. The expected value of  $\rho$  for a pure perpendicular transition was calculated, and the result is also given in figure 5. The calculation assumes a permanent dipole moment of 3.6 D and a rotational temperature of 2.5 K. Rotational constants were obtained from an *ab initio* calculation at the 6-31G\*\* level. The same calculation for nitrobenzene gave rotational constants in very good agreement with Ribeaud *et al.*,<sup>184</sup> however, the calculated permanent dipole of nitrobenzene was 30% larger than experimentally determined values. For o-nitrotoluene, experimental measurements of the permanent dipole varied between 3 and 4 D.<sup>185</sup> If the same 70% scaling factor is applied to our *ab initio* calculation for o-nitrotoluene, the resulting value of the permanent dipole is 3.6 D. This value is in very good agreement with the experiment by Rahman *et al.*,<sup>186</sup> and was thus chosen for use in subsequent calculations.

The experimental polarization ratios in figure 6.7 are slightly less than those expected of a pure perpendicular transition. Thus, a second potential energy surface accessible through a parallel transition is likely present. When 15% parallel character is factored into the calculation, the agreement between theory and experiment is very good. It is worth noting that the rotational temperature of 2.5 K used in this calculation is a cautious estimate. If the rotational temperature were as low as 2.0 K,



Figure 6.7 Polarization ratios for a few rotational transitions of the  $P_2$  branch of the v''=0 band. Calculations of the polarization ratio for a pure perpendicular transition and a transition with 15% parallel character are also shown.

the amount of parallel character would be 40%. The calculated value of 15% should therefore be treated as a lower limit.

The dependence of  $\rho$  on the strength of the orientation field is given in figure 6.8. The experimental points represent the polarization ratio of the P<sub>2</sub>(37.5)/R<sub>21</sub>(16.5) transition of the v''=0 band. All data were normalized with respect to field-free conditions. As the field strength was increased, more molecules became oriented, and the preference for a perpendicularly polarized dissociation beam increased. The solid line in the figure shows the calculated polarization ratio for a pure perpendicular transition, while the dashed line factors in 15% contribution from a parallel transition. The experimental data agrees well with the latter calculation. These results are once again supportive of the presence of a second potential energy surface in the dissociation process.

Our results are consistent with previous observations of nitromethane, nitroethane, 1-nitropropane, and nitrobenzene.<sup>155-173</sup> As mentioned in section 6.1, the dissociation of nitromethane is instantaneous, therefore photofragment translational spectroscopy has been used to determine vectorial information. Butler *et al.*<sup>157</sup> found that the effective direction of the transition dipole of nitromethane at 193 nm was predominantly perpendicular to the  $C_{2v}$  symmetry axis of the NO<sub>2</sub> group, but slightly tilted. Similarly, the observations of Kwok *et al.*,<sup>161</sup> implied a mixing of states in the dissociation mechanism of nitroethane and 1-nitropropane. We have found that a parallel transition contributes 20% in nitrobenzene and 15% in o-nitrotoluene. Since the relationship between the permanent dipole and the transition dipole is similar for



**Figure 6.8** Dependence of the polarization ratio of the  $P_2(37.5)/R_{21}(16.5)$  transition on the strength of the orientation field. As the field strength increased, more molecules became oriented, and the preference for the perpendicular polarization direction of the dissociation laser increased. For comparison, the trends for a pure perpendicular transition and a transition with 15% parallel character are given.

all of these nitrocompounds, localization of the electronic orbitals on the nitro group is implied.

#### 6.6 Conclusions

The dissociation dynamics of o-nitrotoluene was explored through measurements of the NO fragment. Under field-free conditions, o-nitrotoluene yielded NO fragments in v''=0, 1, and 2 states. Upon excitation between 220 and 250 nm, the relative vibrational populations were 1:0.6:0.06. The NO fragments were formed with more vibrational energy than the NO fragment from nitrobenzene as reported by Galloway et al.<sup>167</sup> and Daugey et al.<sup>164</sup> Our results were consistent with observations by Marshall et al. on o-nitrotoluene<sup>169</sup>, in which the NO fragments were vibrationally more excited than those from both nitrobenzene and nitrogen dioxide. Rotational distributions of each vibrational level were non-Boltzmann, and the average rotational energy decreased with increasing vibrational energy. Based on the analysis of the Crim group on nitrobenzene, the energy partitioning in these nitroaromatic compounds was better described by the statistical model than the impulsive model.<sup>167</sup> Preferences for spin-orbit and A-doublet states were observed in the present experiment. The  $F_1/F_2$  ratio was 1.4 while the A'/A" ratio was 1.7. The latter ratio indicated that the unpaired  $\pi$  lobe of the NO fragment was parallel to the plane of rotation. The preference for the F<sub>1</sub> component ( ${}^{2}\Pi_{1/2}$  spin-orbit state) showed the same trend as the NO fragment from dissociation of nitromethane at 193 nm, as reported by Moss et al.<sup>155</sup>

REMPI spectra of the NO fragments following photolysis of oriented nitrobenzene and o-nitrotoluene between 220 and 250 nm led to quantitative assessment of the electronic transitions. From the dependence of the yield of the NO fragment on the polarization direction of the photolysis laser in an orientation field, it was determined that the major contributor for both molecules is a perpendicular transition, i.e. the transition dipole is perpendicular to the permanent dipole of the molecule. However, the degree of enhancement in signal when the dissociation beam was polarized perpendicular to the orientation field fell below calculation of pure perpendicular transitions. Our results indicated ~15% parallel character for o-nitrotoluene and ~20 % parallel character for nitrobenzene. Considering the similarities in the UV absorption spectra of these two compounds and the probable localization of electronic orbitals on the NO<sub>2</sub> moiety, this conclusion was not surprising. These observations are also in good agreement with results on dissociation of nitromethane at 193 nm.<sup>157</sup>

This work has reiterated the advantages of using a uniform electric field to determine directions of transition dipoles. This procedure is only related to the excitation probability of an oriented system under two different polarization directions of the excitation laser. Therefore, this kind of experiment overcomes a fundamental obstacle in studies of the photodissociation processes of large molecules. The polarization ratio is independent of the dissociation mechanism and the dynamics of the upper state. This new approach has no reliance on Doppler or other photofragment translational spectroscopic techniques. It therefore suffers no kinematic constraints, and it can be used for large, complex systems where slow, non-energetic fragments are produced.

# 7. Concluding Remarks

#### 7.1 Summary

The experiments presented in this thesis have demonstrated the feasibility and applications of orientation of linear and asymmetric top molecules with a strong, uniform electric field. Successful orientation can be achieved when the rotational energy of gas phase, polar molecule is overcome by the electrostatic potential energy. Using supersonic expansion to cool the rotational temperatures, orientation of pyridazine, pyrimidine, ICN, BrCN, t-butyl nitrite, nitrobenzene, and o-nitrotoluene has been achieved. The photoexcitation/photodissociation processes of the oriented molecules were then studied using polarization spectroscopy.

Chapter 3 presented experimental data on the  $\pi^* \leftarrow n$  transitions of pyridazine (1,2-diazine) and pyrimidine (1,3-diazine). The transition dipole moment in both cases is perpendicular to the molecular plane, while the permanent dipole lies in the molecular plane. Excitation perpendicular to the orientation field, thereby perpendicular to the permanent dipole and parallel to the transition dipole, resulted in enhanced transition efficiency. Theoretical treatment of asymmetric top molecules in a Stark field was developed, as was a general methodology for determining directions of transition dipole moments from this type of measurement.

The dissociation dynamics of the cyanogen halides was studied via orientation with an electric field, and the results were presented in chapter 4. The CN (light) and I\* (heavy) fragments from photodissociation of oriented ICN were detected with LIF and REMPI techniques. The transition at 266 nm was shown to be purely parallel in nature, while at a 250 nm, some perpendicular character was observed. The ability to achieve selective excitation when more than one potential energy surface is accessible was discussed. Unlike ICN at 266 nm, experimental data on BrCN indicated that the effective transition dipoles of BrCN at 213 and 230 nm have substantial perpendicular components. Furthermore, the invariability of the polarization ratio with rotational quantum number in BrCN implied that all of the contributing surfaces have a similar bending angle and topography. The difference between the two cyanogen halides is most likely attributable to a difference in spin-orbit coupling.

Chapter 5 presented data from the photodissociation of t-butyl nitrite. This work represented our first attempt to use this method for the study of medium sized organic molecules. Results indicated that the vibrationally predissociative  $\pi^* \leftarrow n$  transition at 351.8 and 365.8 nm was accomplished through a pure perpendicular transition, while the  $\pi^* \leftarrow \pi$  transition between 224 and 250 nm was accomplished through a pure parallel transition. In addition, differences in vibrational energy distributions of the NO fragment were observed, and a detailed investigation of the dissociation dynamics and topography of excited electronic states was performed.

Investigations of the dissociation dynamics of nitroaromatic molecules have been challenging in the past due to fast internal conversion, slow dissociation, and low translational energy release upon UV excitation. Both experimental and theoretical efforts had failed to yield reliable results regarding the vectorial properties of dissociation. However, chapter 6 indicated that some of this information can be determined through orientation with a uniform electric field. The directions of the

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transition dipoles of nitrobenzene and o-nitrotoluene between 220 and 250 nm were shown to be predominantly perpendicular to the permanent dipole moments. However, quantitative analysis implied a 15-20% contribution from parallel transitions.

## 7.2 Future Work

The work presented in this thesis describes the development of a new method for measuring directions of transition dipoles of polar molecules. The technique has proven to be quite successful, and may be used to study the behavior of a wide range of molecules upon photoexcitation. In the future, this methodology will be applied to larger, more complex systems. In particular, biologically important molecules such as the nucleic acid bases will be studied. The goal of these experiments will be to provide reliable data for semi-empirical calculations of circular dichroism (CD) of biomolecules, which is important for conformational analysis of proteins, DNA, and RNA.

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