AN ABSTRACT OF THE DISSERTATION OF

<u>James E. Abbott, Jr</u>. for the degree of <u>Doctor of Philosophy</u> in <u>Chemistry</u> presented on <u>November 3, 2006</u>. Title: Polarization Spectroscopy and Photodissociation Studies of Nitroaromatic

<u>Compounds in the Gas Phase</u>.

Abstract approved: _____

Wei Kong

The central purpose of this dissertation was to explore and expand the use of an uniform electric field for orientation and for subsequent spectroscopic investigation of asymmetric polar molecules in the gas phase. The systems of study were nitrobenzene (NB) and the nitrotoluene (NT) isomers. We were able to quantitatively determine the direction of the electronic transition dipole relative to the permanent dipole for these molecules, thus providing quantitative information on the symmetry of the second and third singlet excited electronic states. Transition to the second singlet excited state (S_2) was shown to have a dipole predominantly perpendicular to the permanent dipole, consistent with a localized excitation of the -NO₂ moiety. The transition dipole to the S_3 state for the meta and para isomers was almost completely parallel to the permanent dipole, opposite to that observed for the S_2 transition. The success of these experiments has demonstrated the ability of the Brute Force Orientation technique to quantitatively characterize the transition dipole properties of large molecules. The importance of this technique lies in the fact that most large molecules undergo rapid internal conversion and slow dissociation after absorption, therefore information on the symmetry properties of these systems is otherwise unattainable.

In addition to the determination of the transition dipole direction, we were able to characterize many details of the dissociation process by analyzing the internal energy distribution of the Nitric Oxide (NO) photofragment. The Resonantly Enhanced Multi Photon Ionization spectrum of NO has revealed that the methyl group causes significant perturbation in the dissociation process, while it seems to have minimal effect on the transition dipole direction among NB and NT. All NT isomers showed significantly more vibrational excitation than previously reported for NB. Additionally, the meta and para isomers were observed to have a vibrational inversion behavior for $v'' \ge 3$, with the higher vibrational levels having larger populations. The higher vibrational levels were also found to have higher degree of rotational excitation. A bimodal behavior was also observed in the rotational distribution of several vibrational bands. A preference was observed for the π lobe being in the plane of rotation of the fragment. After a thorough comparison with relevant literature reports, and based on our experimental results, we present a model for the dissociation of NT isomers. We believe the bimodal rotational distribution and vibrational inversion indicate at least two dissociation channels in which isomerization of the nitro group and an NO₂ photofragment play essential roles.

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Polarization Spectroscopy and Photodissociation Studies of Nitroaromatic Compounds in the Gas Phase

by James E. Abbott, Jr.

A DISSERTATION

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Oregon State University

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November 3, 2006.

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

James E. Abbott, Jr., Author

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S.D.G.

CONTRIBUTION OF AUTHORS

Dr. Xianzhao Peng assisted with data collection for material presented in Chapters 3 and 4.

Dr. Yonggang He assisted with data collection and mass determination presented in Appendix B.

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In memory of my mother and dedication to my father

Proverbs 1: 8,9

Polarization Spectroscopy and Photodissociation Studies of Nitroaromatic Compounds in the Gas Phase

Chapter 1

Introduction

1.1 RESEARCH GOALS

The primary goal of this research project is to develop a polarization spectroscopic method of oriented species in a DC electric field for studies of electronic transition dipole properties. Large molecules are characterized by unresolvable rovibronic spectra due to the many energetically accessible states for a given system and internal conversion (IC) or intersystem crossing (ISC) processes. The unresolvable nature makes determination of transition dipole symmetry properties impossible with high resolution spectroscopic techniques. Consequently, methods of polarized radiation have been developed.

There are two basic techniques in using polarized radiation for determination of transition dipole properties. Vector correlation techniques are based on analysis of photofragments upon excitation with polarized radiation. If dissociation occurs in less than the time required for molecular rotation, in the picosecond range or shorter, anisotropy in the spatial distribution of the photofragments can yield transition dipole symmetry information. This method has been very successful for small molecules with an almost instantaneous dissociation. However, it fails for larger molecules that undergo slow dissociation, or exhibit rapid IC or ISC without dissociation. For example, the nitroaromatic compounds of this study dissociate on the nanosecond time scale, and they complete several rotations before dissociation, leading to an isotropic distribution of the photofragments. To obtain the transition dipole information for these large molecules, methods to place steric controls on the molecule before dissociation have been developed. For polar symmetric top molecules, this has been accomplished via hexapole focusing of a molecular beam. Unfortunately, few molecules of general interest fit into this category. On the other hand, orientation in a strong, uniform electric field prior to laser excitation has been developed, and this method of orientation makes it possible to study any polar molecule, provided a sufficiently low rotational excitation can be achieved. This process is termed Brute Force Orientation, and it is the central technique developed in this study.

When orientation is achieved prior to excitation with polarized radiation, the orientation of the molecule in the laboratory frame, and therefore the projection of the molecular frame in the laboratory frame, are readily known. By alternating the laser polarization between parallel and perpendicular relative to the orientation field, we are able to determine the direction of the transition dipole relative to the permanent dipole of the molecule. This then yields information about the symmetry of the transition dipole and the excited electronic state accessed in the transition.

In this study we need a detectable photofragment that we can correlate to a preferred polarization for absorption by the oriented molecule. The detection method can be either Resonantly Enhanced Multi Photon Ionization or Laser Induced Fluorescence depending on the nature of the fragment. The photofragment yield is then compared for excitation with a laser polarized parallel and perpendicular to the electric field and a polarization ratio is obtained. By coupling this experimental ratio with theoretical modeling of the oriented molecule we are able to obtain the angle of the transition dipole relative to the permanent dipole of the molecule.

Before we are able to complete an orientation experiment for a given molecule, we must survey the spectral region we wish to study to determine the optimal experimental conditions. As these surveys are being completed, we are also able to characterize spectroscopic details associated with the photofragmentation process. Hence, additional information on the dissociation mechanism is obtained.

1.2 NITROAROMATIC COMPOUNDS

The nitrobenzene (NB) and the nitrotoluene (NT) isomers are not large in many senses, but they behave as large molecules with rapid internal conversion upon electronic excitation, resulting in unresolvable rovibronic spectra as shown in Figure 1.1. The dissociation of NB and NT is also known to be slow, and vector correlation studies are therefore impossible to derive the direction of the transition dipole. However, the large permanent dipoles of these compounds make them ideal candidates for the use of polarization spectroscopy in a DC electric field.

Experimental measurement of the transition dipole is essential for the calibration of quantum mechanical calculations. Table 1.1 demonstrates this need in the case of nitrobenzene, where calculations using different packages have yielded a wide variety of symmetries for the excited singlet states. In our previous study, we have determined that the PPP, AM1, and MP2/6-31G* calculations produced the proper symmetry for the second singlet excited electronic state (S_2).^{1, 2} Interestingly,



Figure 1.1 Absorption Spectra of Nitrobenzene and the Three Nitrotoluene Isomers. S_1 , S_2 , and S_3 refer to the first, second and third excited singlet transitions for the respective molecule. The intensities of the spectra are normalized at 190 nm for graphing purposes. No information of the relative cross section is represented. The assignments are from Nagakura.³

Table 1.1 Symmetry Species for Nitrobenzene from Theoretical Calculations. This table presents the published calculation results for the excited states of nitrobenzene. There is obvious disagreement between the different techniques and a definite need for experimental determination of the excited state symmetry.

Excited	Method	PPP	SINDO	AM1	MP2/	CAS-
State		(1979)	1/CI	(1988)	6-31G*	SCF
			(1984)		(1995)	(1997)
S ₁	Symmetry	¹ B ₂	¹ B ₂	¹ B ₁	${}^{1}A_{2}$	${}^{1}A_{2}$
S ₂	Symmetry	¹ B ₁	${}^{1}A_{1}$	¹ B ₂	¹ B ₁	¹ A'
S ₃	Symmetry	¹ B ₁	${}^{1}A_{1}$	${}^{1}A_{1}$	${}^{1}B_{2}$	$^{1}A_{2}$

the most recent calculation using CAS/SCF did not capture the essence of this electronic transition. In this study, we will further investigate the effect of methylation and the position of methylation on the direction of the transition dipole. We will demonstrate that, surprisingly, the AM1 calculation has produced the excited state geometry of the S_2 and S_3 states for the nitroaromatic systems studied, while more sophisticated methods disagree with our experimental results.

While completing the analysis of the transition dipole symmetry for the nitroaromatic compounds, we have also studied the dynamics of this dissociation process. This information is important in understanding the explosive nature of the nitroaromatic compounds. Prior to our work, nitrobenzene (NB) has been extensively studied, but there are significant disagreements in the literature over the dissociation process.⁴⁻¹² We have briefly examined NB with an attempt to resolve the discrepancies, but the bulk of our dissociation dynamics work concentrates on the nitrotoluene (NT) isomers. We discovered that the dissociation dynamics of the NT isomers are much more complicated than those previously reported for NB. We have determined that the basic process for dissociation of NT to produce nitric oxide is similar to that of NB, but that the ground electronic state of a NO₂ photofragment plays a larger role in the dissociation than previously proposed for NB. Our observations also provide significant evidence that multiple dissociation channels are being accessed for the excitation wavelengths studied.

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Chapter 2

Experimental Details

2.1 GENERAL SETUP

The experiments presented in this work were performed using a supersonic molecular beam apparatus designed for investigations of molecules in a gas phase, collision free environment. The schematic in Figure 2.1 shows the basic components of a two laser experiment; the primary modification needed to perform a one laser experiment was to remove one of the lasers. The sample was injected into the source chamber through a pulsed, piezo-electric actuated valve. After passing through a skimmer and reaching the reaction chamber, it was intercepted by the counter propagating pump and probe lasers. The ions or fluorescence produced from the probe laser excitation were then detected by a multichannel plate (MCP) detector or a photomultiplier tube (PMT) respectively. A time of flight mass spectrometer (TOF-MS) in the reaction chamber provided the additional mass information for the detected ions. The pulsed analogue signal was then converted into digital data through the data acquisition system and stored in the computer for analysis.

A personal computer was the center of the control system with a timing board and an interfacing data acquisition board connecting all the different aspects of the experiment. A custom visual basic program issued the command to scan the dye lasers, provided the necessary trigger pulses, and recorded the experimental data. The timing board was used as the central time keeper and provided the trigger pulse to the



Figure 2.1 General Schematic of Experimental Apparatus. This figure shows the basic flow path of the sample, laser beams, timing pulses, and signals needed for data acquisition in a two laser experiment. One of the laser systems was removed for one laser experiments.

pulsed valve, and a synchronized pulse generator (DPG, Stanford Research Systems, DG535) controlled the triggers for the lasers, boxcars, and oscilloscope. The sequence of events started with a trigger to the pulsed valve, and then the dissociation laser was fired and the boxcars were ready for data acquisition. Finally, the probe laser was fired and the data were acquired.

2.2 LASER SYSTEM

Q-switched Neodymium Yttrium Aluminum Garnet (Nd:YAG) lasers were the basic light sources of these experiments. The pump or dissociation laser could be either a Nd:YAG (Spectra Physics, GCR 190) pumped dye laser (LAS, LDL 20505), frequency doubled to generate the appropriate wavelength, or the 5th harmonic of a Nd:YAG laser at 213 nm. The probe laser was scanned to reach resonant transitions of a dissociation fragment or the parent molecule, and it was invariably a frequency doubled Nd:YAG (Spectra Physics, GCR 230) pumped dye laser (LAS, LDL 2051) system. Frequency doubling to obtain wavelengths between 213 - 280 nm was achieved using a beta-barium borate (BBO) crystal (β -BaB₂O₄), while for longer wavelengths, a potassium dihydrogen phosphate (KDP) crystal (KH₂PO₄) was used. The doubling crystal was placed in the laser beam and oriented using an Inrad Autotracker III system or a pre-programmed doubling unit. As the dye laser scanned, the angle of the crystal was adjusted through a feedback system in the Autotracker or through a pre-determined calibration function in the doubling unit, so as to maintain a maximum output of the doubled light. The doubled light was separated from the

fundamental beam by either a color filter or a double Pellin-Brocha (PB) prism setup. In the latter setup, two PB prisms were arranged as mirror images of each other to compensate for the change in the pointing direction of the frequency doubled beam. The thus obtained pointing stability enabled scans in wavelength without the need for frequent optical adjustment. The maximum energy output after the PB prisms was approximately 2.0 mJ/pulse for the frequency doubled beam. Table 2.1 lists the various laser dyes used in this set of experiments and the corresponding tuning range of each dye.

In the polarization spectroscopy experiment, the linearly polarized pump beam was passed through a half wave plate (CVI Lasers) to allow adjustment of the polarization direction relative to the vertical electric field between the electrodes. The fluorescence or ionization yields of the parent or fragment molecules obtained under vertical (parallel to the orientation field) and horizontal (perpendicular to the orientation field) excitations were compared, and the ratio obtained was termed the polarization ratio in this work.

2.3 MOLECULAR BEAM

2.3.1 Seeding and Expansion

Supersonic cooling of the sample was achieved by seeding the sample into a helium carrier gas at a high pressure, typically about 2 atm. The carrier gas was

Table 2.1 Summary of Laser Dyes. A Nd:YAG laser was the pump source in all cases; all dye solutions were prepared in methanol. The tuning range and wavelengths of maximum intensity are given for the fundamental output. In the experiment, only the frequency doubled output was used.

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

expanded into the high vacuum source chamber operating at 10^{-5} - 10^{-6} Torr through a pulsed valve with a nozzle diameter of 0.5 mm and an opening duration of ~ 200 µs. The rapid expansion did not allow time for heat to be transferred between the gas and the surroundings, resulting in an adiabatic condition. As the gas expanded, a group velocity developed along the symmetry axis of the nozzle pointing away from the pulsed valve. The work done in the expansion led to rapid cooling of the thermal translational and internal energies of the sample molecules. The resulting rotational temperature was typically in the range of a few Kelvin. The center portion of the molecular beam was extracted by a 0.5 mm diameter skimmer that separated the source chamber from the reaction chamber. The small orifice skimmer performed two essential functions: extraction of the coldest portion of the molecular beam, and isolation of the experimental chamber from the source chamber. This latter function decreased the pumping requirements in the experimental chamber while maintaining it at a higher vacuum.

While a low uniform rotational temperature was crucial to polarization spectroscopy in the gas phase, it was not necessary for studies of photodissociation dynamics. In the latter case, the skimmer was removed and the pulsed valve was pushed closer to the interaction region. This adjustment significantly increased the flux of the molecular beam in the detection region and hence the signal to noise ratio.

2.3.2 Pulsed Valve

The pulsed valve had a stainless steel body, a piezo electric actuator, a connecting rod (plunger), and a viton O-ring at the tip of the plunger. Figure 2.2 shows the basic layout of the valve. When a large negative voltage was applied to the actuator, the thin piezo electric coating contracted radially, causing a concave deformation of the actuator facing the pulsed valve nozzle. The plunger, and hence the O-ring at the tip of the plunger, was then pulled backwards from the seating surface of the valve, opening the seal for gas release. The movement of the plunger was in the μ m range, just enough to slightly unseat the O-ring. This design thus allowed for the fast action with fine control of sample gas flow necessary for experimental control. The pulsed valve was operated at 10 Hz with a pulse duration of approximately 200 μ s.

2.3.3 Vaporization of Non-volatile Species

The nitroaromatic compounds have low vapor pressures at room temperature. Special care was necessary to successfully observe these species in our experiment. Figure 2.3 shows the seeding method used for preparing the sample. An interesting aspect of the sample preparation process is that it was often necessary to place the sample in the system under vacuum for a few days to allow the compound to saturate the gas line. Even after this preliminary action, we still occasionally needed to



Figure 2.2 Layout of the Pulsed Valve. When a negative voltage was applied to the piezo electric material, it contracted and caused the plunger to move back from the seating surface for gas passage. The pressure difference across the nozzle led to supersonic expansion and internal cooling of the gaseous sample.


Figure 2.3 Flow of the Nitroaromatic Sample into the Vacuum Chamber. Helium was bubbled through the liquid sample to seed with the desired species. The gas mixture was then delivered to the pulsed valve through a stainless steel pipe.

physically coat the tubing leading to the pulsed valve with the sample. This need of "passivation" was attributed to adsorption onto the inner surface of the tubing. The solid para-nitrotoluene (p-NT) sample was the most difficult to vaporize, and moderate heating to approximately 363 K was applied.

The rotational temperature of the nitroaromatic molecules was estimated by co-expanding pyrimidine (1,3-diazine) with the nitroaromatic sample through the pulsed valve. The LIF signal of pyrimidine was then simulated to determine the rotational temperature. The size and shape of pyrimidine is similar to that of the nitroaromatic molecules in this experiment, and we expect the expansion to have a similar cooling effect. This piece of information was essential in the data analysis of polarization spectroscopy.

The extreme non-volatility of nucleic acid bases required extensive heating for vaporization. Figure 2.4 shows a modified pulsed valve designed for this purpose. An oven located at the front of the pulsed valve was used for sample heating, and the maximum operational temperature was 573 K. The piezo electric actuator was isolated from the oven by mounting it onto a water cooled copper disk. With this design, we were able vaporize 1,3-dimethyluracil and supersonically cool the sample to a rotational temperature of a few Kelvin.



Figure 2.4 Heated Pulsed Valve. This valve was designed to vaporize non-volatile species while maintaining supersonic cooling. The sample was placed in the oven and heated while the helium carrier gas passed through the valve at approximately two atmospheres of pressure. Cooling water was used to maintain the operational temperature of the piezo electric actuator. Adequate thermal isolation between the piezo electric actuator and the heated oven was essential for the operation of this valve.

2.4.1 Resonantly Enhanced Multi Photon Ionization (REMPI)

2.4.1.1 Basic Method for REMPI

The basic principle of resonantly enhanced multiphoton ionization ¹⁻¹¹ is shown in Figure 2.5. At least two photons are required to achieve ionization. The first photon or group of photons will achieve resonant excitation, while the second photon or group of photons will ionize the excited molecule or atom. The resonant enhancement in the first step and the high detection sensitivity of ions in the second step make this method one of the most sensitive tools in spectroscopy. If the photons in both steps are from the same laser beam, i.e. a one color experiment, the notation is (m + n), where m denotes the number of photons in the first step and n denotes the number of photons in the second step. If the photons for the two steps are from different laser beams, i.e. a two color experiment, the notation is (m + n'). For the studies presented in this work, all processes were (1+1).

The spectroscopic information of a REMPI experiment is carried in the first step of excitation. In the second step, the effect of the photon is to uniformly ionize all of the excited species prepared in the first step. As the first laser scans across different rovibronic transitions, enhanced ion production is directly proportional to the probability of the corresponding transition. Although there are reasons to doubt the



Figure 2.5 Diagram of (1+1) Resonantly Enhanced Multi Photon Ionization (REMPI) Used for NO Detection. Two photons of equal energy were absorbed by the molecule of interest. The first photon resonantly excited the NO to the first excited electronic state, while the second photon further ionized the excited species for ion detection.

assumption of the uniform ionization yield in the second step of REMPI, judicious choices of ionization wavelengths have proven the method possible and effective.

2.4.1.2 Time of Flight Mass Spectrometer (TOF-MS)

A time of flight mass spectrometer works on the basic premise of Newton's first law of motion where an object's velocity is constant unless an external force is exerted on it. This method is for detection of ions that have a given kinetic energy, but have different mass to charge ratios. Under this condition, different masses will have different velocities and hence different time of flight in a field free drift region. In our experiment, the singly ionized ions were formed in the interaction region between the two electrodes as shown in Figure 2.6. They were then accelerated due to a potential difference between the two electrodes. The kinetic energy gained in this region should be equal to the potential energy of the ions when they were formed. After passing though the meshes on the negative electrode and entering the field free region inside the tube, the ions traveled at a constant velocity towards the detector. A heavier ion with a larger mass to charge ratio takes more time to arrive at the detector. By recording the time of arrival of the different ions, we obtained their mass to charge ratios. Although our emphasis was not on mass resolution, this capability was necessary for isolating an ion of a specific mass for analysis.



Figure 2.6 Experimental Diagram Showing the Arrangements of Mechanical and Electrical Components in the Vacuum Chamber.

The process of laser induced fluorescence is similar to that of REMPI, except that in LIF, fluorescence from the resonance state is observed instead of ionization by an additional photon. The schematic energy level diagram of LIF is shown in Figure 2.7.¹²⁻¹⁶ This method requires a fluorescing excited state. Whenever the excitation energy scans through a resonance of the molecular system, an increase in the total fluorescence or phosphorescence will be observed. The fluorescence intensity depends on the absorption probability of the molecular system. Using a scanning laser, the resonance structure of the molecule can be mapped out, and the population distribution at the different levels of the ground state can be determined. This technique can be difficult because of the low fluorescence intensity and low collection efficiency of typical fluorescence detectors. Moreover, knowledge of the fluorescence wavelength is also helpful in determining the proper color filters for rejection of background scattering from the excitation laser.

2.5 BRUTE FORCE ORIENTATION

Brute Force Orientation is a type of field induced orientation where a polar molecule is oriented in a strong, uniform external electric field due to the interaction between the permanent dipole of the molecule and the field. As a free rotating polar molecule enters the uniform field, it experiences a torque from the field. If this torque is large enough, the molecule will be forced to precess around the direction of the



Figure 2.7 Schematic of a Laser Induced Fluorescence (LIF) Experiment. After excitation to an upper state, the total fluorescence signal is collected. The fluorescence intensity distribution as a function of the excitation wavelength thus maps out the resonant levels of the molecular system.

electric field, and the permanent dipole of the molecule is preferentially oriented with the field, as shown in Figure 2.8. This process will only occur if the ratio of the electrostatic potential energy and the rotational energy, $f = \mu E/E_r$, is sufficiently large.¹⁷ Typical values of f are between 0.01 and 0.001 for polar molecules at room temperature.¹⁷ For orientation to occur, however, the field-dipole interaction must dominate, with $f \ge 1$.¹⁷ The rotational temperature of a molecular beam can be reduced to a few Kelvin, leading to f >> 1 for modest field strengths; orientation in a strong electric field thus becomes feasible.^{7, 11, 17-29}

To examine this process quantum mechanically, we first need to consider the kinetic and potential energies, which form the Hamiltonian of the system. The interaction between the permanent dipole of a polar molecule (μ) and an electric field **E** results in a potential well, the depth of which is mathematically determined by μ E. Since rotation is the primary degree of freedom altered in the electric field, we can define the pendular wavefunctions of the molecule in the potential well in terms of the field free rotational wavefunctions. The Hamiltonian in the Stark field is then:

$$H = J^2 - \omega \cos \theta \quad (\text{Eq.2.1})$$

where $\omega = \frac{\mu E}{B}$, and B is the rotational constant of the molecule.¹⁷ As the field strength is increased, the change in energy for the pendular states can be complicated and can lead to level crossings. However, over a certain range of field strength for a given molecule, the change in energies can be approximately described as linearly dependent on the field strength.³⁰ This leads to the description of first order Stark effect.



Conditions for Orientation

- Strong electric field (typically 50 kV/cm)
- 2. Large permanent dipole
- 3. Low rotational temperature

Application of Technique

- 1. Selective excitation of electronic transitions.
- 2. Transition dipole moment directions

Figure 2.8 Basic Requirements of the Brute Force Orientation Method for Aligning a Molecule.

When a molecule passes into the strong uniform electric field and is oriented, it changes from a freely rotating state to a two dimensional harmonic librator where it is free to rotate around the direction of the field. The oscillatory behavior of the molecule in the other two dimensions closely resembles that of the two dimensional harmonic oscillator, provided that the potential well is sufficiently deep. In the limit of an infinite field, the energy levels of a harmonic librator should be equally spaced. Figure 2.9 shows the correlation of the energy levels of a linear molecule from free rotational states to Harmonic Librators. The rotational wavefunctions are mixed by the Stark field to form new Stark states. The total angular momentum is no longer a good quantum number, but the magnetic quantum number remains good. The new states are referred to as pendular states, described by the magnetic quantum number M and a new quantum number v_p , with $v_p = (2J - |M|)$.³¹ For each librator state v_p , there is still a degree of degeneracy of $[v_p/2]$, corresponding to the different values of M. The two dimensional oscillation of the librator produces an equivalent rotation around the field direction, and the angular momentum of this rotation ranges from v_p to 0 (or 1) by a stepsize of 2. To a certain degree, a 2-D librator is the same as the degenerate bending vibration of a linear molecule such as CO₂. It is interesting to note that, unlike a magnetic field, the electric field does not lift the degeneracy in the M value completely. In a low field, the degeneracy is two for each M > 0 level, but in the limit of high fields, the degeneracy further increases due to complete mixing of different states with different total rotational quantum number J.

The selection rule in an electric dipole transition of pendular states is a combination of the standard rotational and vibrational selection rules. Since J is no



Figure 2.9 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. The lines connecting the low and high field states are linear for simplicity. Actual solutions are much more complicated.

longer a good quantum number, the only restriction in angular momentum quantum number is in M, with $\Delta M = 0, \pm 1$. The transition $\Delta M = 0$ is allowed when the electric field of the photon is parallel to the external field, and the transition $\Delta M = \pm 1$ is allowed when the polarization direction of the excitation laser is perpendicular to the field.³¹ From the correlation diagram in Figure 2.9, we can see that the $\Delta M = 0$ transition can only be achievable if $\Delta v_p = \pm 2$, and $\Delta M = \pm 1$ is only possible for $\Delta v_p = \pm 1$. In comparison, for a 1-D harmonic oscillator, the selection rule is $\Delta v = \pm 1$ in the harmonic approximation. If anharmonic behavior is manifest, overtone transitions with $\Delta v = \pm 2, \pm 3...$ become allowed. In an electric field, the potential is of the form of $\cos \theta$ with a high degree of anharmonicity. This anharmonicity makes transitions with $\Delta v_p = \pm 1, \pm 2$ possible when the electric field is low. As the field strength is increased, the system becomes increasingly harmonic. Based on the harmonic oscillator selection rule, the $\Delta v_p = \pm 2$ transition should become progressively less probable, especially for states deep in the potential well. Since transitions with $\Delta v_p = \pm 2$ are associated with $\Delta M = 0$ where the laser should be polarized parallel to the electric field, as the field strength increases, the probability of absorption for parallel polarized light should decrease. This absorption probability of polarized light for pendular state transitions has been proposed as a parameter in determining the degree of orientation.³¹ Electronic transitions are independent of this effect, because electronic energy level spacing is much larger than the field energies, thus are not effected by the field. For our experiments we utilize a $\Delta v_p = 0$ and

 $\Delta M = 0$ selection rule for the pendular states when investigating electronic transitions.

The emphasis of our experiment was to use the thus achieved molecular alignment to derive the direction of the electronic transition dipole. This was accomplished by measuring the orthogonal projections of the transition dipole in a space fixed lab frame, then transforming the projections into the molecular frame with the appropriate theoretical treatment. This transformation process through the Euler angles is presented in Figure 2.10. This figure demonstrates that the spatial orientation of the transition dipole is dependent on the orientation of the permanent dipole in the lab frame. If the permanent dipole has a preferred orientation in space, as is the case when Brute Force Orientation is employed, the transformation process allows for a complete analysis of the obtained polarization ratio and determination of the transition dipole, relative to the permanent dipole.

Details of the coordinate transformation are known from general physics. We assigned the electric field direction as the lab frame Z-axis. The permanent dipole of the molecule was assigned to the molecular z-axis, and the transition dipole was assigned to be in the x-z plane of the molecular frame for simplicity. The permanent dipole will precess around the Z-axis with in a cone defined by the angle θ . Additionally, the transition dipole will precess around the permanent dipole, forming a cone of angle α . The symbols ϕ and χ were used to denote the azimuthal angles of the lab and molecular frames respectively. Transformation of the molecular coordinate system can then be achieved via the rotation matrix



Figure 2.10 Transformation of Molecular Frame to Laboratory Frame for an Aligned Molecule. This diagram shows the relevant Euler angles. The transition dipole was placed in the x-z plane for mathematical simplicity.

$$\begin{bmatrix} Z \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} C\phi C\theta C\chi - S\phi S\chi & -C\phi C\theta S\chi - S\phi C\chi & C\phi S\theta \\ S\phi C\theta C\chi + C\phi S\chi & -S\phi C\theta S\chi + C\phi C\chi & S\phi S\theta \\ -S\theta C\chi & S\theta S\chi & C\theta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (\text{Eq. 2.2})^{32}$$

where $C = \cos$ and $S = \sin$.

In the molecular frame, the transition dipole is given as

$$\boldsymbol{\mu}_{t} = \boldsymbol{\mu}_{t} \begin{pmatrix} \sin \alpha \\ 0 \\ \cos \alpha \end{pmatrix}. \quad (\text{Eq. 2.3})$$

In practice, to obtain the direction of the transition dipole, we needed to know the degree of molecular alignment and relate the spatial distribution of the permanent dipole to the probability of excitation under different polarization directions of the excitation laser. Kong and Bulthuis have developed a model to predict the distribution of the molecular permanent dipole in an electric field.³³ In this model, the population in each pendular state was assumed to be in thermal equilibrium at the temperature of the molecular beam. With knowledge of the permanent dipole of a molecule, rotational temperature, and field strength, the distribution of the permanent dipole can be determined relative to the field direction. The inherent cylindrical symmetry required a distribution function that is dependent only on the polar angle θ . The equation is given by

$$P(\cos\theta) = \int_{0}^{2\pi} P(\cos\theta, \phi) d\phi = \frac{1}{2} \left[\sum_{n=1}^{\infty} a_n P_n(\cos\theta) \right] \quad (\text{Eq. 2.4})^{33}$$

where a_n represents the expansion coefficients. i.e., the multipole values, and P_n represents the Legendre polynomials. Odd values of n correspond to orientation of the permanent dipole and even values correspond to alignment. In particular, alignment does not distinguish the difference between "head" and "tail", while orientation is a dipolar property. The principle of our experiment dictated that we were only sensitive to the alignment of the molecule. More specifically, only a_2 could be probed in a single photon process using linearly polarized light.³³

Once the distribution function was determined, the transition probabilities under parallel and perpendicular polarizations of the excitation laser could be obtained. Absorption of linearly polarized light follows:

$$A_{\parallel}(\alpha) \propto \int_{0}^{2\pi} d\phi \int_{0}^{2\pi} d\chi \int_{0}^{\pi} P(C\theta) \left[S\theta C\chi S\alpha - C\theta C\alpha \right]^{2} S\theta d\theta \quad (\text{Eq. 2.5})$$
$$A_{\perp}(\alpha) \propto \int_{0}^{2\pi} d\phi \int_{0}^{2\pi} d\chi \int_{0}^{\pi} P(C\theta) \left[C\phi C\theta C\chi S\alpha - S\phi S\chi S\alpha - C\phi S\theta C\alpha \right]^{2} S\theta d\theta \quad (\text{Eq. 2.6})$$

Using these results, a ratio of light absorbed perpendicular to the electric field to that parallel to the field ρ , i.e., the polarization ratio, is given by:

$$\rho(\alpha) = \frac{A_{\perp}(\alpha)}{A_{\parallel}(\alpha)}.$$
 (Eq. 2.7)

This was the quantity derived from our experiment. By varying the angle between the two dipoles for the theoretical polarization ratio and comparing with experiment, we were able to determine the direction of the transition dipole. This method has resulted in good quantitative agreement between experiment and theory.

2.6 SPECTROSCOPY OF NITRIC OXIDE

Nitric oxide was the photofragment detected in our study of nitroaromatic compounds; and characterization of the NO photofragement with REMPI allowed us to study the dissociation process in detail. The energy disposal upon photoabsorption is of interest in systems where the fragments are of biological significance, or the decomposition reactions are known to be highly energetic. In this study, we characterized the rotational, vibrational, Λ -doublet, and spin-orbit populations to obtain insight into the decomposition mechanism of the relevant species. In this section, some relevant spectroscopic information of NO will be discussed.

2.6.1 Energy Levels of NO

The electronic configuration of NO is

$$(\sigma_{1s})^{2}(\sigma_{1s}^{*})^{2}(\sigma_{2s})^{2}(\sigma_{2s}^{*})^{2}(\sigma_{2p_{z}})^{2}(\pi_{2p_{y}})^{2}(\pi_{2p_{x}})^{2}(\pi_{2p_{y}}^{*})^{1}.^{34}$$

There is an unpaired electron in the π^* orbital, and thus the radical has a total electronic spin of $S = \frac{1}{2}$ and an orbital angular momentum projection along the internuclear axis of $\Lambda = 1$. Hund's case (a), as shown in Figure 2.11, both the orbital angular momentum and the spin angular momentum are strongly coupled to the internuclear axis.³⁵ For hund's case (a) is a reasonable description for low rotational states, because the spin-orbit coupling constant A is 124.2 cm⁻¹, considerably larger than the rotational constant of 1.7046 cm⁻¹.³⁵ For high J states, a progression to



Figure 2.11 Hund's Case (a). This diagram depicts the angular momenta of a diatomic molecule. J is the total angular momentum, L is the orbital angular momentum of the electron, S is the spin angular momentum of the electron, N is the nuclear rotational angular momentum of the molecule, Λ is the projection of L along the internuclear axis, Σ is the projection of S along the internuclear axis, and Ω is the vector sum of Λ and Σ along the internuclear axis. The key feature of Hund's case (a) is that there is a strong coupling of both the spin and orbital electronic angular momentum to the internuclear axis.

case (b) occurs where the electron spin is no longer coupled to the internuclear axis. Using case (a) the resulting projection of the total electronic angular momentum along the internuclear axis is $\Omega = \frac{3}{2}$ or $\frac{1}{2}$, depending on the relative orientation of the spin and orbital angular momenta. Each spin-orbit doublet component, ${}^{2}\Pi_{1/2}$ or ${}^{2}\Pi_{3/2}$ denoted as F₁ or F₂ respectively, is further split into two symmetry adapted parity states. The first allowed electronic transition, which was used in our detection of NO, involved the promotion of the unpaired electron to a σ orbital. The excited electronic state, $A^2\Sigma^+$, is also split into F_1 and F_2 components, corresponding to the e and f parity. The two states are degenerate, arising from coupling of the spin with the rotational angular momentum in Hund's case (b). The $A^2\Sigma^+ \leftarrow X^2\Pi$ transition is referred to as the gamma band of NO, and there are twelve rotational branches possible for each vibronic transition. Figure 2.12 shows example transitions for the twelve rotational branches involving $F_1 \leftarrow F_1$, $F_2 \leftarrow F_2$, $F_1 \leftarrow F_2$, $F_2 \leftarrow F_1$ transitions from the ground to electronically excited state. These branches are labeled using a subscript representing the spin-orbit component of both the initial and final state. Transitions from F1 to F1 or F2 to F2 correspond to the six main branch transitions. Transitions from F_1 to F_2 or F_2 to F_1 correspond to six satellite branches. The transition frequencies of four of the satellite braches completely overlap with four of the main branches: Q11 overlaps with P21, R11 overlaps with Q21, Q22 overlaps with R12, and P22 overlaps with Q12. This overlap arises from the double degeneracy of F_1 and F_2 in the $A^2\Sigma^+$ state.



Figure 2.12 Energy Level Diagram of the NO Radical. This figure also shows the initial and final states of the 12 branches of the vibronic transition. The spacing of the levels is not to scale. The total angular momentum is denoted J, and N is the nuclear rotational angular momentum. The label P refers to the total parity, and P_e refers to the electronic parity. All of the levels in the ${}^{2}\Sigma^{+}$ state are doubly degenerate, except for J = ${}^{1}\!/_{2}$, with *e* and *f* parity associated with the F₁ and F₂ states respectively.

The term values for the ${}^{2}\Sigma^{+}$ state can be calculated using

$$F_1(e) = B(J - \frac{1}{2})(J + \frac{1}{2})$$
 (Eq. 2.8),
 $F_2(f) = B(J + \frac{1}{2})(J + \frac{3}{2})$ (Eq. 2.9)

and for the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ components, 36

$$F_{1} = E_{\frac{1}{2}} = -\frac{A}{2} + B(J + \frac{1}{2})^{2} - \frac{B^{2}[(J + \frac{1}{2})^{2} - 1]}{A} \quad (\text{Eq. 2.10}),$$

$$F_{2} = E_{\frac{3}{2}} = \frac{A}{2} + [B(J + \frac{1}{2})^{2} - 2] + \frac{B^{2}[(J + \frac{1}{2})^{2} - 1]}{A}. \quad (\text{Eq. 2.11}).$$

The absorption intensity of a rovibronic transition is given by³⁵

$$I = I_0 N_{v'',J} \langle v' | v'' \rangle^2 |R_e|^2 S_J \quad \text{(Eq. 2.12)}$$

where I₀ is the intensity of the incident radiation, $N_{v,J}$ is the population in the given rotational and vibrational level, $\langle v' | v'' \rangle^2$ is the Franck-Condon Factor, $|R_e|^2$ is the electronic transition probability, and S_J is the rotational line strength factor, or Hönl-London factor. The overlapping satellite branches start in the same level of the ground state as the main branches they overlap with. This means that the overlapping branches should have the same initial state population. Based on Eq. 2.12, the only term that is different for the pair of overlapping branches is the line strength factor, S_J . If the experimental intensity I is divided by the sum of S_J for the overlapping branches, we can derive the population of the ground state, in spite of their overlapping nature.

2.6.2 Rotational Population and Average Rotational Energy

Based on the previous section, to obtain the rotational population distribution of a vibrational state, we first needed to assign the observed transitions and thus to obtain the relevant Hönl-London factors. Congestion of the NO spectrum, due to multiple branches and band head structures, significantly increased the difficulty of spectral assignment. The vibrational excitation of the NO fragment further resulted in hotbands overlapping with the $A^2 \Sigma^+ (v'=0) \leftarrow X^2 \Pi (v''=0)$ band and transitions beginning in v" = 3 and v" = 4 overlapping with the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=2)$ band. We used the LIFBASE simulation package to assist with spectroscopic assignment and to obtain the Hönl-London factors.^{37, 38} Since the Franck-Condon factor and the electronic transition probability were the same for a given vibrational band, the population of a rotational level was directly proportional to the intensity in the REMPI spectrum after correction with the Hönl-London factor. The resulting relative populations were then fit to a Boltzman distribution using the linear regression method by fitting ln(Intensity/Hönl-London factor) vs. J(J+1). The slope of the fitting result was inversely proportional to the equivalent rotational temperature of the molecule. An average rotational energy of the NO fragment was then obtained by calculating a weighted average truncated to the J = 79.5 level:

$$E_{rot} = c_1 E_{J=0.5} + c_2 E_{J=1.5} + c_3 E_{J=2.5} \dots c_{80} E_{J=79.5} \quad (\text{Eq. 2.13})$$
$$\overline{E}_{rot} = \sum_{J=0.5}^{79.5} c_{J+0.5} E_J \quad (\text{Eq. 2.14})$$

where $c_{J+0.5}$ was the normalized population and E_J was the rotational energy for a given state J.

2.6.3 Vibrational Population

Overlapping hotband transitions, for example, $A^2 \Sigma^+(v'=1) \leftarrow X^2 \Pi(v''=1)$ and $A^2 \Sigma^+(v'=2) \leftarrow X^2 \Pi(v''=2)$ bands in the region of the

 $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band, pose a serious challenge for spectroscopic assignment of rotational transitions, but they provide crucial information in deriving relative populations of the related vibrational levels. Since the overlapped bands were recorded in the same wavelength region under the same experimental conditions, direct comparison of vibrational populations was possible provided that the relevant Franck-Condon factor for each vibrational band and the Hönl-London factor for each rotational transition were known. In practice, we chose the same rotational level in each branch for such a comparison, and the effect of the Hönl-London factor was also canceled out. The relative population of a chosen vibrational level was obtained by dividing the intensity of the observed transition by the Franck-Condon factor.

For some of the NT isomers, analysis of vibrational levels with v'' > 2 was attempted but the results were inconsistent. Populations for v'' = 3 and 4 were found from the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=3)$ band and the $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=4)$ band that overlapped with the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=2)$ band. In addition, the v''=3 level was also observed from the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=3)$ band in an extended scan of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=2)$ band. Unfortunately, these two methods produced different results and we therefore chose not to include them in our discussion.

When the relative vibrational populations were obtained, they were normalized and used to calculate the average vibrational energy. The energy for each level was calculated using

$$E_{v} = \omega_{e}(v + \frac{1}{2}) - \omega_{e}x_{e}(v + \frac{1}{2})^{2} + \omega_{e}y_{e}(v + \frac{1}{2})^{3} \quad (\text{Eq. 2.15})$$

The weighted vibrational energies for each level were then summed to obtain the average vibrational energy.

2.6.4 Λ-Type Doubling

A-type doubling in NO is due to the coupling of the rotational motion of the diatomic molecule with the angular momentum of the unpaired electron in the π orbital. This relationship has been discussed in detail by Andresen and Rothe.³⁹ Briefly, this coupling results in states with different parity based on the orientation of the π orbital relative to the plane of rotation. If the π lobe is out of the plane of rotation, the electronic state is assigned the "+" electronic parity (π^+), while an in plane π orbital results in π^- electronic parity. Among the 6 main branch transitions, incidentally, all Q branches originate from π^+ state, while the P and R branches originate from π^- states. The intensity ratios of these branches are therefore reflective of the relative populations in the different parity states. Preferential population of one of the parity states is indicative of a preferred geometry of the transition state during

dissociation.³⁹ In particular, the relative population in the Λ -type doublet is generally used to examine the planarity of the transition state during dissociation.

Another interpretation of the π^+ and π^- states can be obtained using group theory. The symmetry group of NO, including its π orbital, is C_s, as shown in Figure 2.13. In this point group, the direction of the rotational angular momentum is chosen to be the x-axis, and rotation around the x-axis, R_x , belongs to the A' species, while R_z and R_v belong to the A" species. Rotation around either z or y is antisymmetric with respect to reflection in the plane perpendicular to the x-axis. The π orbital of the molecule has two independent orientations in the C_s geometry: parallel to the x-axis (A") or in the plane of rotation (A'). The transition dipole associated with a $\sigma \leftarrow \pi$ transition will need to be perpendicular to the internuclear axis, determined by the orientation of the π electron involved in the transition. If the π orbital is in the plane of rotation, the transition dipole will be along the y-axis of the NO system. This will result in a change in J and hence favor P and R branches. If the π orbital is along the x-axis and parallel to the angular momentum of the system, no change in J can occur, thus a Q branch transition is favored. Thus different branches originate from different orientations of the electron lobe. By analyzing the populations of the different rotational branches, populations in the A' or A" symmetry can be obtained.



Figure 2.13 Symmetry of the NO Molecule Including the Unpaired π Orbital. This figure demonstrates that the molecule and its π system are of C_s symmetry. The plane of the figure is both the horizontal mirror plane of the C_s point group and the plane of rotation of the molecule. Part "a" of this figure shows the π system oriented in the A" irreducible representation and part "b" shows the π system oriented in the A' irreducible representation.

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Dissociation Dynamics of the Nitrotoluene Isomers

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Chapter 3

Dissociation Dynamics of the Nitrotoluene Isomers

3.1 INTRODUCTION

Extensive studies of dissociation dynamics of organic compounds containing the nitro group $(-NO_2)$ have been conducted in vapor and condensed phases.¹⁻⁵⁰ These studies are motivated by a fundamental interest in the explosive nature of many nitro containing compounds, ⁵¹⁻⁵⁷ detection of these compounds as pollutants, ⁵⁸⁻⁶² and delivery of NO in biological systems.^{63, 64} To understand the explosive and bond dissociation characteristics of nitroaromatic molecules, it is necessary to study the process in the isolated environment afforded by a high vacuum, gas phase experiment. The absence of the external effects typically found in the condensed phase allows us to isolate the nitroaromatic properties at the molecular level; this aids in the understanding of the fundamental energetics of the system and lays a foundation for gaining an understanding of the more complex behavior observed in other phases. Nitrobenzene (NB) and nitrotoluene (NT) are prototypical systems for understanding the fundamental effects of the nitro and methyl groups on the nature of the highly energetic dissociation process of nitroaromatic compounds. While nitrobenzene has been extensively studied, there are significant conflicts in the literature on how this process evolves after the absorption of one or more photons. The NT isomers have also been examined, though not to the same extent as NB. In the present study, dissociation of NB and the three NT isomers are examined in the gas phase, and the

results are compared as the methyl group is added and moved relative to the nitro group on the aromatic ring.

Some of the earliest work in the gas phase on dissociation of nitro containing organic compounds was performed on nitromethane due to its simple form and small molecule behavior.^{9, 35, 37-39, 41, 44} Houston's group studied the dissociation of nitromethane in the gas phase at 193 nm and observed two dissociation channels that produced NO₂ and NO. The first channel led to an electronically excited NO₂($^{2}B_{2}$) that subsequently dissociated to $O({}^{3}P)$ and $NO(X^{2}\Pi)$. The second channel produced NO2 in an unidentified excited electronic state that dissociated upon absorption of a second 193 nm photon to produce NO($A^2\Sigma$). There was no evidence of excited vibrational states observed for the NO photofragment in the ground electronic state, and the limit on the population in the v"=1 state was estimated to be less than 10 percent.⁹ This is in contrast to previous reports on the photodissociation of the ground electronic state of NO₂ in the gas phase, where an inversion of the vibrational population was reported with a maximum vibrational population in v'' = 7 by one source and v'' = 5 by another.^{65, 66} These studies on NO₂ also demonstrated a correlated behavior in the rotational energy of NO, where the more populated vibrational states of the NO fragment also had more rotational excitation.

Nitrobenzene is the simplest of the nitroaromatic compounds and has been extensively studied both theoretically and experimentally.^{11-22, 54, 63, 67-93} Dissociation studies of NB have yielded several decomposition pathways. Crim's group proposed three dissociation channels based on the rearrangement of the nitro group to a nitrite upon excitation at 193 nm:

$$C_6H_5NO_2 \rightarrow C_6H_5 + NO_{2,}$$

 $C_6H_5NO_2 \rightarrow C_6H_5O + NO, \text{ and}$
 $C_6H_5NO_2 \rightarrow C_5H_5 + CO + NO.^{14-16, 18}$

Their data indicated a preference for the formation of the NO₂ fragment relative to NO.¹⁵ Recent ultrafast electron diffraction (UED) studies by Zewail's group examined the structural rearrangement of nitrobenzene during dissociation at 266 nm. The authors found no indication of NO₂ formation, but exclusive formation of NO and phenoxy radicals through the isomerization pathway.⁶³ This mechanism of single channel dissociation is in conflict with several previous mass spectrometry results, which showed a variety of fragments during dissociation.^{13, 15, 17, 22}

Studies of the NO photofragment from NB have consistently shown that the fragment is produced highly rotationally excited, but the distribution of vibrational population is controversial.^{14-17, 19, 22} Two groups observed NO only in the ground electronic and vibrational energy levels^{14-16, 22} and from this it was concluded that less than 10% of the NO photofragment was in excited vibrational levels.¹⁴⁻¹⁶ Singhal's group, however, identified NO from the photodissociation of NB in v'' = 0 - 3 of the ground electronic state, demonstrating a significantly higher vibrational excitation than previously reported.¹⁷ The vibrational populations of NO decreased from the highest in v'' = 0 to the lowest in v'' = 3, as would be expected from a somewhat thermal dissociation process.¹⁷ Rosenwaks' group later quantified the population ratios to be 1:0.3:0.1:0.02 for v'' = 0 - 3 respectively.¹⁹

The nitrotoluene isomers have not been as extensively studied as NB. The methyl group is expected to have little effect on the properties of the molecule because

of the abundance of lone pairs and π electrons in the molecular system. This is somewhat verified by the similarity shown in the UV/VIS absorption spectra of all four nitroaromatic compounds presented in Figure 3.1. The assignment of the excited singlet states to the features of this spectra is based on that of Nagakura et al.⁹³ In Figure 3.1, as the methyl group is added and moved from the ortho to the para positions, there are observable red shifts of the spectral feature, indicating that the methyl group does have some effect on the molecular system. In this figure, no compensation was made for the vapor pressure in the cell, and the vertical scale was arbitrarily normalized at 190 nm. (The para isomer is solid at room temperature, while the NB and the ortho and meta-NT isomers are liquid). No relative cross sectional information is therefore implied by the plot.

Work by our group on o-nitrotoluene (o-NT) identified significant similarities to NB and some differences.^{7, 21} The NO fragment was found to have a higher degree of vibrational excitation than that reported for NB^{14-16, 22}, with up to v" = 2 observed, while the transition dipole orientation properties for accessing the S₂ potential surface were essentially the same.^{7, 21} This increased vibrational excitation is consistent with the result by Singhal's group, except that the authors also observed the v" = 3 vibrational level.⁴ Additional mass spectrometry studies performed on the NT isomers by Tönnies' group using single laser excitation at 206 nm and 412 nm found no evidence of NO production from the ortho and meta isomers, and very little from the para isomer.⁹⁴ The lack of NO signal is not surprising since NO does not have significant absorption cross sections in the 206 nm or the 412 nm regions. Additional theoretical work was performed on the NT isomers by Yang's group using


Figure 3.1 Absorption Spectra of Nitrobenzene and the Three Nitrotoluene Isomers. S_1 , S_2 , and S_3 refer to the first, second and third excited singlet transitions for the respective molecule. The intensities of the spectra were normalized at 190 nm for graphing purposes. No information of the cross section is represented. The assignments are from Nagakura.⁹³

Density Functional Theory (DFT), yielding dissociation energies for the C-NO₂ bond of the ortho and para isomers.¹¹ These calculations were in good agreement with the experimental work by Golden's group, where the dissociation energies for NB and the ortho and para-NT isomers in the gas phase were obtained using a CO₂ laser in a pyrolysis setup.⁹⁵

In this present work, we examine NB and the three isomers of NT using a 1+1 REMPI of the NO photofragment produced from photodissociation of the parent molecule. We performed a 1-laser experiment on the ortho-nitrotoluene (o-NT) isomer and 2-laser experiments on the meta-nitrotoluene (m-NT) and para-nitrotoluene (p-NT) isomers. The o-NT experiment focused on dissociation initiated from the S₂ potential surface. The m-NT and p-NT experiments investigated dissociation initiated from both the S₂ and S₃ potential surfaces. The combination of these experiments allowed for a thorough evaluation of the effects of the methyl group on the basic nitroaromatic system.

The results obtained from dissociation of the NT isomers were similar to those obtained for NB, but with key differences. The energy in the rotational degree of freedom for the NO photofragment was similar up to the v'' = 2 state. The vibrational excitation was significantly larger than that observed from the dissociation of NB. The vibrational population distribution showed evidence of an inversion behavior above v'' = 2 for the NO photofragment; and states up to v'' = 5 were clearly observed. No vibrational inversion has been reported for the NO fragment from the dissociation of NB. Coupled with the vibrational inversion behavior was a rotational correlation, where the rotational excitation of NO was higher for higher vibrational levels. This

rotational result was in direct contrast to results reported for dissociation of NB. This rotational and vibrational inversion behavior was observed to become more dominant as the methyl group was moved from the ortho to the para position on the aromatic ring. Density Functional Theory calculations were used to develop a model as to why the inversion behavior was more dominant as the methyl group was moved to the para position on the aromatic ring. We propose that the inversion behavior observed in this study is associated with the possibility that the NO₂ photofragment plays a more important role in the production of NO from the NT systems than from NB. Results of the Λ -doublet analysis show that the NO fragments from photodissociation of NT and NO₂ are created in a similar bond cleavage event. Evidence of at least two dissociation channels is presented.

3.2 EXPERIMENTAL SETUP

Details of the experimental setup have been discussed previously.^{7, 21} In summary, a differentially pumped vacuum chamber was used to produce a supersonically cooled molecular beam. Room temperature NB (Aldrich 99+%), o-NT (Aldrich 99+%), m-NT (Aldrich 99+%), and heated p-NT (Aldrich 99+%, 363 K), were seeded into the helium carrier gas with a stagnation pressure of 1340 torr. The sample was introduced into the chamber through a piezoelectric actuated pulsed valve. The supersonically cooled molecular beam was characterized by seeding pyrimidine (1,3-diazine) into the carrier gas and coexpanding it with the nitroaromatic sample. From the rotationally resolved LIF spectrum of the $\pi * \leftarrow n$

transition of the pyrimidine, a rotational temperature of 2 - 3 K was suggested for molecules in the detection region.

The lasers used in these experiments were frequency doubled Nd:YAG pumped dye laser systems. For the NB and o-NT experiments, a single laser system was used to dissociate the sample molecule and detect the NO photofragment. The laser scanned over the wavelength region for the transition to the S₂ state of the nitroaromatics and simultaneously covered the rovibronic transitions of NO to the $A^{2}\Sigma^{+}$ excited electronic state for 1+1 REMPI detection. The m-NT and p-NT experiments were performed using a two laser set up. The dissociation laser and probe laser were set to counter propagate through the interaction region with a time delay of 20 ns. The dissociation laser was operated at 5 Hz and the probe laser was operated at 10 Hz to allow subtraction of the background from the probe laser. The probe laser was a pulsed Nd:YAG (Spectra Physics GCR 230) pumped dye laser (LAS, LDL 2051), frequency doubled to probe NO fragments between 218 nm and 300 nm by 1+1 REMPI through the $A^2\Sigma^+$ excited electronic state. To generate the required wavelength for photodissociation, either the Nd:YAG laser was used to pump a frequency doubled dye laser (LAS, LDL 20505), or the second and third harmonics of the Nd:YAG laser were mixed using a BBO crystal to generate 213 nm. The dissociation laser wavelengths were chosen based on the UV/VIS spectra in Figure 3.1. The wavelengths of 245 nm for m-NT and 249 nm for p-NT corresponded to the maxima in the cross-section for excitation to the S_2 state. To access the S_3 potential surface, we used a convenient wavelength from our laser system at 213 nm.

The ions produced in the REMPI process were collected in a time of flight mass spectrometer. After passing through the field free region, the ions were collected on a chevron type channel plate detector. The signal from the channel plate was then transmitted to a boxcar integrator (SRS 250). Output from the boxcar was collected by a custom visual basic program on a personal computer.

3.3 RESULTS

3.3.1 meta-Nitrotoluene (m-NT)

3.3.1.1 Dissociation of m-NT from S_2 at 245 nm

The rotational and vibrational energy distributions were measured and analyzed for the NO photofragment from the dissociation of m-NT. For dissociation at 245 nm, transitions involving v"=0 - 5 were observed. The spectra obtained are presented in Figures 3.2 and 3.3. Characterization of the vibrationally excited states with v" > 3 was not possible due to poor signal to noise ratios.

The dissociation of m-NT at 245 nm led to more vibrational excitation of the NO photofragment than was previously observed in nitrobenzene^{15, 16, 22}, as seen in Figure 3.4. The increase in vibrational excitation allowed clear detection of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$ and $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=2)$ bands overlapping with the high rotational lines in the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band. The overlap is shown in Figure 3.2 for the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$ band in the expanded section



Figure 3.2a (Top) Spectrum of the NO Fragment Produced by Dissociation of m-NT at 245 nm. This spectrum contains the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$, $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$, and $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=2)$ bands of NO.

Figure 3.2b (Bottom) Expanded View of the Spectrum of the NO Fragment Produced by Dissociation of m-NT at 245 nm. This section shows the presence of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$ band mixed with peaks of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band. The unassigned peaks were composed of mixtures of the two bands.







Figure 3.3 Spectra of the NO Fragment Produced from Dissociation of m-NT at 245 nm. Spectrum **a.** shows the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=1)$ band. No other vibronic transitions were observed in this wavelength region because of unfavorable Franck-Condon factors. Spectrum **b.** shows the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=2)$ band, which also included transitions from the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=3)$ band.



Figure 3.4 Relative Vibrational Populations of NO from the Dissociation of m-NT at 245 nm. The data was standardized to the population at $v^{"}=0$. The population ratios were 1: 0.35: 0.081 for $v^{"}=0-2$ respectively.

of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band. Due to congestion of the

 $A^{2}\Sigma^{+}(v'=0) \leftarrow X^{2}\Pi(v''=0)$ band at low rotational levels and overlap from hotbands at high rotational levels, the number of rotational lines that were isolated and resolved in the experiment were limited. This situation had an adverse effect on the statistics of data analysis.

The rotational energy information was extracted by fitting the data to a Boltzmann distribution, as shown in Figure 3.5. All branches of the NO REMPI spectrum were averaged together, and a linear regression of ln(Intensity/Hönl-London factor) vs. J(J+1) was performed. The rotational temperatures obtained were, 3600 ± 430 K for v" = 0, 5100 ± 670 K for v" = 1, and 3300 ± 640 K for v" = 2. The corresponding average rotational energies are summarized in Table 3.1 for all three isomers. Although the data have a strong Boltzmann character, which is consistent with the slow dissociation process observed from other nitroaromatic compounds, some deviations are also observable. This could be due to any combination of the following: the processes not being completely thermal, saturation of the NO transitions by the probe laser, or NO being generated through multiple pathways.

Figure 3.6 shows the relative populations in the Λ -doublet. These results demonstrate a definitive preference for the NO fragment to be in states that lead to P and R rotational branches. The preferred Λ -doublet correlates to an A' symmetry with the unpaired electron located in the plane of rotation. This preference is typically interpreted as representative of a planar geometry of the transition state during dissociation.



Figure 3.5 Boltzmann Plot of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ Band of NO from Dissociation of m-NT at 245 nm. The ln(Intensity/Hönl-London factor) was plotted verses J(J+1). This plot shows a strong Boltzmann character to a moderately high rotational quantum number J. The line is the fitting result for the Q1 + P21 branch.

Percent Percent Average Average of of Trot Rotational Vibrational **v**" Available Available Energy **(K)** Energy Energy Energy (cm^{-1}) (cm^{-1}) (%) (%) o-NT 0 3400 ± 320 2200 ± 170 ---------1 3200 ± 340 2100 ± 190 1-laser ------2 390 ± 59 210 ± 41 -------Total $\mathbf{2100} \pm \mathbf{170}$ 4.7 1760 ± 90 4.6 -m-NT ___ 0 4200 ± 1100 2600 ± 430 213nm ------Total 2600 ± 430 4.7 1200 ± 300 2.7 --0 2300 ± 210 245nm 3600 ± 430 ----___ 1 5100 ± 670 2900 ± 220 ------2 3300 ± 640 2100 ± 330 ------Total 2400 ± 220 1600 ± 360 6.0 4.0 p-NT 0 2700 ± 200 1800 ± 120 213nm --------1 3700 ± 380 2300 ± 180 ------2 3700 ± 750 2300 ± 300 -------Total 2000 ± 150 1600 ± 170 --4.2 3.5 0 2900 ± 280 1900 ± 150 249nm ------- 3300 ± 240 2100 ± 120 1 ---2 4700 ± 580 2800 ± 160 -------Total 2000 ± 140 5.4 1500 ± 160 3.9

Table 3.1 Summary of Rotational and Vibrational Energy Distributions of Isomers ofNitrotolueneAll values are from experiments performed by our own group.



Figure 3.6 Population Ratios in the Λ -doublet for the Different Vibrational States of the Ground State of NO from the Dissociation of m-NT at 245 nm. This ratio shows a preference for the A' state, which indicates that the unpaired electron was preferentially in the plane of molecular rotation.

3.3.1.2 Dissociation of m-NT from S_3 at 213 nm

Similar to the result at 245 nm, dissociation of m-NT at 213 nm led to highly rotationally and vibrationally excited NO photofragments. The spectrum for the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band is shown in Figure 3.7. Vibrational levels with v''=0-2 were observed. The expanded region in Figure 3.7 shows the presence of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$ band in the spectrum. Due to a poor signal to noise ratio for the v''=2 transitions, only relative populations of the v''=0 and v''=1 levels could be obtained, and the result is shown in Figure 3.8. Using the same method previously discussed for rotational analysis of the NO photofragment, a rotational temperature of 4200 ± 1100 K was determined for the v''=0 level from the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ transition. There was not enough data to determine the rotational energy of any of the excited vibrational states. Analysis of the Λ -doublet and spin-orbit populations did not yield any preference within the limit of our experimental error.

3.3.2 para-Nitrotoluene (p-NT)

3.3.2.1 Dissociation of p-NT from the S₂ State at 249 nm

The spectra for NO produced from dissociation of p-NT at 249 nm are provided in Figures 3.9 - 11. Similar to the results of the meta isomer, the NO fragment was significantly vibrationally and rotationally excited, with evidence of



Figure 3.7a (Top) Spectrum of the NO Fragment Produced by Dissociation of m-NT at 213 nm. This spectrum contains the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$, $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$, and $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=2)$ bands of NO.

Figure 3.7b (Bottom) Expanded View of the Spectrum of the NO Fragment Produced by Dissociation of m-NT at 213 nm. This segment shows the presence of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$ band mixed with peaks from the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band. The peaks assigned were isolated transitions; while the unassigned peaks were composed of mixtures of the two bands.



Figure 3.8 Relative Vibrational Populations of NO from the Dissociation of m-NT at 213 nm. The data was standardized to the v'' = 0 level, and the ratio of the populations was 1: 0.19.



Figure 3.9a Spectrum of the NO Fragment Produced by Dissociation of p-NT at 249 nm. This spectrum contains the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$, $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$, and $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=2)$ bands of NO.

Figure 3.9b Expanded View of the Spectrum of the NO Fragment Produced by Dissociation of p-NT at 249 nm. This segment shows the presence of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$ band mixed with peaks of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band. The peaks assigned were isolated peaks of the assigned transitions; while the unassigned peaks were composed of a significant mixture of the two bands.







Figure 3.10 Spectra of the NO Fragment Produced by Dissociation of p-NT at 249 nm. Spectrum **a.** shows the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=1)$ band. No higher excited states were observed in this data section because of small Franck-Condon factors for transitions originating from other vibrational states. Spectrum **b.** shows the band region of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=2)$ transition, which also includes peaks from the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=3)$ transition.



Figure 3.11a Spectrum of the NO Fragment Near the Region of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=3)$ Band Produced by Dissociation of p-NT at 249 nm. This spectrum demonstrates that the NO photofragment was highly vibrationally and rotationally excited.

Figure 3.11b Expanded View of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=3)$ Band Region. This shows the presence of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=4)$ band and the $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=5)$ band within the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=3)$ band region despite their small Franck-Condon factors.

vibrational populations in v'' = 0 - 5 levels. Quantitative characterization of the v'' = 0, 1, 2 levels was possible; and the relative populations are presented in Figure 3.12. The v''=3 - 5 levels were clearly observable in the regions for the

$$A^2 \Sigma^+(v'=0) \leftarrow X^2 \Pi(v''=2)$$
 transition and the $A^2 \Sigma^+(v'=0) \leftarrow X^2 \Pi(v''=3)$

transition illustrated in the expanded view in Figure 3.11. Evidence of the

$$A^{2}\Sigma^{+}(v'=0) \leftarrow X^{2}\Pi(v''=4)$$
 and $A^{2}\Sigma^{+}(v'=0) \leftarrow X^{2}\Pi(v''=5)$ bands was also
observed but not quantifiable. Attempts for a quantitative comparison of the
populations in the v''=3 and v''=2 levels were made by comparing the transition
intensity of the $A^{2}\Sigma^{+}(v'=1) \leftarrow X^{2}\Pi(v''=3)$ band and the

$$A^2 \Sigma^+(v'=0) \leftarrow X^2 \Pi(v''=3)$$
 band with that of $A^2 \Sigma^+(v'=0) \leftarrow X^2 \Pi(v''=2)$.

However, the results are inconsistent and are therefore not presented. However, compared with the spectrum from m-NT at 245 nm, the signal to noise ratio for the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=3)$ band from p-NT was much improved.

The Franck-Condon factor for the $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=5)$ transition is only one fifth that of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=3)$ transition⁹⁶, and the presence of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=4)$ and the $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=5)$ bands is therefore suggestive of an inversion in the vibrational population. The inverted vibrational excitation could be interpreted as evidence of NO being produced, at least in part, from a dissociation process involving NO₂ as an intermediate product; this point will be examined in more detail in the discussion section.



Figure 3.12 Relative Vibrational Populations of NO from the Dissociation of p-NT at 249 nm. The data was standardized to the population at v"=0. The ratios of the populations were 1: 0.26: 0.083 for v"=0-2 respectively.

The rotational temperatures of the different vibrational states were determined to be 2900 ± 280 K for v" = 0, 3300 ± 240 K for v" = 1, and 4700 ± 580 K for v" = 2. This correlation between vibrational and rotational excitation is unusual, since we typically expect that higher vibrational levels should have lower rotational excitation. This result indicates non-thermal behavior in the dissociation process. A close inspection of Figure 3.13 reveals that for the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band, the data should be best fit by at least two Boltzmann temperatures, one for the high J component shown in the diagram and the other for the low J component. This bimodal rotational energy distribution provided additional evidence that the NO product originated from different dissociation channels. However, not all branches demonstrated such a clear biomodal distribution. Thus, in this analysis we only focus on the high rotational temperature component, partly to maintain consistency in our comparison with other nitroaromatic molecules.

The population ratios for the Λ -doublet are shown in Figure 3.14. The result demonstrated a clear preference for the P and R branches with A' symmetry. Similar to m-NT, the unpaired electron had a preference for being in the plane of rotation of the NO molecule during dissociation. The spin-orbit ratio indicated a slight preference for the F₁ state in the v" = 1 level, but the v" = 0 and v" = 2 states did not exhibit any preference within our experimental error.



Figure 3.13 Boltzmann Plot of the NO $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ Band from Dissociation of p-NT at 249 nm. The ln(Intensity/Hönl-London factor) was plotted verses J(J+1). The fitting result of the Q1 + P21 branch was included with the rotational temperature. This result showed a Boltzmann character, however, the data would be best fit by two rotational temperatures, one for the high J component shown in the diagram and the other for the low J component.



Figure 3.14 Population Ratios of the Λ -doublet in the Different Vibrational Levels of NO from Dissociation of p-NT at 249 nm. This ratio reflects the relative populations in the A' and the A" state; the preference for the A' state is an indication that the unpaired electron was preferentially in the plane of molecular rotation.

3.3.2.2 Dissociation of p-NT from S_3 at 213 nm

The dissociation of p-NT at 213 nm yielded similar results as those at 249 nm. The spectra of the NO photofragment are presented in Figures 3.15 and 3.16, and the relative populations in the v'' = 0, 1, 2 levels are shown in Figure 3.17. A high degree of vibrational excitation was demonstrated by the presence of the

 $A^{2}\Sigma^{+}(v'=1) \leftarrow X^{2}\Pi(v''=1)$ and the $A^{2}\Sigma^{+}(v'=2) \leftarrow X^{2}\Pi(v''=2)$ bands in the region of the $A^{2}\Sigma^{+}(v'=0) \leftarrow X^{2}\Pi(v''=0)$ band, as shown in the expanded section in Figure 3.15. Evidence for the third excited vibrational state, v''=3, was observed in the region of the $A^{2}\Sigma^{+}(v'=0) \leftarrow X^{2}\Pi(v''=2)$ band. Given the limited signal to noise ratio, however, we were unable to quantify the relative population in the v''=3 level. Qualitatively, the Franck-Condon factor of the $A^{2}\Sigma^{+}(v'=1) \leftarrow X^{2}\Pi(v''=3)$ transition is less than one third of that of the $A^{2}\Sigma^{+}(v'=0) \leftarrow X^{2}\Pi(v''=2)$ band; and the definitive peaks originating from v''=3 in the spectrum indicate a relatively large population in the v''=3 vibrational level. We believe that this result offers tantalizing evidence that the vibrational population actually rises again at v''=3, i.e., the vibrational population is inverted for the levels with v'' > 2.

The NO fragment is highly rotationally excited, with rotational temperatures of 2700 ± 200 K for v" = 0, 3700 ± 240 K for v" = 1, and 4700 ± 580 for v" = 2. This behavior of increasing rotational temperature with increasing vibrational quantum number has been observed from photodissociation of NO₂. This result provides



Figure 3.15a (Top) Spectrum of the NO Fragment Produced by Dissociation of p-NT at 213 nm. This spectrum contains the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$, $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$, and $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=2)$ bands of NO.

Figure 3.15b (Bottom) Expanded View of the Spectrum of the NO Fragment Produced by Dissociation of p-NT at 213 nm. This segment shows the presence of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$ band mixed with peaks of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band. The peaks assigned were isolated transitions of the assigned band; while the unassigned peaks were mixtures of the two bands.

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Figure 3.16 Spectrum of the NO Fragment Produced by Dissociation of p-NT at 213 nm for the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=1)$ Band. No higher excited states were observed in this wavelength region because of small Franck-Condon factors for transitions originating from other vibrational levels.



Figure 3.17 Relative Vibrational Populations of NO from the Dissociation of p-NT at 213 nm. The data is standardized to the population at v'' = 0. The ratios of the populations are 1: 0.37: 0.081 for v'' = 0 - 2 respectively.

additional evidence that the NO photofragment was produced, at least in part, by sequential dissociation of an NO₂ photofragment.

The Λ -doublet ratios were analyzed only for the v" = 0 and v" = 1 levels as the spectra related to the v" = 2 level were too noisy for this type of analysis. The $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=1)$ band shows preference for the A' symmetry with a A'/A" ratio of 1.8 ± 0.2 , but the other levels do not exhibit a definitive preference within the experimental error. The v" = 0 state did indicate that there was a slight preference for the F₁ spin-orbit state, as listed in Table 3.2.

3.3.3 Dissociation of ortho-Nitrotoluene (o-NT)

The dissociation dynamics and electronic transition dipole symmetry of the o-NT molecule have been studied previously by our group.⁷ The high vibrational excitation in the meta and para isomers piqued our interest in taking a more careful look at the population distribution of o-NT. The spectra previously published by our group are presented in Figures 3.18 and 3.19.⁷ The expanded region shown in Figure 3.18 demonstrates the presence of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$ band, which was not identified in the previous analysis. Reanalysis of this data, by the same methods used for the other NT isomers, led to a change in the v'' = 0 to v'' = 1 population ratios from a 1 : 0.60 ratio to 1 : 0.30 respectively. Results for v'' = 2 are unaltered as there were insufficient peaks to perform this type of analysis. This additional piece of information resulted in a slight changes to the rotational temperatures: 3400 ± 320 K for v'' = 0, 3200 ± 340 K for v'' = 1, and 390 ± 59 K for v'' = 2. Some concern is

Table 3.2 Summary of A-doublet and Spin-orbit Ratios. The F_1/F_2 ratio signifies the ratio of the populations in the ${}^{2}\Pi_{1/2}$ state relative to the ${}^{2}\Pi_{3/2}$ state. The A'/A" ratio compares the populations in the Q branch relative to that in the P and R branches. The preference for the A' symmetry is an indication that the unpaired electron was preferentially in the plane of rotation of the NO fragment.

	F_1/F_2	A'/A"	
o-NT v''=0	1.8 ± 0.4		
o-NT v''=1		1.7 ± 0.5	
m-MT 249nm			
v"=0		1.5 ± 0.2	
v"=1	1.6 ± 0.5	1.5 ± 0.2	
v"=2		1.7 ± 0.3	
p-NT 249nm			
v"=0		1.5 ± 0.2	
v"=1	1.3 ± 0.1	1.7 ± 0.2	
v"=2		1.4 ± 0.2	
p-NT 213nm			
v"=0	1.5 ± 0.4		
v"=1		1.8 ± 0.2	



Figure 3.18a Spectrum of the NO Fragment Produced by Dissociation of o-NT in a 1laser Experiment. This spectrum contains the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$, $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$, and $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=2)$ bands of NO.

222.37

222.32

222.42

Wavelength(nm)

222.47

222.52

222.57

Figure 3.18b Expanded View of the Spectrum of the NO Fragment Produced by Dissociation of o-NT in a 1-laser Experiment. This segment shows the presence of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$ band mixed with peaks of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band. The peaks assigned were isolated peaks of the assigned transitions; the unassigned peaks were composed of a significant mixture of the two bands.

2.5

2.0

1.5

1.0

0.5

0.0

(Arbitrary Units)

0.1000 0.0000

222.22

222.27

Intensity

Intensity (Arbitrary Units) 82







Figure 3.19 Spectra of the NO Fragment Produced by Dissociation of o-NT in a 1-laser Experiment. Spectrum **a.** shows the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=1)$ band transition. No higher excited states were observed in this data section because of small Franck-Condon factors for transitions originating in higher excited states. Spectrum **b.** shows the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=2)$ band region.

warranted for the value of the v'' = 2 level, since in this one laser experiment, to detect the v'' = 2 level, the laser wavelength has to be scanned to the red of the S₂ state and close to the absorption region of the S₁ state. In addition, the signal to noise ratio of the spectrum was less than ideal. The Boltzmann analysis in Figure 3.20 also revealed the possibility of a bimodal rotational temperature distribution. For consistency in comparison among all the nitroaromatics considered in this project, only the high J component was included in this discussion.

Some numerical changes in the Λ -doublet and spin-orbit ratios from the previous values are obtained, but the general trends are consistent. The v" = 0 state yielded a F₁/F₂ ratio of 1.8 ± 0.4, indicating a preference for the ${}^{2}\Pi_{1/2}$ spin-orbit state. The v" = 1 state has a Λ -doublet ratio of 1.7 ± 0.5, indicating that the P and R branches are preferred and that the unpaired electron tended to be in the plane of rotation. No other levels yielded information for the electron orientation and spin-orbit preference within the experimental error evaluated to the 95% confidence level.

3.3.4 Dissociation of Nitrobenzene

Our initial emphasis in the photodissociation study of nitrobenzene centered around the direction of the transition dipole, and only surveys of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band were performed. Qualitative analysis of this region, however, revealed the definitive presence of the $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=1)$ band and possibly the $A^2\Sigma^+(v'=2) \leftarrow X^2\Pi(v''=2)$ band. These observations are



Figure 3.20 Boltzmann Plot for the NO $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ Band for Dissociation of o-NT in a 1-laser Experiment. The ln(Intensity/Hönl-London factor) is plotted verses J(J+1). This plot shows a strong Boltzmann character to a moderately high J. The line is the fitting result for the average F1 data. The low J portion of this plot would be best fit by an additional, separate rotational temperature.

contradictive to those by Crim's¹⁶ and He's²² groups, but they support the results of Singhal's¹⁷ and Rosenwaks'¹⁹ groups.

3.4 DISCUSSION

3.4.1 Comparison of Dissociation Products

A summary of the rotational and vibrational energy distributions in Tables 3.1 and 3.3 shows that the energy partitioned to the vibrational degree of freedom for the NT systems is essentially the same up to the second excited vibrational level. This offers support for the idea that the basic mechanism of dissociation is the same among the different isomers. This observation was consistent with our previous result based on polarization spectroscopy. The orientation of the electronic transition dipole relative to the permanent dipole was concluded to be essentially the same for all listed members of the nitroaromatic systems.

Similarities in the rovibrational distribution from different NT isomers and electronic states support a statistical redistribution of the absorption energy prior to dissociation. Our polarization studies have demonstrated an orthogonal relation between the electronic transition dipoles of the S₂ and S₃ states. Localized excitation of the NO₂ moiety has been proposed for the S₂ state, and a charge transfer to the aromatic ring has been proposed for the S₃ state.^{7, 21} Despite these differences, the vibrational distributions of the NO fragment from the two excited states were largely similar. This similarity in vibrational and rotational excitation of NT dissociated on

Table 3.3 Summary of Rotational and Vibrational Energy Distributions. The values reported are literature values for NB^{16, 22} and from our own experiments for the three isomers of nitrotoluene.

	v"	Trot (K)	Average Rotational Energy (cm ⁻¹)	Percent of Available Energy (%)	Average Vibrational Energy (cm ⁻¹)	Percent of Available Energy (%)
NB						
226nm	0	3700 ± 350		6.8 ¹⁶		< 2.1
266nm	0	3300 ± 300		6.1 ²²		< 2.5
280nm	0	2300 ± 200		5.4 ¹⁶		< 2.7
o-NT	0	3400 ± 320	2200 ± 170			
Total			2100 ± 170	4.7	1526 ± 190	3.5
m-NT						
213nm	0	4200 ± 1100	2600 ± 430			
Total			2600 ± 430	4.7	1200 ± 300	2.7
245nm	0	3600 ± 430	2300 ± 210			
Total			2400 ± 220	6.0	1600 ± 360	4.0
p-NT						
213nm	0	2700 ± 200	1800 ± 120			
Total			2000 ± 150	4.2	1600 ± 170	3.5
249nm	0	2900 ± 280	1900 ± 150			
Total			2000 ± 140	5.4	1500 ± 160	3.9

the S_2 and S_3 potential surfaces further supports the idea that the dissociation process was similar on both potential surfaces. There must be a fast internal relaxation process upon photoabsorption that has erased the memory of the initial excitation process. This result agrees with the slow dissociation observed for all nitroaromatic molecules.

The fraction of the total energy partitioned into the rotational degree of freedom was similar for all members of the nitroaromatic systems. The rotational temperatures obtained from the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ band for all systems and at different dissociation wavelengths are shown in Figure 3.21. The rotational temperature of NB decreased as the excitation energy decreased,^{16, 22} while the NT isomers were indifferent to the initially accessed electronic state. The p-NT isomer was observed to have a slightly lower rotational temperature than the other NT isomers, and this may be related to higher vibrational excitation in p-NT.

Analysis of the rovibrational population has yielded information about the dissociation processes. Table 3.1 and Figure 3.22 contain the rotational distribution for each vibrational level. The most significant trend observed in this data set was the increase in rotational excitation with increasing vibrational excitation. This trend was the most noticeable for p-NT. At 249 nm, the highest quantifiable rotational temperature was for the v'' = 2 level, but Figure 3.11 further indicates that the next higher vibrational level may actually have an even higher rotational excitation as the population seems to have a maximum in the short wavelength, high J region of the spectra and the expanded view shows evidence of v'' = 4 and 5 populations. For m-NT, the data for dissociation at 213 nm did not yield information on the rotational






Figure 3.22 Comparison of the Rotational Temperatures of the v'' = 0 - 2 Levels from the NO Photofragment Generated from m-NT and p-NT. This chart shows the NO rotational temperatures produced by the selective excitation to the S₂ and S₃ states of the meta and para isomers of nitrotoluene. In general, the rotational excitation is essentially the same, except that for p-NT, a higher rotational excitation is correlated with a higher vibrational level. The trend is particularly clear for the dissociation from the S₂ state of p-NT.

excitation of the excited vibrational levels. At 245 nm, the highest observed rotational temperature was in the v'' = 1 level. This correlation of rotational and vibrational excitation is opposite from that observed in nitrobenzene.

Galloway et al. proposed a pathway for the NO fragment from photodissociation of NB involving the rearrangement of the $-NO_2$ moiety into a -ONO nitrite intermediate state.¹⁶ They also calculated the energy distribution among the different degrees of freedom using the statistical and impulsive models. Table 3.4 lists their calculation results and our experimental values for the NT isomers. Due to the similarities between NB and NT we used the results of these models for comparison. The statistical model predicts that approximately 4.2 % of the available energy will be in the rotational degree of freedom and 2 % in vibration. This result does come close to the observed values. The rotational prediction noticeably underestimated the values for dissociation on the S₂ surface, but it was fairly close for the S₃. The vibrational prediction was noticeably lower for all of the observed distributions that were well characterized in our experiment. Although the impulsive model seems better in the vibrational prediction, it was still a underestimate, especially considering the fact that we have ignored all vibrational levels above v'' = 2 in this analysis. The rotational energy prediction from the impulsive model was incompatible with our experimental observations.

Boltzmann type behavior observed in this experiment agrees well with the statistical model. The small deviations from a Boltzmann distribution indicate that the process is either not completely statistical or may involve multiple dissociation

Table 3.4 Comparison of the Statistical and Impulsive Models for Direct NOProduction through Isomerization . The experimental result qualitatively followed thestatistical model, but discrepancies are noticeable.

	m-NT		p-NT		o-NT	Statistical Model	Impulsive Model
	213 nm	245nm	213 nm	249 nm			
Er	4.7 %	6.0 %	4.2 %	5.4 %	4.7 %	4.3 %	26 %
Ev	2.7 %	4.0 %	3.5 %	3.9 %	4.6%	2.1 %	3.0 %

channels. This latter possibility is supported by the observed bimodal distribution in dissociation of o-NT, p-NT, and NB.²²

The observed A-doublet and spin-orbit ratios are summarized in Table 3.2. In almost all cases, the unpaired π electron from NO strongly prefered to be in the plane of rotation with an A' symmetry. The transition state for NO production must originate from a geometry in which the NO breaks apart from the transition state in a bending motion with the π orbital preferentially in the plane of bending, as shown in Figure 3.23. The preference for the lower spin-orbit state indicates that the process was not truly thermal, as an almost one to one ratio would have been statistically expected.

3.4.2 Dissociation Channels

3.4.2.1 Available Energy

To understand the production pathway for nitric oxide from the dissociation of nitroaromatic molecules, a general description of the bond energy was necessary. We considered two possibilities of NO production, one from sequential dissociation via the NO₂ radical, and the other from direct dissociation via the rearrangement to a nitrite structure. The energies required for the dissociation of nitro and nitrite compounds resulting in the elimination of NO₂ are presented in Figure 3.24. These bond dissociation energies (BDE) were calculated using the Gaussian 03



Figure 3.23 Dissociation Process that Produces NO with an A' Symmetry. The axis used is that for the NO product formed with the π bond in the plane of rotation. The O-N-O system is in a single plane and may be bound via the singly bonded oxygen to additional atoms that may or may not lie within this plane. With the high degree of rotational excitation, a bending vibrational mode is likely part of the transition state dynamics. The arrow around the axis represents the angular momentum of the NO after bond scission.



Figure 3.24 Bond Dissociation Energies of the Nitro and Nitrite Isomers of NB and NT. This diagram shows the energy required to cleave the C-N bond for the nitro group or the C-O bond for the nitrite group. The energy available was 480 kJ/mol for a 249 nm photon. All of these dissociation channels were possible for the dissociation wavelengths used in this experiment.

computational package with the DFT/B3LYP method at the 6-311G++dp level and corrected for zero point energies.⁹⁷ Experimental values have been determined for NB, p-NT, and o-NT. These values were used to generate a scaling factor for the corresponding molecule. An average of the o-NT and p-NT scaling factors was used for m-NT calibration. The calculation for each nitrite compound was scaled using the same factor as that of the corresponding nitro isomer.⁹⁸ Our calculated values for NB, o-NT, and p-NT agree with those computed by Shao et al.¹¹ The result in Figure 3.24 indicates that it is easier to remove NO₂ in the nitrite form than in the nitro form for m-NT and p-NT. Moreover, the ortho effect caused by the methyl group's proximity to the nitro group in o-NT, leads to a lower dissociation energy for the nitro compound than that for the nitrite compound.

For direct production of NO via rearrangement to the nitrite compound, we have calculated the dissociation energy of the O-N bond using the same approach, and the results are shown in Figure 3.25. We used the experimental BDE of phenyl nitrite to obtain the scaling factor. The values in Figure 3.25 indicate that it is energetically easier to remove NO than to remove NO₂ from the parent molecule. This has been attributed, in part, to the stability of the phenoxy radical from the dissociation of phenylnitrite.⁶³ We thus expect that in this statistical process, direct dissociation of NO from a nitrite isomer might be a dominant channel. The excess energy from the dissociation laser could explain the high rotational excitation in the NO photofragment.

On the other hand, the above analysis does not rule out the possibility of NO₂ production, and the report from Crim's group actually considered the NO₂ channel the



Figure 3.25 Bond Dissociation Energies for Cleavage of the O-N bond of the Nitrite Isomers of NB and NT. This diagram shows the relative dissociation energy for the production of NO directly from dissociation of the parent molecule. The energy available was 480 kJ/mol for a 249 nm photon.

dominant pathway for NB. The dissociation energy of ground state NO₂ is approximately 306 kJ/mol. Our experiment at 249 nm provided an energy of 480 kJ/mol, with approximately 295 kJ/mol required for cleavage of the C-O bond from the phenylnitrite intermediate. If NO was produced through sequential dissociation of a NO₂ photofragment, a second photon would be required, from either the dissociation or probe laser.

To unravel the mechanism of NO production in the three isomers of NT, we will refer to the dissociation mechanisms of similar systems, including NB, nitromethane, methylnitrite, t-butyl nitrite, and NO₂. Since the rovibrational distributions of NO from both S_2 and S_3 surfaces were similar, we will focus our discussion on the S_2 state.

3.4.2.2 Comparisons with Nitrobenzene

At first glance, the nitrotoluene isomers appear to dissociate in the same fashion as NB, with strong similarities in product rotational and vibrational excitation. However, upon careful examination, we see that there are several differences. Dissociation of NB has been shown to produce NO, vibrationally excited to the third excited state, when a single laser scans over a long wavelength range.^{17, 19} Some concerns, however, should be given to these results as they were not performed with the dissociation laser parked at a constant location on the potential energy surface at a single wavelength. Studies with the dissociation laser at a single wavelength have not yielded any observable vibrational excitation.^{15, 22} The NO photofragment from NB showed no evidence of vibrational population inversion; and the first excited vibrational level was observed to have a population of about one third of that of the ground vibrational level. The NT isomers demonstrated more vibrational excitation than that reported for NB and they had a greater preference for vibrational inversion as the methyl group was moved further away from the nitro group on the aromatic ring. The rotational excitation profile of the NO photofragment from the NT isomers was significantly different from that of NB, with a relatively constant rotational temperature across different dissociation wavelengths for a given vibrational level. Of greater contrast was the increasing rotational excitation in the exited vibrational states; this phenomenon has not been observed in NB.

The existing model for dissociation of NB to produce NO and NO₂ is through the isomerization pathway detailed by Glenewinkel-Meyer and Crim,¹⁸ The nitro group isomerizes to a nitrite structure after the absorption of a photon with subsequent dissociation of the parent molecule. This mechanism has recently been supported by the experiment using ultrafast electron diffraction by Zewail's group.²² The authors identified this process as the exclusive dissociation pathway at 266 nm. Our own calculations of the bond dissociation energies presented earlier also agree with the conclusion that isomerization is the most likely route for dissociation leading to NO. However, the energies from Figure 3.24 also hint that there is an increased preference for the production of NO₂ via the isomerization pathway as the methyl group moves from the ortho to the para position, since there is significant stabilization of the C-N bond in the m-NT and p-NT isomers. The discrepancies in the rovibrational distribution between NB and the isomers of NT could be caused by the existence of the NO₂ channel in NT. With the absorption of another photon, NO₂ could further dissociate into NO and O, resulting in additional rotational and vibrational excitation in the observed NO fragment.

3.4.2.3 Comparison to Nitromethane, Methylnitrite, and t-Butyl nitrite

Studies of the simpler nitro and nitrite compounds, such as nitromethane, mythlnitrite and t-butyl nitrite (tBN), have been reported, and comparisons with results from these simpler compounds may provide some inspiration in understanding the nitroaromatic systems. Unfortunately, there has been no report on the internal energy distribution of NO from dissociation of nitromethane in the S₂ state. The experimental results suggest a quantum yield of 0.7 for the production of NO₂ and a quantum yield of approximately 0.13 for NO.⁴⁶ Dissociation from S₃ at 193 nm indicated that the NO photofragment was formed with a relatively high rotational excitation, but a low vibrational excitation.⁹ Additional studies further revealed that multiple dissociation channels existed and NO was formed in both the ground and excited electronic states.^{9, 39, 41, 42, 44} The pathway for the formation of NO in different electronic states involved NO₂ in different excited electronic states as an intermediary. We are unaware of any Λ-doublet analysis of the NO photofragment.

Direct comparisons with the methylnitrite literature were impossible in the wavelength region of this study, because ground state methylnitrite absorbs in a different region. It is therefore no surprise that the internal energy distribution from dissociation of methylnitrite is very different from that of the NT isomers.⁹⁹⁻¹⁰³ In the

350 - 370 nm range, the NO fragment from methylnitrite tends to have high rotational excitation and a non-inverted vibrational population, with observed levels up to v" = $3.^{99, 102}$ The rotational excitation from dissociation at 266 nm showed a strong bimodal behavior.¹⁰¹ Most importantly, the NO photofragment prefers the orientation of the π-orbital in an A" symmetry,^{100, 102, 104} opposite to that observed from dissociation of the NT isomers. This difference suggests that the transition state geometry for the dissociation of methylnitrite was significantly different from that of the NT isomers. This result is important in understanding the isomerization pathway in NT, because it supports the idea that the nitrite group was not in its ground state, but might have been in vibrationally excited states before the dissociation of the NT isomer occured. Vibrational excitation in a bending mode involving the O-NO bond is necessary to understand the extreme rotational excitation of the NO fragment.

t-Butyl nitrite, on the other hand, demonstrated more similarity in production internal energy distribution to that of nitrotoluene than either nitromethane or methyl nitrite.^{105, 106} It was found that dissociation initiated by absorption to the S₂ feature was extremely wavelength dependent, with a strong bimodal rotational distribution in both the v" = 0 and v"= 1 levels of the NO photofragment. For dissociation at 250 nm, the Λ -doublet of NO was found to have a preference for the A" symmetry, in close agreement with observations on methylnitrite. However, at wavelengths \leq 236 nm the Λ -doublet ratio was observed to prefer the A' symmetry, similar to that observed for the NT isomers. As the excitation energy was increased, a greater preference for formation of NO in the first excited vibrational level was observed. The similarity between the tBN and the NT isomers seems to imply, that if the NT isomers passed through a nitrite form, the aromatic nitrite would be in a state similar to the S_2 state of tBN prior to dissociation.

3.4.2.4 Comparison with NO₂

To assess the role of the possible NO_2 fragment in the production of NO, the most relevant comparison is perhaps with the photodissociation process of NO₂. Several groups have studied photodissociation of NO₂ at 248 nm,^{65, 66, 107} and they all have identified that the NO photofragment was formed with an inverted vibrational population. The most populated vibrational level was found to be $v'' = 5^{66, 107}$ or $v'' = 7.6^{5}$ The higher vibrational levels were also observed to have higher rotational excitation, with the highest rotational excitation at v'' = 6.⁶⁶ Although the degree of rotational excitation from dissociation of NO₂ was not as high as that from NT, there are still important similarities. Analysis of the Λ -doublet populations of the NO photofragment from NO₂ yielded a preference for the A' symmetry with an A'/A" ratio of approximately 1.5.⁶⁶ This value is almost identical to that observed for the NT isomers in Table 3.4. In addition, the spin-orbit ratio was also similar for the two types of systems, slightly preferring the lower spin state.⁶⁶ Moreover, the similarity in the trend of population distribution seemed to enhance as the methyl group was moved from the ortho to the para position on the aromatic ring. This was supported by a better signal to noise ratio for bands with v'' > 2 in m-NT and p-NT.

3.4.2.5 Summary of Dissociation Channels

We propose that there are at least two distinct dissociation channels for the production of NO from the NT isomers. The basic reactions are:

$$C_7H_7NO_2 + h\upsilon \rightarrow C_7H_7O + NO$$

and

$$C_7H_7NO_2 + h\upsilon \rightarrow C_7H_7 + NO_2$$

 $NO_2 + h\upsilon \rightarrow NO + O$

where the first photon is produced by the dissociation laser and the second from either the dissociation or the probe laser. The rotational excitation observed for the vibrational levels of v'' = 2 and below from dissociation of the NT isomers was in good agreement with that seen for NB by Daugey et al.¹⁹ However, the vibrational inversion and high rotational energy in high vibrational levels with v'' > 2 is well explained by sequential dissociation of the NO₂ fragment. Photodissociation of NO₂ from the ground state cannot explain the high levels of rotational excitation observed in NO from NT; but a vibrational excitation of the bending mode of NO₂ is energetically possible and could account for the additional rotational excitation.

We believe that the dominant channel for the v" = 0 - 2 levels was essentially the same as that seen for NB. In this channel, NO is preferentially produced directly from isomerization via the nitrite intermediate. The exceptionally high rotational excitation in NO could be related to the internal excitation of the NO₂ fragment, since there is sufficient energy from a single photon for additional vibrational and rotational excitation. Dissociation from an excited NO₂ would allow for more internal energy to be imparted to NO upon fragmentation initiated by a second photon. We believe this sequential dissociation of vibrationally excited NO₂ is responsible for the vibrational inversion observed for the NO photofragment.

3.5 CONCLUSIONS

Dissociation of nitrobenzene and the three nitrotoluene isomers have been examined. The dissociation process of these molecules was similar, yielding similar energy distributions in the rotational degrees of freedom. However, significant vibrational excitation was observed in the nitrotoluene isomers, indicating that perturbations of the molecular wavefunction by the methyl group attached to the aromatic ring were significant in the dissociation process. The most surprising result was that the p-NT isomer showed the largest perturbation in the dissociation process, while it would be expected to be the least affected by the methyl group. The UV/VIS spectra in Figure 3.1 are consistent with this observation in that the p-NT spectra has the greatest deviation from the NB absorption spectra. The presence of vibrational inversion for the NT isomers and the bimodal distribution of rotational temperatures observed in NB, o-NT, and p-NT indicate that the NO photofragment was produced through at least two dissociation channels. Further work is necessary to characterize and quantify these processes.

3.6 FUTURE WORK

This work has revealed many new and interesting facts about the nitroaromatic compounds. The doors have been opened for a variety of experiments to pinpoint the exact details of what is happening in the photodissociation process. The first level of future experiments is to investigate the vibrationally excited states and thoroughly explore the degree of vibrational excitation not quantified in this study. The effect of the power of the dissociation laser needs to be examined and quantified. A significant variation in the internal energy distribution of the NO photofragment is expected if two photons are required for the production of a portion of the NO fragment. This data could facilitate the deconvolution of the different dissociation channels and allow both the direct and the indirect pathways to be characterized. An improved S/N ratio and precise measurement of the laser power are needed for the success of this experiment. Reexamination of the effect of the laser power on the NO fragment is also necessary for NB to determine if the difference in the vibrational excitation of the NO photofragment, as reported previously,^{15, 17, 19, 22} is due to a multiple photon process. Effects of the probe laser power may also be important in the secondary dissociation of NO₂ to produce NO. The improved S/N ratio will also allow for a more detailed study of the dissociation initiated on the S₃ potential surface.

In addition to a more detailed study with laser spectroscopy, a time resolved study of the dissociation process via ultrafast electron diffraction would be useful in determining the process of structural rearrangement. Use of different dissociation wavelengths could elucidate the wavelength dependence of the dissociation process. Comparison of these results to those of NB would be beneficial in determining the effect of the methyl group on the dissociation process. Characterization of NB dissociation, initiated at different dissociation wavelengths and dissociation powers, by UED is needed to understand the processes producing different photofragments and clarify discrepancies between the UED results and several mass spectrometry results for NB. The use of a narrow line width nanosecond laser for dissociation might aid in understanding the origin of the observed single dissociation channel using UED at 266 nm.⁶³

3.7 ACKNOWLEDGEMENTS

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Symmetry Properties of Electronically Excited States of Nitroaromatic Compounds

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Chapter 4

Symmetry Properties of Electronically Excited States of Nitroaromatic Compounds

4.1 ABSTRACT

We report polarization spectroscopy of oriented gas phase nitroaromatic compounds, including nitrobenzene and the three isomers of nitrotoluene. Orientation of supersonically cooled molecules was achieved in a uniform electric field. The dependence of the yield of NO on the polarization direction of the excitation laser was used to derive the direction of the transition dipole. The transition to the S_2 state centered at 250 nm demonstrated increased yield when the excitation laser was polarized perpendicular to the orientation field. The transition dipole was therefore characterized to be near perpendicular to the permanent dipole. The transition to S_3 demonstrated an opposite behavior, indicating that the transition dipole for S_3 is primarily parallel to the permanent dipole. Quantitative analysis of the polarization dependence further revealed that in both cases, the transition dipole is not strictly parallel or perpendicular to the permanent dipole, and the tilt is about 20 to 30°. This result demonstrates the sophisticated nature of electronically excited states of nitroaromatics. It is therefore not surprising that only two previous theoretical calculations agree with our results, while other calculations and experimental work in condensed phases do not.

4.2 INTRODUCTION

Understanding the physical and chemical properties of electronically excited states is important in deciphering many chemical and biological reactions. For this purpose, experimental techniques and theoretical methods have been developed.^{1,2} To date, a detailed picture of electronic and nuclear motions in electronically excited states can be obtained for small molecules. However, for medium and large sized molecules, this is a largely underdeveloped field. Although with increasing computational power calculations of large systems have become possible, experimental calibrations of these calculations, in particular, results from the gas phase that can be directly compared with theory, are essentially unavailable, with only a few exceptions.³⁻¹⁷ Experimental efforts in the condensed phase are subject to environmental effects: not only can the transition intensity and energy vary, but also the order of electronic orbitals.^{18, 19} Precautions are therefore required in using these results for calibration purposes.

In an effort to derive the symmetry information of excited states of medium to large sized molecules, we have developed a spectroscopic method through polarized excitation of oriented gas phase molecules in a strong electric field.²⁰ When the rotational temperature of the gas phase molecules is cooled to a few Kelvin in a supersonic molecular beam, the electrostatic interaction between the permanent dipole and a strong external field can create a high potential barrier for molecular rotation.²¹⁻

orientation. Once the transformation from the molecular frame to the laboratory frame is fixed through orientation of the molecular frame, all properties of the molecular frame are uniquely projected to the laboratory frame and the polarization dependence of the overall excitation probability directly reflects the direction of the transition dipole. In practice, the overall excitation probability can be obtained from the fluorescence intensity in an laser induced fluorescence (LIF) experiment,²⁴ the ionization yield in resonantly enhanced multiphoton ionization (REMPI),^{25, 26} and in case photofragmentation occurs upon excitation, the yield of a photofragment.²⁷⁻³¹ This method allows direct determination of the direction of the transition dipole without knowledge of the dynamics of the excited state. Even when the photodissociation pathway is unknown, the dependence of the photofragment on the polarization direction of the dissociation laser can still reveal the direction of the transition dipole.^{32, 33} This method is therefore particularly applicable for studies of large molecules where the dynamics of the upper state typically involve fast internal conversion, slow dissociation, and subsequent low translational energy release. In contrast, techniques developed for small molecules, such as vector correlation or high resolution spectroscopy,^{34 - 38} are subjected to time and kinematic constraints and are therefore inapplicable for large systems. In order for a correlation to exist between the transition dipole and the recoil velocity of the fragment, the dissociation event has to be instantaneous and the fragment has to carry a substantial amount of kinetic energy. To determine the direction of the transition dipole using high resolution

spectroscopy,³⁹ the lifetime of the upper state has to be long enough to allow partial resolution of the rotational profile.

In this work, we present results on polarization spectroscopy of nitroaromatic molecules, including nitrobenzene (NB) and the three isomers of nitrotoluene (NT). Although these molecules are not considered large systems, they demonstrate properties of large systems. Figure 4.1 shows their absorption spectra in the gas phase with assignment based on reference 40. No correction of the vapor pressure difference among the different species was performed, and the intensities of the spectra were normalized at 190 nm. The featureless spectra render rotational profile analysis impossible, and even the assignment of electronic transitions is still ambiguous.^{40, 41} In some reports on nitrobenzene, a much weaker absorption band centered at 350 nm was identified as the first excited singlet state,⁴¹ while others ignored this band and assigned the S_1 state to the next higher energy band centered at 280 nm.⁴⁰ This inconsistency in experimental data resulted in further discrepancies in theoretical reports. $^{42-46}$ Some treated the weak bands as symmetry forbidden transitions or low lying triplet states,⁴² while others categorized the bands as singlet states with small oscillator strengths.⁴⁶ Moreover, the planarity of nitrobenzene in the excited states is also of some concern.^{46, 47} Upon excitation to both S_2 and S_3 , fragmentation was observed.⁴⁸⁻⁵³ All fragments were reported to demonstrate isotropic distribution,



Figure 4.1 Absorption Spectra of Nitrobenzene (NB) and the Three Isomers of Nitrotoluene (NT). The intensities of the spectra were normalized at 190 nm, so no information on the absorption cross section is represented here. The assignment for the three electronic transitions is based on reference 40.

signifying a slow dissociation process.⁵⁴ The majority of the fragments, including NO₂ and O atoms, were of low kinetic energy, while the minor product NO was reported to carry a high translational energy when the excitation wavelength was around 220 nm. Thus no vector correlation exists between the fragment recoil velocity and the transition dipole. Moreover, the pathway for the production of NO is still unclear.^{55 - 58}

Attempts to derive the directions of the transition dipoles and thereby the symmetry of the excited states were made both theoretically^{42 - 47, 55} and experimentally in the past.^{40, 59 - 64} The transition to the S₁ state (Figure 4.1) in nitrobenzene was considered perpendicular to the symmetry axis in all previous experimental work ^{40, 59, 64} and theoretical reports.^{42 - 55} For the S₂ state, experimental reports assigned it a ¹A₁ state,^{40, 59, 64} while some theoretical results assigned it ¹B₁ or ¹B₂ ^{42, 55} Since all previous experimental work was carried out in the condensed phase, environmental effects plague these results. Theoretical calculations, on the other hand, are known to provide unreliable data for the absolute transition energy, so calculated results were often adjusted to fit early experimental data, sometimes even the ordering of the calculated states was deliberately switched.⁴²

Work on nitrotoluene is much less extensive in comparison to that on nitrobenzene.⁴⁵ Given the abundance of lone pairs and π electrons, the effect of methyl substitution should be inconsequential, but shifts in the absorption spectra are clearly visible in Figure 4.1. Correspondence of electronic states in these systems awaits experimental confirmation. Our systematic investigation in the gas phase will

provide an unadulterated version of the electronic states of this series of molecules. In particular, we report that contrary to previous reports from condensed phase studies,^{40, ^{59, 64} the transition to S_2 is perpendicular to the permanent dipole, while the transition to S_3 is parallel to the permanent dipole. All four aromatics demonstrate similar behavior. Limited by the absorption cross sections, we did not attempt to derive any polarization information for the S_1 state.}

4.3 EXPERIMENTAL SETUP

The experimental setup has been explained in previous publications.^{32, 33} The equipment was a standard differentially pumped high vacuum chamber, and the electrodes for orientation were located in the reaction chamber separated from the source chamber via a skimmer of 1 mm in diameter. The gap between the electrodes was 6 mm, and the resulting maximum field was 50 kV/cm. The stagnation pressure of the helium carrier gas was maintained at 1400 torr, and the rotational temperature of the molecular beam was measured to be ~2.5 K based on partial rotationally resolved REMPI and LIF spectra of pyrimidine. The nonvolatile nitroaromatic compounds were mostly used at room temperature without heating, except for p-nitrotoluene when a low grade of heating outside the pulsed valve was applied to speed up the vaporization process. The NO products were detected using REMPI via the A state, and a detailed analysis of the vibrational and rotational distributions of the NO products will be published in the future. Typically, a few rotational levels of different vibrational states of NO were picked for orientation studies. The choice of rotational

lines was somewhat arbitrary, mainly determined by the symmetric lineshape of a particular transition and its separability from other lines. The polarization ratio was obtained by integrating the whole NO peak in the high field under different polarization directions of the excitation laser. Variation of the polarization direction of the probe laser did not produce any observable alignment effect. As pointed out in previous discussions,²⁷ the permanent dipole moment of NO is so small that for the typical rotational levels investigated in this experiment, the effect of the orientation field can be ignored.

4.4 RESULTS

Table 4.1 summarizes the polarization ratios for m-nitrotoluene. These ratios represent the yield of NO when the polarization direction was perpendicular and parallel with respect to the direction of the orientation field. A larger than unity value signifies preferred excitation under perpendicular polarization, while a smaller than unity value signifies the opposite. Dissociation of nitro compounds produces NO with high rotational excitation, and given the dense rotational lines of NO and the many branches of the electronic transition, each peak measured in this experiment includes a few rotational transitions from different branches. From Table 4.1, the polarization ratios are specific for each dissociation wavelength, and they are independent of the

Table 4.1 Experimental Polarization Ratios (ρ) of m-Nitrotoluene.

Dissociation Wavelength	Peak Assignment	$ \begin{array}{c} \rho \\ NO (v = 0) \end{array} $	$\frac{\rho}{NO(v=1)}$
	R21(16.5)/R1(21.5)/P2(37.5)	1.43 ± 0.08	
245 nm (S ₂)	R2(25.5)/Q1(29.5)/Q2(31.5)	1.41 ± 0.09	
2 10 mm (52)	R21(27.5)/Q1(39.5)/Q2(40.5) /P2(47.5)/P12(55.5)	1.43 ± 0.12	
	R21(20.5)/R1(25.5)/R2(27.5) /Q1(31.5)/P1(38.5)/P12(47.5)		1.41 ± 0.06
	R21(16.5)/R1(21.5)/P2(37.5)	0.69 ± 0.05	
213 nm (S ₃)	R2(25.5)/Q1(29.5)/Q2(31.5)	0.70 ± 0.04	
	R21(27.5)/Q1(39.5)/Q2(40.5) /P2(47.5)/P12(55.5)	0.70 ± 0.05	

rotational and vibrational state of NO. It is therefore reasonable to combine the data from different quantum states of NO and derive an overall polarization ratio for each electronic state.

Table 4.2 lists all the polarization ratios of the four nitroaromatic compounds. For NB and o-NT, only the S₂ state was investigated using the same laser for dissociation and detection, and the results have been presented previously.^{32, 33} For m-NT and p-NT, both S₂ and S₃ states were investigated using two different lasers, one for dissociation and one for detection. Also listed in Table 4.2 are calculation results for each system.²⁰ The permanent dipole of the ground state and the rotational constants used in the calculation were obtained from our own *ab initio* calculation using Gaussian 98 on the MP2 6-31G** level. The permanent dipoles were scaled down by a factor of 70%, consistent with our previous treatment.^{32, 33} The rotational temperature was assumed to be 2.5 K.

In general, all polarization ratios for the S_2 state are similar for the four nitroaromatics, and perpendicular excitation relative to the orientation field is preferred. For the S_3 state, the polarization ratios are almost a direct reversal of those of the S_2 state, and parallel excitation is preferred. In all cases, the experimental values differ from the calculation results, which assumed a pure perpendicular transition for S_2 or a pure parallel transition for S_3 . These deviations are out of the error limit of our measurement, signifying that the transition dipole is not strictly parallel or perpendicular to the permanent dipole. For NB, if the C_{2v} symmetry is
Species	NB	o-NT	m-NT (245 nm, S ₂)	m-NT (213 nm, S ₃)	p-NT (249 nm, S ₂)	p-NT (213 nm, S ₃)
ρ (exp)	1.43 ± 0.04	1.46 ± 0.04	1.42 ± 0.06	0.70 ± 0.03	1.47 ± 0.07	0.72 ± 0.03
ρ (cal) ¹	1.62	1.54	1.61	0.62 ^f	1.72	0.58 ^f
$\sin^2(\alpha)^2$	0.16 ± 0.04	0.08 ± 0.04	0.16 ± 0.06	0.85 ± 0.06	0.18 ± 0.06	0.76 ± 0.05
a (°) ³	67 ± 3	70 ± 5	62 ± 5	28 ± 5	65 ± 4	30 ± 4
μ _p (Debye) ⁴	3.9	3.6	3.9		4.2	
A $(cm^{-1})^5$	0.1315	0.0748	0.0882		0.1290	
B (cm ⁻¹) ⁵	0.0429	0.0422	0.0329		0.0272	
$C (cm^{-1})^5$	0.0324	0.0271	0.0241		0.0225	

Table 4.2 Polarization Ratios (ρ) of Nitrobenzene and Nitrotoluene.

¹ Other than noted for dissociation at 213 nm (S₃ state) of m- and pnitrotoluene (shaded area), all calculations assumed a pure perpendicular transition with $\alpha = 90^{\circ}$.

- ² Fraction of parallel transitions.
- ³ Angle between the transition dipole and the permanent dipole.
- ⁴ Permanent dipole used in the calculation.
- ⁵ A, B, C are rotational constants from our *ab initio* calculation at the MP2 (6-31G**) level.

^f Calculations assumed a pure parallel transition.

preserved during the electronic excitation, this deviation signifies the existence of multiple excitations to electronic states of different symmetry.

Based on the methodology developed from our previous work,²⁰ the polarization ratio ρ is related to the angle α between the overall transition dipole μ_t and the permanent dipole μ_p via:

$$\sin^2 \alpha = \frac{2 \left[\rho(\alpha) - \rho(0) \right]}{\left[1 - \rho(0) \right] \left[2 \rho(\alpha) + 1 \right]} ,$$

where $\rho(0)$ is the expected polarization ratio when μ_t is parallel to μ_p . The value of $\sin^2 \alpha$ represents the amount of perpendicular transition (relative to the permanent dipole) in the overall transition dipole moment. From Table 4.2, the S₂ state is predominantly a perpendicular transition and the contribution of a parallel component amounts to 8 - 18 %, while S₃ is almost the opposite. The resulting angle between the permanent dipole and the transition dipole is therefore ~ 65° for S₂ and ~30° for S₃.

Figure 4.2 shows the voltage dependence of the polarization ratios for the R2(25.5)/Q1(29.5)/Q2(31.5) line of NO from dissociation of m-nitrotoluene at 245 nm. The dashed line is a calculation result after factoring in a 16% contribution from a parallel transition. The agreement between theory and experiment further supports the above conclusion.



Figure 4.2 Voltage Dependence of the R2(25.5)/Q1(29.5)/Q2(31.5) Line of NO from Dissociation of m-Nitrotoluene at 245 nm. The polarization ratios are defined by the yield of NO under perpendicular (to the orientation field) and parallel polarizations of the dissociation laser. The solid line is a calculation assuming a pure perpendicular transition using parameters listed in Table 4.2, and the dashed line factors into a 16% contribution from a parallel transition.

4.5 ANALYSIS

The nature of electronically excited states of nitroaromatics has remained elusive in the past. Discussions in the literature were mainly based on experimental work in the condensed phase or pure theoretical calculations.^{40 - 47, 59, 64} Three types of transitions have been suggested, including local excitation of the -NO₂ moiety, local excitation of the benzene ring, and charge transfer between the two chromophores. Our results on the direction of the transition dipoles should help clarify the situation.

We believe that the S₂ state of nitrobenzene should correspond to local excitation of the $-NO_2$ moiety, with the transition dipole predominantly perpendicular to the permanent dipole and lying in the plane of the ring. A charge transfer state would involve a transition dipole parallel to the symmetry axis, opposite to our experimental observation. The -NO₂ moiety is isoelectronic with an allyl anion on the simple Hückel level, so its electronic configuration should be $(b_1)^2(a_2)^2(b_1)^0$ in the C_{2v} symmetry for nitrobenzene.⁶⁵ The first excited state is from the a_2 orbital to the b_1 orbital with a transition dipole of b_2 symmetry. The transition dipole moment is therefore perpendicular to the symmetry axis and in the plane of the $-NO_2$ moiety. Similarly, in the D_{6h} symmetry of benzene, the electronic configuration is $(a_{2u})^2 (e_{1g})^4$, and the first excited electronic configuration is $(a_{2u})^2 (e_{1g})^3 (e_{2u})^1$. The first two electronic transitions occur at 254 nm for the ${}^{1}B_{2u}$ state and 203 nm for the ${}^{1}B_{1u}$ state.⁶⁶ Both states are symmetry forbidden in the original D_{6h} symmetry, but when the molecular frame is distorted to a C_{2v} symmetry,⁶⁷ both are allowed with transition dipoles perpendicular $({}^{1}B_{2u})$ and parallel $({}^{1}B_{1u})$ to the symmetry axis. These two

transitions should be relatively weaker than the allowed transition localized at the -NO₂ moiety. It is therefore reasonable to assign the weak transition centered at 280 nm, the S₁ state in Figure 4.1, a local excitation of the benzene ring to the ${}^{1}B_{2u}$ state, corresponding to ${}^{1}B_{2}$ in the C_{2v} group, and the transition dipole is perpendicular to the symmetry axis in the plane of the benzene ring. The higher energy state of the ring (${}^{1}B_{1u}$) contributes as a symmetry species of A₁ in the C_{2v} group, so it is a parallel transition along the symmetry axis. We believe this is the origin of the parallel component in the predominantly perpendicular transition to the S₂ state.

The S₃ state can be assigned as a mixture of the charge transfer state from the a₂ orbital of the -NO₂ moiety to the e_{2u} orbital of the benzene ring and an excitation of the π orbitals localized on the ring. Upon distortion into C_{2v}, the degenerate e_{2u} orbital of benzene splits into two orbitals of a₂ and b₁ symmetry. Transitions from the a₂ orbital of the -NO₂ moiety to these two orbitals contain a parallel component and a perpendicular component, as do the transitions on the ring to the electric dipole allowed E_{1u} state. Given the fact that local excitation of the benzene ring is centered at 180 nm,⁶⁶ its contribution to S₃ should be substantial. The dominant parallel component of this transition is therefore the (E_{1u}) A₁ \leftarrow A₁ of the ring and the a₂ \leftarrow a₂ charge transfer from -NO₂ to the ring. The perpendicular component contributes less than 20% of the overall transition strength, and it could correspond to the transition of the a₂ orbital of the -NO₂ moiety to the b₁ orbital of the ring, and the (E_{1u}) B₂ \leftarrow A₁ of benzene. Our experiment cannot distinguish the difference between the in-plane and the out-of-plane transitions when they are both perpendicular to the permanent dipole.

Nitrotoluenes do not have the same symmetry as nitrobenzene, but their absorption spectra are similar and their polarization ratios follow the same trend as those of nitrobenzene. It is therefore reasonable to assume that for all four nitroaromatic compounds, the S₂ state is predominantly a local excitation of the -NO₂ moiety, while the S₃ state is a mixture of the charge transfer state from the a₂ orbital of the -NO₂ moiety to the benzene ring and an excitation of the π orbitals localized on the ring. Figure 4.3 summarizes the directions of the transition dipoles and the permanent dipoles. The sizes of the permanent dipoles from our own ab initio calculation are listed, and the scaled permanent dipoles used in the calculations of Table 4.2 are also shown in brackets. Our treatment derives the direction of the transition dipole in the molecular frame, we rely on the direction of the permanent dipole of the ground state, which can usually be determined with a high precision.

It is interesting to review the literature reports on the direction of transition dipoles of the two electronic states S_2 and S_3 . In a polarization study of nitrobenzene, three electronic transitions were identified, and the S_1 and S_2 states labeled in Figure 4.1 were reported to be perpendicular and parallel to the symmetry axis.^{64, 68} A later work by Nagakura *et al* believed that the S_2 state was largely a charge transfer state from the ring to the -NO₂ moiety.⁴⁰ The transition dipole should therefore be parallel to the direction of the permanent dipole, in agreement with the earlier report.^{64, 68}



Figure 4.3 Permanent Dipoles and Transition Dipoles of Nitrobenzene and Nitrotoluene. The numbers listed on top of the single headed arrows are the permanent dipoles obtained from our calculation on the MP2 6-31G** level, while the numbers in the brackets are the dipoles used in the calculation of Table 4.2. The transition dipole directions for the S_2 states are represented by double headed arrows with their directions labeled relative to those of the permanent dipoles.

The S₃ state was assigned a mixture of local excitation of the -NO₂ moiety and the $B_{1u} \leftarrow A_{1g}$ transition of benzene.⁴⁰ These conclusions were derived based on a theoretical calculation and the solvent shift of the absorption bands. Given the level of the calculation, it is not surprising that the symmetries of both states are contradictory to our result from the gas phase. In a later experiment by Sinha and Yates using electro-optical spectroscopy in solutions of dioxane and cyclohexane,⁵⁹ the S₁ state was assigned ${}^{1}B_{1}$, while the S₂ state was ${}^{1}A_{1}$. The disagreement of this work with our gas phase studies might be a manifestation of the solvent effect in the condensed phase. In theoretical attempts, the order of the excited states was typically adjusted based on early experimental results, since the energy of the excited states was believed to have large uncertainties.⁴² Taking into account the complications in experiments conducted in the condensed phase, the fact that most calculations are in disagreement with our gas phase results should not be a surprise.⁴³⁻⁴⁵ The calculation by Malar and Jug included both singlet and triplet states, 42 and the transition to the S₂ state of Figure 4.1 was actually the 4th singlet excited state in energy, and its symmetry species was $^{1}B_{2}$. Crim's group reported two singlet allowed transitions with B_{1} and B_{2} symmetry.⁵⁵ If we assume that the B_1 state corresponds to S_1 , while B_2 corresponds to S_2 , as suggested by the authors, their results are in qualitative agreement with our observation. However, no calculation of the S₃ state was included in this calculation. In a later work by Takezaki *et al.*⁴⁶, the S₁ transition near 280 nm was reported to be

the third singlet excited state with a symmetry of A_2 , a forbidden transition in the C_{2v} group.

Polarization spectroscopy of oriented gas phase molecules offers a universal approach to deriving the direction of the transition dipole. As long as the molecules can be effectively oriented, the polarization ratio of the excitation probability should reveal the direction of the transition dipole. In this experiment, the pathway for the generation of the NO fragment is unclear, but the relative production of NO under different polarizations should only be proportional to the excitation probability and insensitive to its pathway. The polarization ratio is therefore independent of the dynamics of the upper state. Moreover, large molecules are particularly suitable for this type of investigation, mainly because of the ease of orientation, as pointed out in our previous calculation.²⁰

4.6 CONCLUSION

We report the directions of transitions dipoles for two electronically excited states of nitrobenzene and nitrotoluene. Although the mechanism of dissociation of the upper state is still unclear, the polarization ratios of the NO product allow for determination of the symmetry of the upper state. The S_2 state is dominated by a perpendicular transition relative to the permanent dipole, while the S_3 state is dominated by a parallel transition. Moreover, quantitative analysis based on our calculation demonstrates that the excitation may not be just a simple single electron two state event, particularly in the case of nitrobenzene. A minor component

perpendicular to the predominant transition also exists for both states. Based on a simple Hückel analysis, we believe that the S_2 state is mostly local excitation of the -NO₂ moiety, while the S_3 state is a mixture of a charge transfer state from the -NO₂ moiety to the benzene ring and a local excitation of the ring.

4.7 ACKNOWLEDGEMENT

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Chapter 5

Conclusions

5.1 SUMMARY

The experiments presented in this dissertation contain two major aspects: Brute Force Orientation for determination of transition dipoles in large asymmetric top molecules; analysis of product internal energy distributions for mechanisms of photodissociation. Successful orientation of large molecules, when sufficiently cooled, was observed. The symmetry property of the electronic transition dipole of nitrobenzene and the three nitrotoluene isomers has been determined. Additional study of the internal energy distribution of the photodissociation product NO has produced new insight into the dynamics of dissociation.

In chapter three, the dissociation dynamics of the nitroaromatic compounds were detailed by studies of the internal energy distribution of the nitric oxide photofragment. In all cases, NO was produced highly rotationally and vibrationally excited. Analysis of the NO rotational distributions indicated a bimodal rotational distribution for several of the systems studied. This can be interpreted as evidence for multiple dissociation channels. For the nitrotoluene isomers, evidence of sequential dissociation of the NO₂ fragment upon absorption of another photon was observed. This observation is supported by the similarity in fragment internal energy distribution between NO₂ and the nitrotoluenes, including the spin-orbit ratio, Λ -doublet ratio, vibrational population inversion, and high rotational excitation in excited vibrational states. Bond dissociation energy calculations were used to investigate the possibility of dissociation via isomerization of the nitro group to a nitrite moiety. The calculation offered rationale for isomerization being a more likely pathway for m-NT and p-NT, as compared to NB. The ortho effect on the o-NT molecule was also evidenced in these calculations, resulting in an increased stability for the nitrite isomer. Further support for the isomerization hypothesis is found in the similarity with Λ -doublet ratios of NO produced in t-butyl nitrite dissociation.

Chapter four focused on the determination of the excited state symmetries of the S_2 and S_3 states of the nitroaromatic compounds. This was obtained by determining the orientation of the transition dipole relative to the permanent dipole of the system for a given electronic transition. We first oriented the molecule in a strong, uniform electric field and then probed its absorption probability via the yield of the NO product. The direct experimental result was a polarization ratio representing a preference for absorption of light polarized either parallel or perpendicular to the orientation field. In combination with theoretical modeling, we determined that the S_2 state is primarily a local excitation of the NO₂ moiety with a perpendicular transition dipole. The S_3 state involved charge transfer from the NO₂ moiety to the benzene ring, with a predominantly parallel transition dipole. Both transitions indicated that they were not purely perpendicular or parallel, and the transitions are not single electron events involving only two localized states.

In combining the results of the orientation experiment with those from the dissociation dynamics, we were able to show that the dissociation process for the nitrotoluene isomers is fairly independent of the initial potential energy surface. Our

results indicate that memory of the excitation event has been largely erased when the molecule dissociates. This is consistent with rapid internal conversion after absorption but prior to dissociation, and it is further corroborated by the long dissociation time observed for these molecules. The dissociation event is largely statistical, and most of the dynamical effect, such as preference in Λ -doublet population, is associated with the sequential dissociation of the NO₂ fragment.

5.2 FUTURE WORK

After the success of the nitroaromatic experiments, a redesign of the molecular beam source has been completed to allow for vaporization of nucleic acid bases under extreme heating conditions. Preliminary results have succeeded in observing 1,3-dimethyl uracil in the gas phase. A low rotational temperature was obtained and effective orientation was achieved. However, fragmentation was also observed, and the next step will be to accurately determine the molecular formula of the observed fragment, and ultimately, to characterize the transition dipole of the oriented species.

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APPENDICES

Appendix A

Brute Force Orientation Figures



Figure A.1 Polarization Ratios for m-NT at Different Rotational and Vibrational Lines of NO. This plot shows the preference for a parallel transition for the S_3 transition and a perpendicular transition for the S_2 transition. The different blue bars represent different rotational lines for the NO produced from dissociation at the listed wavelength in nm. The ratios presented are perpendicular to parallel.



Figure A.2 Polarization Ratios for p-NT at Different Rotational and Vibrational Lines of NO. This plot shows the preference for a parallel transition for the S_3 transition and a perpendicular transition for the S_2 transition. The different blue bars represent different rotational lines for the NO produced from dissociation at the listed wavelength in nm. The ratios presented are perpendicular to parallel.

Appendix B

1,3-Dimethyl Uracil Experiment

After completion of the nitroaromatic experiment series we moved to orientation of nucleic acid bases with the use of the heated pulsed valve discussed in Chapter 2. Uracil and thymine proved to be difficult to detect in the gas phase, so 1,3dimethyl uracil (DMU) was selected because of its higher vapor pressure.

Signal was rapidly found using this sample in the heated pulsed valve with mild heating. We did find that signal went away when the sample was heated above its melting point. The meaning of this data was uncertain because we determined through later experiments that we had been studying a contaminant of some sort. The contaminant has not been identified at the present time, but may be a form of the DMU dimmer. In the future we hope to determine the species investigated and publish these results for that system. The mass peak used for all of the detection and measurements was found to be between 91 and 92 amu using pyrimidine as a calibration molecule for the mass spectrum. The signal was found to be dependent on at least 2 photons, but up to six may have been involved. The orientation results are presented for the unknown parent molecule. The rotational temperature of pyrimidine in the expansion was ~1.8 K indicating that the parent was rotationally cold; this is consistent with the orientation effect observed.



Figure B.1 Averaged Mass Spectrum. The pulsed valve dependent peak labeled was used for the orientation and REMPI experiments. The estimated fragment mass is 91 atomic mass units. The parent DMU was not observed in this set of experiments.



Figure B.2 REMPI Spectrum of Mass 91 Peak. This is the REMPI spectrum attained for the mass 91 fragment when scanning the laser.


Figure B.3 High Resolution UV/VIS Spectra of Vapor Phase 1,3–Dimethyl Uracil. These spectra were taken with a Shimadzu UV/VIS spectrometer with an evacuated sample cell heated to the listed temperatures.



Figure B.4 Spectra Comparing One and Two Laser Mass Results. Spectrum **a** is of a two laser mass spectrum and is contrasted to the one laser signal of spectrum **b**.



Figure B.5 Polarization Ratio Plot for 1,3-Dimethyl Uracil Experiment. This plot indicates that the observed molecule had a preference for absorbing light polarized perpendicular to the permanent dipole of the molecule. The ratio of perpendicular to parallel was 1.28 ± 0.09 . The wavelengths listed correspond to peaks in the REMPI spectrum used for the orientation analysis.