INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.

2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame. If copyrighted materials were deleted you will find a target note listing the pages in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.
Dietz, Thomas Gordon

RESONANT MULTIPHOTON IONIZATION OF LARGE MOLECULES IN SUPersonic BEAM ENVIRONMENTS

Rice University Ph.D. 1981

University Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106
RICE UNIVERSITY

RESONANT MULTIPHOTON IONIZATION OF LARGE MOLECULES IN SUPersonic BEAM ENVIRONMENTS

by

Thomas Gordon Dietz

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

[Signatures]

Richard E. Smalley
Professor of Chemistry
Chairman

Robert F. Curl
Professor of Chemistry

F. H. Bunting, Associate
Professor of Physics

HOUSTON, TEXAS

AUGUST 1981
Abstract
Resonant Multiphoton Ionization of Large Molecules in Supersonic Beam Environments
by Thomas Gordon Dietz

Time-of-flight detected resonant two photon ionization (R2PI) in supersonic beams is investigated. The advantages of the method are the high sensitivity, spectral selectivity and the lack of extensive fragmentation in the mass spectra. To obtain these properties the molecular system must meet several restrictions. Stable intermediate electronic states, which are greater than half of the adiabatic ionization energy generally are detected with these advantages, with a single photon field supplying the energy to populate the intermediate state and to form the photoions. Modulation of the ionization efficiency is observed when a rapid decay channel is available to the intermediate state, which is no longer coupled to the photon field. These properties are illustrated by the behavior of aniline, bromobenzene, and metal carbonyl systems.

Two-color ionization removes many of the restrictions inherent to one-color R2PI. High efficiency is maintained for a broader class of molecules by allowing the ionization photon to provide the energy spanned by the intermediate state and the ionization continuum levels. Experiments which scan the ionization laser energy, provide information regarding the nature of the ionization step in benzene and naphthalene. The predominantly step-like direct ionization structure observed, indicates that this is the dominant ionization process. Thus the
relevant selection rules governing the propensity of an intermediate state to ion transitions are largely of a vibrational nature.

The two-color ionization method has been specifically applied to studies of collision-free vibrationally excited triplet state levels formed in the molecular beam. By varying the time delay between the pump and ionization lasers, the decay of excited state populations can be monitored. This time evolution data has been unavailable through conventional methods due to the experimental difficulties imposed by the long-lived, non-fluorescent nature of these states. As the decay rate of these states are highly sensitive to excess vibrational energy, the presence of collisional perturbation tends to distort the true non-radiative decay rates. In the molecular beam environment, the decay of triplet levels, isoenergetic with initially pumped $S_1$ vibronic states, have been monitored as a function of the excess vibrational energy in several aromatic systems. It is found that the slope of this excess energy dependence does not extrapolate well to the zero energy value determined by low temperature crystal measurements. This effect appears to be a result of intramolecular vibrational redistribution in the triplet manifold, causing a dilution of good accepting mode character. Although the states initially populated by $S_1 - T_1$ intersystem crossing are likely to be good accepting modes for the $T^\dagger - S_0$ transition, the presence of fast IVR will result in a distribution of most of this vibrational energy amongst the statistically more prevalent poor accepting low frequency modes.

Two-color R2PI is a very general technique and allows for the
detection of many exotic species. Molecular beams are capable of producing distributions of cluster species formed in the initial stages of the supersonic expansion. One area of great promise is the study of metal cluster species by this method. Preliminary experiments investigate the utility of both laser vaporization and photolysis of metal containing organometallic species, as sources for these metal atom clusters, which are detectable by photoionization methods.
Acknowledgement

'We get by with a little help from our friends...' and I must thank the many friends who have helped me through my stay at Rice. Mike Duncan, my principal coworker on the projects in this thesis, was extremely helpful, both in the physical completion of the experiments and in the many fruitful discussions we had concerning the science of our results. Greg Liverman's efforts were instrumental to the success of the experiments as he spent many hours developing the computer software that enabled the rapid and efficient collection of the mass spectral data. He and his wife also provided a social outlet, as they shared much of their free time in Betty's and my company. Dave Powers, John Hopkins, Steve Beck, and Dave Monts all helped out by providing an environment in which I was continually challenged and encouraged. Many thanks to Jim Newman, whose valuable assistance with the operation of the spinwriter and the software necessary to its use saved me many hours and much money in the production of the final copy contained in this volume. To Professor Rick Smalley, I thank you for sharing with me your many insights into the field of chemical physics. To all of my professors and teachers of the past 25 years, I thank you for your patience and guidance.

Most of all, I would like to thank my wife, Betty, who has supported and encouraged me throughout my graduate and undergraduate studies. In addition, it is she who typed a large amount of the text into the computer, and proofread the resultant copy for my numerous
spelling and grammatical errors. Her dedication is recognized and sincerely appreciated.
# Table of Contents

Chapter 1. Introduction 1

Chapter 2. Experimental 10

2.1 Vacuum Hardware 10
2.2 Supersonic Beams 13
2.3 Pulsed Beams 16
2.4 Time-of-Flight Mass Spectrometer 23
2.5 Laser Sources 31
2.6 Electronics and Computer Data Acquisition 33

Chapter 3. Resonant Two-Photon Ionization 35

3.1 Introduction 35
3.2 Monohalobenzenes 38
  3.2.1 Introduction 38
  3.2.2 Results 39
  3.2.3 Discussion 49
3.3 Metal Carbonyls 52
  3.3.1 Introduction 52
  3.3.2 Results 54
  3.3.3 Discussion 65
3.4 Aniline 68
  3.4.1 Introduction 68
  3.4.2 Results 70
3.4.3 Discussion

Chapter 4. Two-Color Ionization Studies

4.1 Introduction

4.2 Threshold Experiments
  4.2.1 Introduction
  4.2.2 Naphthalene
  4.2.3 Benzene

4.3 Triplet State Dynamics
  4.3.1 Introduction
  4.3.2 Substituted Benzenes and Benzene
    4.3.2a Results
    4.3.2b Kinetic Model
    4.3.2c Vibrational Energy Dependence of Triplet Decay Rates
    4.3.2d Tert-butylbenzene: Fragmentation Processes in R2PI
    4.3.2e Oligomers

4.3.3 Pyrazine and Pyrimidine
  4.3.3a Introduction
  4.3.3b Results and Discussion
  4.3.3c Conclusion

4.3.4 Conclusion
Chapter 5. Metal Clusters

5.1 Introduction 156

5.2 Laser Vaporization 157
   5.2.1 Method 157
   5.2.2 Results and Discussion 158

5.3 Photophysics of Transition Metal Complexes 166
   5.3.1 Introduction 166
   5.3.2 Results and Discussion 168

Chapter 6. Summary 175

References 176

Appendix 1 186
CHAPTER 1

INTRODUCTION

The development of laser sources in the last 20 years has catalyzed interest in many new fields of chemical physics. The most glorified of the possibilities for laser application has been the idea of laser specific chemistries. The feasibility, economics, and subjects of this laser chemistry has yet to be developed and is still a subject of high interest and considerable debate. However, the area where lasers may make their largest lasting impact is with the sensitive and selective detection techniques that have become possible only through use of the unique properties of laser light sources.

In the past, the nature of conventional light sources limited spectroscopy to relatively low fluence conditions. In this circumstance, possible detection methods are largely restricted to absorption and emission studies. Absorption experiments are hindered by the requirement that sizable fractions of the input light must be absorbed. In numerous systems, which have small absorption cross-sections for transitions to excited state levels, extremely high molecular densities or long path lengths are required for this technique to be of general use. Detection of emission from excited states proves to be far more attractive in terms of overall sensitivity, however this technique is far from ideal and somewhat limited. Most molecules emit from their excited states with far from
unit efficiency due to the presence of non-radiative decay channels, which in some instances may reduce emission yields to zero. Detection efficiency is modulated by the emission yield and 'dark' molecular states with small yields are virtually undetectable. Furthermore, collection of molecular emission by an optical system and the conversion into electrical signals by phototubes is a very inefficient process. Finally, the ultimate sensitivity of both of these techniques is restricted by the low light fluences available, as in low pressure gases only a small fraction of the incident photons will be absorbed to populate excited states.

The most sensitive of conventional non-laser techniques is mass spectrometry. While this technique boasts high sensitivity (approaching 0.1% detection efficiency in low pressure gases) and mass selectivity, several features of mass spectral data are unattractive. Electron beams are the typical means of ion production in most mass spectrometers, and the high energies required for maximum ion production results in non-selective ionization. The high energy electron beams (typically 70 ev) usually provide several times the bond energies of typical chemical species and wholesale fragmentation is generally observed. Fragmentation patterns are usually complex and mixtures of similar molecules may be difficult to separate due to the presence of common functional groups. Often pre-separation techniques, such as gas chromatography, become necessary compliments the mass spectral method.

The recent availability of high peak power tuneable dye lasers has
encouraged the development of new types of spectroscopically selective detection. These laser sources simultaneously allow the sensitive detection of molecular excited states, based on spectroscopic techniques, as laser outputs combine high power and narrow bandwidths. The high photon fluences characteristic of laser sources, enable the selective population of excited states with high efficiency. Additionally, multiple photon absorptions and non-linear processes are feasible under laser fluence conditions.\(^1\) A particularly attractive possibility is the use of high power lasers to form ions. When a sufficient number of photons are absorbed by a molecule, ionic states of that molecule become energetically accessible and a photoion can be created. This method of multiphoton ionization was first demonstrated by Johnson and coworkers.\(^2\)

As the ionization energies of most molecules fall in the range of 7–11 electron volts, absorption of several (2–4) visible or ultraviolet photons can produce ionization. Photoionization by one-photon absorption is well known, but this type of excitation is typically non-selective as little or no sharp structure is observed above the ionization potential due to the continuous nature of the ionic manifold. The large vacuum ultraviolet photon fluences necessary for a high probability of direct one photon ionization are very difficult to obtain with either conventional or laser light sources. Multiphoton absorption effectively extends the range of laser outputs, as many states can be accessed by two photons instead of one.

The early MPI experiments of Johnson et al.\(^2\) required extreme
laser conditions to accomplish ionization by absorption of three or more photons. These severe conditions however, have been found to be unnecessary for the efficient ionization of molecular species. Extreme laser fluences produce undesirable fragmentation by enabling subsequent absorptions by the ionic states$^{3-7}$. Nonetheless there is a spectral dependence of the total ionization yield due to the inherent structure in molecular spectra. This is a significant advantage of laser excitation over electron beam ionization sources. The need for extreme laser fluences was dictated by the high order processes studied in the initial multiple photon ionization work. For three photon or greater absorptions two or more intermediate states are encountered. The rate of ion formation is limited by the products of cross-sections for photon absorption at each intermediate level, which are typically as small as $10^{-82}$ cm$^6$ sec$^2$ for three photon resonances.$^7$ Absorption cross-sections for one photon resonant states are much larger, typically around $10^{-18}$ cm$^2$. It is not surprising that under the fluence conditions required to populate a state by a multiphoton transition ($10^{25} - 10^{28}$ photons/cm$^2$-sec), the resultant ions will absorb additional photons causing extensive fragmentation. Decay from intermediate states to levels which are no longer coupled to the photon field is a second factor which limits the total rate of ion formation and efficiency. A much more efficient method of ion production would restrict itself to stable resonant states, as this method avoids the pitfalls of unfavorable intermediate states. The additional constraint that only two photon absorptions are utilized provides for a reduced
degree of fragmentation, due to the relaxation of laser fluence conditions. The properties of this type of resonant two-photon ionization (R2PI)\textsuperscript{8-15} are explored and elucidated by several experiments in this thesis.

An energy level diagram relevant to the R2PI method is illustrated in Figure 1.1. In this simplified picture, a laser pumps an electronic intermediate state greater than half way between the zero point level of the molecule and ground state of the ion. This level can decay along several paths. Emission of a photon and relaxation to the ground electronic state, such as in fluorescence, is probable if the radiative rate is competitive with non-radiative channels. The radiationless channels, internal conversion and intersystem crossing to other low lying electronic states, occur without the emission of photons. Finally, when the rate of up-pumping by the laser field is competitive with any of these paths, ionization occurs upon absorption of a second photon.

For most molecular systems, a suitable choice of laser sources enables the detection of excited states of molecules with high efficiency (up to unit efficiency). Molecules are selectively excited depending on the frequency of the pump laser source and the absorption spectra of the excited state molecules to be detected. A mass spectrometer is often interfaced to these experiments to collect the resultant ions and provide mass resolution. The mass determination serves to separate species which have absorptions in overlapping spectral regions. However, in the R2PI experiment, the mass spectral
FIG. 1.1 Energy level diagram of the resonant two-photon ionization process. Intermediate levels pumped by $\omega_1$ can be ionized by subsequent absorption of a second photon ($\omega_2$). Non-radiative decay of the intermediate state modulates the ionization yield. Conversion of electronic energy into vibrational motion, as in the $T^+$ state illustrated, is responsible for the attenuation of the ionization yields.
data takes on added importance as the total ionization energy is minimal and thus the formation of predominantly parent ions is often observed. The net result is that R2PI detection is a method which boasts all the advantages of mass spectroscopy, while adding excitation selectivity through control of the narrow band laser frequency.

Concurrent and parallel to the development of laser ionization methods, the technology of supersonic beam expansions has encouraged a renewed interest in large molecule spectroscopy.\textsuperscript{16,17} A supersonic beam provides a unique environment, in which molecules of low internal temperature can be probed in the absence of intermolecular perturbations. Under these conditions complex spectra are often reduced to easily analysed patterns. Interesting studies of excited state molecular dynamics as well as the unraveling of spectroscopic problems benefits from the availability of these collision-free low temperature molecules. The results of beam studies have added significantly to the general knowledge of large molecule physics. However these experiments place severe demands on the detection system due to the very low gas densities required for true collision-free conditions.

This thesis is concerned with the development of R2PI techniques, with the goal of its utilization for the study of the dynamics of rarified molecules cooled by supersonic expansion sources. The marriage of these two experimental techniques has enabled several unique studies of molecular systems to be undertaken. The experiments discussed within this work attempt to point out the type of information
that can be obtained within the constraints of this powerful experimental system.
CHAPTER 2

EXPERIMENTAL

The experimental apparatus used for the study of beam cooled gas phase molecules is illustrated in Figure 2.1. The apparatus consists of several vacuum chambers, a pulsed nozzle source, and a photoionization mass spectrometer along with the requisite high peak power lasers, and computer data acquisition system.

2.1 VACUUM HARDWARE

The source chamber of the supersonic beam apparatus is a stainless steel cylinder of 90 centimeters in diameter and 90 centimeters tall. Its large dimensions have been chosen in order to minimize possible interference to the supersonic expansion by molecules which have scattered off the walls of the vacuum chamber. The chamber is pumped by a 20 inch diffusion pump (Varian HS-20) that provides a pumping speed of 20,000 liters/sec for helium. Under no-load conditions, pressures of $\sim 1.0 \times 10^{-6}$ torr are routinely obtained, whereas with the pulsed beam operating at 10 hertz and 5-10 atmospheres backing pressure, the average pressure ranges from $1-3 \times 10^{-5}$ torr. The pulsed nozzle source is mounted inside the vacuum chamber on a translator which allows alignment along three orthogonal axes. A conical skimmer is also mounted in this chamber upstream of the nozzle at a distance of
FIG. 2.1 Schematic diagram of the supersonic beam system used in this work.
15 centimeters from the center of the chamber. Experiments can be conducted in this chamber by fluorescence detection, or upon the skimmed molecular beam in two smaller chambers past the first skimmer.

The small 11.5 inch x 11.5 inch square chambers are isolatable from the main expansion chamber by a gate valve which allows maintenance of high vacuum conditions during periods of nozzle servicing. These chambers are pumped by individual 6 diffusion pumps (Varian VHS-6) and are maintained at pressures less than \(3.0 \times 10^{-8}\) torr. Liquid nitrogen trapping in both chambers provides additional pumping for condensible species. This is especially important in the detection chamber as background gas can be efficiently detected by the photoionization time-of-flight mass spectrometer (PITOFMS) which is mounted there. A copper shroud in contact with the LN\(_2\) dewar surrounds the source of this instrument, trapping the majority of diffusion pump vapors before they can enter the source region. The details of the time of flight source will be described in a later section of this thesis.

2.2 SUPersonic Beams

A supersonic beam is formed by the expansion of gas from a high pressure region through an orifice into a region of low pressure vacuum. This type of expansion produces several effects which are extremely attractive to the molecular spectroscopist studying the
photochemistry of large molecules.16-19 The high frequency of collisions in the transition between the high pressure gas and the collisionless regime downstream of this source, act to convert the initially random kinetic motion of the gas into directed mass flow. The directional properties of the supersonic expansion is apparent in the characteristic \( \cos^2 \theta \) intensity distribution about the beam axis.17a The expanded gas has a large velocity component parallel to this axis and a small component in the perpendicular direction. The net effect is a narrowing of the parallel velocity distribution of the expansion gas from that of the initial thermal Boltzmann distribution of the source gas. The parallel velocity components that result can be fit to a Boltzmann distribution which is characteristic of translational temperatures of a few \( ^\circ \text{K} \). The speed of sound in an ideal gas is proportional to the square root of the gas temperature, which for the expanding gas is lower than the parallel velocity component, hence the terminology, supersonic beam.

When a polyatomic molecule is expanded in a free jet, not only is the translational temperature reduced, but the internal degrees of freedom, such as rotations and vibrations are efficiently quenched. Molecules of the size of benzene and naphthalene have been studied extensively under supersonic beam conditions and the extent of cooling of internal energy is found to be large. This work has shown that rotational temperatures of less than \( 10^\circ \text{K} \) can be obtained for large polyatomic molecules under moderate conditions with the same molecular beam source used in this work.18,19 Absolute vibrational temperatures
are difficult to determine, but no hot bands with intensities greater than 1% of the major cold bands were observed for any of the molecules studied in this apparatus. This cooling of internal degrees of freedom serves an important function, reducing the difficulties of rotational and sequence congestions which plague room temperature studies.

The supersonic expansion can also cause a large degree of complexation and stabilization of many weakly bound species. This is a direct result of so-called three-body collisions, which are the interaction of three particles to form a partially relaxed complexed molecule. These species are cooled further by the expansion, allowing the observation of species which are only bound by weak Van der Waals forces. A large body of research has developed, probing the nature and structure of this interesting class of molecules. However, the fertility of this new area has just recently been recognized, as a wider class of dimer and oligomer compounds are beginning to be studied to elucidate the nature of the bonding interactions.\textsuperscript{20,21}

The properties of supersonic nozzle expansions have been related to both nozzle orifice diameter and the source pressure.\textsuperscript{17a} These relations prove to be extremely useful in determining optimum experimental designs.

\[
\begin{align*}
\text{Temperature} & \quad (\text{PD})^{-1} \\
\text{Complexation} & \quad (\text{P}^2\text{D}) \\
\text{Throughput} & \quad (\text{PD}^2)
\end{align*}
\]

Depending on the cooling and complexation conditions which are required these parameters can be varied to yield the desired results. However
the finite capabilities of vacuum systems places several restrictions upon the possible choice of nozzle parameters. A continuously operated nozzle requires that the orifice dimensions be kept to a minimum in order to prevent pump overload and hence, is restricted to the use of high backing pressures to obtain strong cooling properties. Most large molecules have relatively low vapor pressures at moderate temperatures and the source pressure must be increased by addition of a second gas. Rare gases are used for this purpose as they provide strong cooling and are difficult to dimerize. Seeded beams of helium have been used for all of the experiments described in this work.

2.3 PULSED BEAMS

A pulsed supersonic expansion presents several advantages over that of a continuously operating expansion. The high pressure that is required to obtain cooling of large polyatomic molecules in a continuous expansion also tends to induce a large degree of complexation due to the \( p^2 \) dependence. A careful balance between cooling, complexation, and throughput must be determined for the successful use of continuous jet expansions. Stronger cooling properties, without the associated complexation, requires large diameter orifices, backed by lower pressures. The approach taken has been to use a pulsed nozzle to achieve this goal. The effective throughput, being reduced by a duty cycle factor, allows a corresponding increase in the peak throughput, enabling the increase of
the nozzle diameter up to 1 millimeter. A valve design developed in our laboratory\textsuperscript{18,19} operates with this diameter at up to 20 atmospheres backing pressure at repetition rates of 10 hertz. The cooling characteristics of these nozzles have been shown to be far superior to the smaller continuous nozzles.\textsuperscript{19} A second advantage of the pulsed nozzle is that the peak beam intensity can be much larger than the continuous beam. This additional density can be critical in experiments where signal to noise is a problem.

The design of the pulsed nozzle used for the experiments described in this thesis has been documented previously.\textsuperscript{18,19} Briefly, the nozzle is a variation of a design by Gentry and Giese.\textsuperscript{22} The valve is opened by passing a high current pulse through a hairpin loop formed by two conductors, one of which seals upon an o-ring seal. The high current pulse causes opposing magnetic fields to be generated, creating a repulsion between the two conductors, allowing gas to flow through the o-ring seal and the nozzle orifice. The original valve of Gentry and Giese produced a pulse with a 10 mircosecond duration (FWHM), however the modified valve used for this work, differs in pulse duration and intensity, yielding a 300 mircosecond flat topped pulse. Figure 2.2 is a diagramatic representation of the valve design. The valve firing is accomplished by discharging a 6 microfarad capacitor charged to 2 kilovolts with a thyatron switch (EG G HY-1102). Two types of conductors have been used as the top conductor. The pulse duration of the valve is dependent upon this choice, with aluminum\textsuperscript{23} and spring steel/copper generating pulses of 100 and 300 mircosecond pulses.
FIG. 2.2 Schematic of the Gentry-type pulsed nozzle. A. Stainless steel baseplate B. Copper return conductor C. Copper spacer D. Copper-plated spring steel or spring aluminum strip E. Teflon insulation F. Viton o-ring G. Teflon spacer H. Copper high voltage input lead I. Clamping bars J. Clamping screws.
respectively. The major advantage that has been found in the use of aluminum is its added thermal conductivity, which allows the valve to be operated at 10 hertz repetition rates, twice that safely obtainable with the spring steel/copper conductors.

The ability to skim the molecular beam pulse enables experiments to be conducted downstream of the expansion chamber and isolated from background gas residual from previous nozzle pulses. A tightly collimated beam is also necessary for the propagation of the molecular beam through the source of the time-of-flight mass spectrometer. Any scattering of the beam off of the time of flight surfaces will create sizable background signals from hot seed molecules and destroy the advantages of the molecular beam environment. The beam is skimmed by two conical nickel skimmers of 5 and 3 millimeter diameters before entering the detection chamber. The molecular beam pulse profile has been measured before and after skimming and little or no distortion of the skimmed pulse shapes is normally observed. Only at small nozzle to skimmer distances and high source pressures are there any indications of destructive skimmer interactions. A typical skimmed beam profile is presented in Figure 2.3. Absolute beam intensity measurements also indicate that the beam intensities are not effected by skimming. The measured intensity of a helium beam in this apparatus has been found to be $\sim 10^{23}$ particles/steradian-second, which is roughly 100x more intense than reported for any previous beam.$^{18a}$

The advantages of the supersonic beam environment as a spectroscopic medium are multiple. Most of the intermolecular
FIG. 2.3 Skimmed molecular beam profile as monitored by the photoionization signal of naphthalene.
perturbations operative in thermal mediums are completely removed. This advantage allows several experiments to be conducted that require these unique conditions. The cooling of internal degrees of freedom, complimented by the absence of collisional relaxation processes, allows dynamical studies of truly isolated molecules. Long lived states that are efficiently quenched by collisions are difficult to observe conventionally, but in the molecular beam they can be probed several hundred microseconds after their formation in the skimmed beam. Conversely, very short lived molecular states can be probed in the same beam environment. The narrow velocity distributions of these beams reduces the doppler widths of optical transitions. This type of subdoppler spectroscopy coupled with the simplified rovibronic spectra, allows line shape studies, free from trivial sources of broadening. Photofragmentation spectroscopy is a third unique possibility, as the spatial and directional properties of beam molecules allow studies of ejected photofragments. An off beam axis detector allows determination of high resolution data about the angular, translational, and internal energy distributions, as well as information on branching ratios of various photochemical channels.

2.4 TIME-OF-FLIGHT MASS SPECTROMETER

The density of helium carrier gas in the detection chamber has been determined to be equivalent to that of a static gas at $10^{-4}$ torr. Detection of the lower concentration seed gas molecules (typically 0.1
- 1% of the carrier) points to the need for extremely sensitive detection methods for the majority of molecular beam experiments. The recent advent of high pulsed power lasers and the development of multiphoton ionization techniques has filled this void.

The successful combination of the resonant two-photon ionization method with a flow-through mass spectrometer increases the data available in the supersonic beam experiment. There are numerous mass separation technologies from which time-of-flight mass spectroscopy has been chosen. Several other workers have also reported the advantages of using time-of-flight technology for photon detection. The time-of-flight (TOF) technique separates ions into time resolvable ion packets, by acceleration of the ions through an electric field and subsequent dispersion in a free flight region. The advantage of this type of mass separation is that an entire mass spectra can be obtained for every ionization laser pulse. As the pulsed nozzle source and high peak power lasers are limited to modest repetition rates, TOF detection will increase the experimental speed over that of most other mass spectral designs, while reducing potential confusion due to the limited nature of the data set.

Figure 2.4 shows a detailed cross-section of the photoionization time of flight mass spectrometer (PITOFMS). The ions formed in the ionization region are pushed into the acceleration region by the field between the repeller plate and the draw-out grid. They are then accelerated through the flight tube grid and into the deflection region. The field between the two deflection plates serves to
FIG. 2.4 Vertical cross-section of the photoionization time-of-flight mass spectrometer. The heavy black arrow shows the molecular beam path. The laser beam propagates in the direction normal to the plane of the diagram. A. Repeller plate B. Draw-out grid C. Flight-tube grid D. Deflection plates E. Flight tube F. Support rods G. Copper cryoshield H. Stainless steel liquid nitrogen Dewar I. Ion multiplier.

The grids and plates are spaced as follows: A-B = 2.54 cm, B-C = 1.27 cm, C-I = 112 cm.
counteract the translational energy of the molecular beam. The ions are detected by an ion multiplier (Johnson MM-1) the output of which is amplified by two fast tenfold amplifiers (LeCroy VV-100) and read by a 20 MHz transient digitizer (LeCroy 2256S).

In normal operation, the following voltages are placed on the grids and plates:

<table>
<thead>
<tr>
<th>Grid/Plate</th>
<th>Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repeller plate</td>
<td>+3100 V</td>
</tr>
<tr>
<td>Draw-out grid</td>
<td>+2660 V</td>
</tr>
<tr>
<td>Flight tube</td>
<td>0 V</td>
</tr>
<tr>
<td>Flight tube</td>
<td>0 V</td>
</tr>
<tr>
<td>Deflection plates</td>
<td>100–500 V</td>
</tr>
</tbody>
</table>

The mass spectrometer materials are either stainless steel or ceramic with the exception of the teflon insulation on the wire leads and the copper cyrotrap shield. The grids are 70 lines per inch, 90% transmission stainless steel mesh (Buckbee Mears).

A two stage acceleration design was chosen because it enhances the mass resolution of the device.\(^{25}\) The resolution of our instrument has been demonstrated by its ability to separate the isotopes of bromobenzene at masses 156 and 158. A mass spectra typical of those obtained in this mass spectrometer is illustrated in Figure 2.5. However, the overall resolution of the PITOFMS instrument is probably much greater than this would indicate. The resolution of a TOF mass spectrometer is determined by the initial space and velocity distributions of the ions.\(^ {25}\) The excitation laser has a finite diameter (typically 2 mm) and the ions formed at the upper and lower
FIG. 2.5 The photoionization mass spectrum of bromobenzene illustrates the mass resolution of the time-of-flight mass spectrometer. Two isotopes at 156 and 158 amu are resolved.
edges of the laser will not obtain the same acceleration. The resultant arrival times at the ion detector will differ accordingly. The spatial spread of the ions can be reduced considerably by tightening the laser waist in the ionization region. The velocity distribution is determined by the gas temperature and at room temperature this is the limiting factor. Through use of a supersonic beam source, this energy distribution is significantly reduced, as the translational temperature is nearly zero. In order for ions created in the beam to reach the multiplier, a voltage must be applied to the deflection plates. This effectively eliminates much of the signal due to background gas, since only a small fraction of these molecules are traveling at the same speed and in the same direction as the molecular beam. The total resolution of the instrument reflects the sum of the time spread from all sources, including the laser beam diameter, the transit time dispersion of the multiplier and amplifier, and the time resolution of the transient digitizer. At present, the resolution is limited by the time dispersion in our detectors and signal processing equipment and not by a time spread in the ion packets reaching the detector.

Laser beams may be admitted into the apparatus either perpendicular to or coaxially with the molecular beam. In experiments where two dye lasers were used, the tunable laser always crosses the molecular beam to minimize the effects of beam walk caused by tuning a doubling crystal. Experiments where an excimer laser was necessary, were configured such that the excimer laser crossed perpendicular to
the beam axis. In two laser timing experiments, careful alignment with fixed apertures insured that the axial laser beam was colinear with the molecular beam, as the initially excited molecules may travel up to several centimeters before detection by the second laser pulse.

2.5 LASER SOURCES

A neodymium doped yttrium aluminum garnet (Nd:YAG) laser (Quanta-Ray DCR1-a) equipped with harmonic generation crystals and beam separation optics was used as the pump laser to generate tuneable radiation. The harmonics of the 1.06 micron fundamental output are well suited to this application due to their high peak powers and the wide range of dyes which they efficiently pump. The second and third harmonics pump dye lasers, whose outputs range between 400–700 nanometers. The harmonics are also useful as excitation sources for molecules which have broad absorptions at these wavelengths. The output power available from this laser range up to 200, 100, and 50 mj/pulse for the second, third and fourth harmonic respectively. The output pulse duration ranges from 8 nanoseconds for the second harmonic to 3 nanoseconds for the fourth harmonic, all of which provide several megawatt peak output powers.

The majority of the experiments in this thesis require tuneable radiation, as the cooling of the supersonic expansion generally reveals very sharp absorption spectra. The output of a commercial dye laser (Quanta-Ray PDL-1) generates this light with a bandwidth of 0.3 cm$^{-1}$. 
This laser is typically frequency doubled into the ultraviolet with an angle tuned KD\textsuperscript{P} (potassium deuterium phosphate) crystal. The laser frequency can be scanned through use of a computer controlled stepper motor. Relative frequency measurements are obtained by directing part of the visible laser output through a solid quartz etalon (37.6 GHz free spectral range) and monitoring the transmission fringes with a photomultiplier tube (RCA 1P28). Relative laser power measurements were made in a similar fashion, by monitoring a fraction of the doubled output with a second phototube. Both frequency and laser power measurements are stored by the computer system along with the corresponding photoionization signals. Absolute laser power measurements were made using several detectors including a Coherent Radiation 210 power meter, a Molelectron J302-DW joulemeter, and a Scientech model 360001 power meter. When frequency doubled outputs were used the residual visible light was filtered with a Corning 7-54 filter to remove complications from possible multiple color absorptions.

In the triplet lifetime experiments, a second laser source is necessary in order to provide optimum photoionization efficiency. The requirement of large per photon energies and high peak power makes excimer lasers the ideal choice. The excimer laser was a Lumonics TE861 which provided outputs at a number of ultraviolet wavelengths. The Ar\textsuperscript{F} and F\textsubscript{2} laser transitions at 1930\AA{} and 1570\AA{} respectively were used exclusively, as they provide the highest per photon energies. The unfocused laser output was collimated to a 2 mm x 5 mm beam spot
adjusted to overlap the molecular beam in the time-of-flight source. Pulse to pulse power variations were measured by a photodiode and accounted for in the data acquisition.

2.6 ELECTRONICS AND COMPUTER DATA ACQUISITION

Synchronization of the pulsed nozzle, lasers and computer data retrieval was accomplished by the use of analog (BNC 8010) and digital (Evans Associates 4145-2) delay generators. In several experiments, the timing precision needed to be on the order of 10 nanoseconds, in order to insure overlap of the output of two lasers. In these experiments, such as in the determination of state lifetimes, the pertinent delays were set with the computer controlled digital delay generators (See Appendix 1). This hardware allows programming of the desired delay between 0-1 microseconds in 10 nanosecond intervals with \( \pm 1 \) nanosecond jitter. All other delays were set with the BNC pulse generators with accuracy to 0.1% of the total delay.

A computer data acquisition system was interfaced to the experiment to collect and digitize the data. The system is centered around a Camac-based LS11/2 minicomputer (Standard Engineering MIK-11/2). A mass spectral record for every laser shot is obtained by the transient digitizer and the computer extracts the appropriate signal channels. Laser power and relative frequency marker measurements are digitized by a 32 channel multiplexed analog-to-digital converter (Bi-Ra 5301). Data can be output through
the use of an eight-channel digital-to-analog converter (Kinetic Systems 3112) for plotting of data on strip chart recorders. The experiment is monitored and controlled with a graphics terminal (Lear Seigler ADM-3A with Retro-Graphics). The resultant data is stored on double density floppy disks (Digital Systems Design DSD-440).
CHAPTER 3

RESONANT TWO-PHOTON IONIZATION

3.1 INTRODUCTION

In this and later sections we will explore some of the advantages and limitations of resonance enhanced two-photon ionization (R2PI) as an alternative to laser induced fluorescence (LIF) for detecting excited molecular species in low concentration gases. The study of molecular species in even intense molecular beams, such as those produced by pulsed supersonic expansions, requires the use of very sensitive detection methods. Multiple photon ionization techniques offer some very attractive advantages over LIF in this regard, however, many of these schemes use two or three photons to access the excited state of interest, often reducing the overall detection efficiency. The R2PI method makes use of only one resonant intermediate state to gain its high sensitivity. The R2PI scheme is analogous to a one-photon absorption experiment. One photon is absorbed by the molecule, placing it in an excited state. The excited molecule then absorbs, rather than emits, as is the case in LIF, a second photon. The total energy of the molecule is now greater than the ionization potential, and an electron is ejected, leaving the molecular ion in a vibrational level of the ground state ion. This scheme may be realized
with a single color light source if the energy of the resonant state is more than half that of the ionization limit$^{8-15}$ or with two laser photons of different frequencies, as will be discussed in the next chapter.

There are two broad classes of molecules for which a comparison between R2PI and LIF would be instructive:

1. Molecules with an intermediate state having a lifetime that is shorter than or on the order of the laser pulse width.

2. Molecules with an intermediate state having a lifetime that is much longer than the laser pulse width.

Molecules in class (1) typically have a very low fluorescence quantum yield due to fast nonradiative decay processes. These 'dark' molecules have been observed heretofore only in absorption experiments. Using R2PI, the absorption spectrum of these molecules may be observed in a supersonic molecular beam with the same clarity as fluorescing molecules are observed using LIF. Like LIF, certain conditions must be fulfilled in order to obtain an absorption spectrum using R2PI. The excited state should not have a decay rate that is faster than the up-pumping rate to ionization, the cross-section for ionization from the excited state should be constant over the spectral region of interest, and saturation of the transition between the ground state and the excited state must be avoided. These criteria are qualitatively the same as those required when an absorption spectrum is desired using LIF techniques. However, the criteria are more stringent for LIF. If the excited state decay rate is too large, no signal is observed. A
large decay rate may be overcome in a R2PI experiment by increasing the laser power until the up-pumping rate exceeds the decay rate. From a knowledge of this up-pumping rate, which is a function of the laser fluence and the ionization cross-section, the decay rate may be calculated.

Molecules in class (2) can be subdivided further into two subsets. Low lying singlet states usually do have reasonable quantum yields for fluorescence and many have been extensively studied by LIF techniques. A comparison of the intensities of spectral features as observed in R2PI and LIF can provide sufficient information for the calculation of relative fluorescence quantum yields. The intensities observed in the LIF experiment are subject to the fluorescence quantum yield of the state under consideration, however, the R2PI experiment, under the conditions outlined above, can accurately produce the true absorption intensities.

A second subset of class (2) molecules do not generally have good emission yields, due to small radiative rates. For example, triplet states do not exhibit strong emission to the the ground state due to the spin forbiddenness of the $T_1 \leftrightarrow S_0$ transition. These states are generally very long-lived, but are nonetheless extremely difficult to detect by direct methods. Supersonic beam experiments utilizing photoionization detection are an excellent probe of these states, allowing dynamical studies to be conducted in an environment where external perturbations are largely removed. The utility of triplet state detection by multicolor R2PI methods will be described in detail.
in Section 4.2.

3.2 MONOHALOBENZENES

3.2.1 Introduction

Bromobenzene and iodobenzene were chosen for study as an example of case (1) molecules due to their short-lived intermediate state lifetimes. Several workers have attempted to observe fluorescence from the monosubstitutes halobenzenes, and only fluorobenzene has been shown to have a significant fluorescence quantum yield. The major radiationless decay channel from the lowest excited singlet state ($\pi\pi^*$) is believed to be intersystem crossing to a triplet state. The absorption spectra of both bromo- and iodobenzene have been observed, the former being characterized by sharp vibrational features and the latter being characterized by the lack thereof. The iodobenzene absorption spectrum is complicated by the fact that a $\sigma^* \leftarrow n$ absorption on the C-I bond overlaps the lower part of the $\pi^* \leftarrow \pi$ absorption in the region of 250-300 nm. This $\sigma^* \leftarrow n$ transition is believed to have an absorption cross-section that is two times greater than the $\pi\pi^*$ cross-section. In the 1-iodoalkanes the $\sigma^* \leftarrow n$ band, extending from 35,000 to 45,000 cm$^{-1}$, is invariant with respect to the length of the alkane chain, and is completely devoid of structure. The corresponding absorption in the bromoalkanes, and presumably bromobenzene, is displaced some 12,000 cm$^{-1}$ to the
blue. For both molecules the $^1\text{B}_2 - ^1\text{A}_1$ origin is more than half of the energy of the lowest ionization potential, which allows the use of a single laser for the R2PI experiments.

The first singlet state lifetimes of bromo- and iodobenzene have not been measured. The lifetimes of the iodobenzene $\pi\pi^*$ state is expected to be shorter than that of bromobenzene due to the larger spin-orbit coupling induced by the iodine atom. An upper limit for the lifetime for bromobenzene has been obtained by performing a delayed two-photon experiment. A study of the known monohalobenzene lifetimes and up-pumping rates allows estimation of the lifetimes for the singlet states of both molecules.

The experiments on the monohalobenzenes point out the profound advantage that R2PI provides in the detection of short-lived nonfluorescent electronic states. Molecules which until the advent of R2PI were undetectable in low pressure environments are now detected with high overall sensitivity, allowing studies of their collision-free spectroscopy and dynamics, along with many potential analytical applications.

3.2.2 Results

The mass spectrum of bromobenzene obtained when the laser (4 MW/cm²) was tuned to resonance at the origin of the $S_1$ transition at 36,991.5 cm⁻¹ is presented in Fig. 3.1. The fragmentation pattern was invariant with respect to the photon energy over the $^1\text{B}_2 - ^1\text{A}_1$ absorption. The peak mass 77 is the $\text{C}_6\text{H}_5$ fragment and the
FIG. 3.1 Resonance enhanced two-photon ionization mass spectrum of bromobenzene obtained when the laser was tuned to the $^1B_2 \leftrightarrow ^1A_1$ origin at 36,991.5 cm$^{-1}$. The parent ion is predominantly formed. A small amount of fragment at mass 77 is observed, as well as an impurity signal from naphthalene present in the addition lines.
peak mass 128 is the \( \text{C}_{10}\text{H}_8 \) ion from naphthalene, an impurity in the gas handling system. In general, the R2PI process produces predominantly parent ions, as Fig. 3.1 illustrates, provided the laser flux is not excessive. At higher laser fluence (177 MW/cm\(^2\)) the benzene ion peak becomes much larger, but further fragmentation is not observed. This is in agreement with other results \(^{14,24}\) for R2PI, but is quite different from conventional electron bombardment mass spectroscopy, which produces wholesale fragmentation for most molecules.

The bromobenzene sample that was used contained benzene as an impurity (\(\sim 1\% - 2\%)\). Resonances due to transitions from vibrationally hot benzene molecules were observed as \( \text{C}_{6}\text{H}_6 \) ions in the mass 78 channel in the vicinity of 38,500 cm\(^{-1}\). The intensities of these benzene hot bands were found to be less than 1\% of that of the benzene vibronic origin, however, the ion signal due to these hot bands was approximately the same as that due to bromobenzene excited at its origin. Without the mass separation afforded by a mass spectrometer, this impurity signal would have greatly complicated the analysis of the bromobenzene spectrum. The advantages of mass correlated detection becomes even more obvious when analysis of isomeric compounds is important, as the frequency dependence of ionization signals can provide the necessary structural information.

The R2PI spectrum of the \( ^1\text{B}_2 \rightarrow ^1\text{A}_1 \) transition of bromobenzene from the origin at 36,991.5 cm\(^{-1}\) to the KDP cut-off at 38,532.0 cm\(^{-1}\) is shown in Fig. 3.2. The spectrum is the average of three separate scans, each having been corrected for dye laser power fluctuations.
FIG. 3.2 Resonance enhanced two-photon ionization spectrum of the $^1B_2 \leftarrow ^1A_1$ bromobenzene absorption. The frequency scale is relative to the origin at 36,991.5 cm$^{-1}$. 
For these corrections we assumed that the R2PI intensity was proportional to the square of the laser power. This assumption should be valid because it is unlikely that we are saturating the $1B_2 \leftrightarrow 1A_1$ transition at the laser powers (4 MW/cm$^2$) used in the experiment. The individual scans are composed of the data points obtained at 0.0048 nm wavelength intervals. Each data point is the average of the signal obtained from 10–15 laser shots. A comparison of the individual scans to the average indicates that the relative intensities are reliable to within ±20%. Table 3.1 contains a list of the observed vibronic bands, their assignments, and intensities. The modes are numbered using Wilson’s system and were assigned in accord with other work in our laboratory. Our observations agree quite well with other observations of the bromobenzene $1B_2 \leftrightarrow 1A_1$ system except for the absence of a strong cold band at 234 cm$^{-1}$ reported by Prakash and Singh and Walzerstein. The absence of this feature from our cold spectrum indicates that it is a hot band. In the jet-cooled spectrum no vibrational hot bands are observed with intensities greater than about 1% of the cold bands, eliminating any confusion in the band assignments.

The spectrum is dominated by the origin and the ring breathing mode $6_b(b_2)$. The combination bands $6_b$ with the totally symmetric vibrations $12, 18_a$, and $9_a$ are also quite prominent. The assignment of the fundamental band at 1018 cm$^{-1}$ to the $9_a$ motion is at variance with previous workers. The motivation for the reassignment is based on an analysis of a series of fluorescence spectra of the alkyl
Table 3.1
Vibrational assignments and relative intensities for the $^1B_2(\pi\pi^*) \leftrightarrow ^1A_1$ R2PI spectrum of bromobenzene.

<table>
<thead>
<tr>
<th>Relative position (cm$^{-1}$)</th>
<th>Relative Intensity$^b$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>100</td>
<td>$0^0$</td>
</tr>
<tr>
<td>3.5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>240.5</td>
<td>9</td>
<td>$16_b^2$</td>
</tr>
<tr>
<td>249.1</td>
<td>4</td>
<td>$6_a^1$</td>
</tr>
<tr>
<td>518.9</td>
<td>69</td>
<td>$6_b^1$</td>
</tr>
<tr>
<td>620.8</td>
<td>3</td>
<td>$16_b^26_a^1$</td>
</tr>
<tr>
<td>877.7</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>925.3</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>931.4</td>
<td>30</td>
<td>$12_a^1$</td>
</tr>
<tr>
<td>960.3</td>
<td>43</td>
<td>$18_a^1$</td>
</tr>
<tr>
<td>1019.1</td>
<td>23</td>
<td>$9_a^1$</td>
</tr>
<tr>
<td>1139.7</td>
<td>5</td>
<td>$6_b^11^1$</td>
</tr>
<tr>
<td>1146.9</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1172.7</td>
<td>7</td>
<td>$16_b^212^1$</td>
</tr>
<tr>
<td>1200.8</td>
<td>4</td>
<td>$16_b^218_a^1$</td>
</tr>
<tr>
<td>1207.6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1253.2</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>1435.7</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1450.6</td>
<td>25</td>
<td>$6_b^112_a^1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1467.7</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1477.6</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>1493.1</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>1537.5</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>1552.2</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>1559.2</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>1569.5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1574.3</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1578.3</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

---

\(a\) Relative to the origin at 36,991.5 cm\(^{-1}\) (Ref. 35).

\(b\) Relative to the intensity of the origin.
benzenes. The intensities observed in our experiment follow the same general pattern observed in the absorption experiments, but the absence of quantitative intensity information from the older work prohibits comparison.

A delayed, two-laser experiment was undertaken to determine the temporal evolution of the bromobenzene singlet state. The dye laser was tuned to the origin of the bromobenzene transition, and the fourth harmonic of a second Nd:YAG laser was time delayed to probe for residual singlet state population. The intensities of the two lasers were adjusted such that the R2PI signal obtained from both lasers was greater than that obtained from either individually. A definite two-laser signal was obtained only when the two lasers were temporally overlapped. The minimum delay for which the two pulses were not overlapped was approximately 10 nsec due to the combined laser pulse widths and jitter. At this delay the observed ion signal was approximately the same as that due to one laser alone, giving an upper limit of 10 nsec for the \( ^1B_2 \) \((\pi\pi^*)\) lifetime.

The lifetime of iodobenzene is expected to be shorter than that of bromobenzene, and observation of the \( ^1B_2 \leftrightarrow ^1A_1 \) absorption by R2PI would therefore require a higher laser flux. A lens was placed in the UV dye laser beam to form a waist of approximately 0.3 mm at the center of the PITOFMS chamber. The laser flux was thereby increased to about 177 MW/cm\(^2\). The gain of the ion detection system was also increased by a factor of 5. Assuming that the cross-sections for both iodobenzene transitions, absorption and ionization, are similar to those for
bromobenzene, the increased laser flux and electronic sensitivity yield an overall sensitivity increase of 200 over the conditions used during the bromobenzene experiment. In spite of this increased sensitivity we were unable to observe any ions produced from iodobenzene anywhere in the reported region\textsuperscript{36} of the \( \text{1B}_2 \leftarrow \text{1A}_1 \) absorption (36,760 to 38,580 cm\(^{-1}\)).

3.2.3 Discussion

The most important aspect of the bromobenzene data is that it demonstrates the ease with which the R2PI technique detects a nonfluorescent molecular species with high sensitivity. The results of the delayed two-photon experiment allow determination of an upper limit of 10 nsec on the bromobenzene singlet lifetime. The absence of vibronic linewidths larger than the laser linewidth places a lower limit on that lifetime of about 2.5 picoseconds. Fluorobenzene is the only monohalobenzene for which lifetime and quantum measurements are available.\textsuperscript{28,29} Fruitless attempts to observe fluorescence from chlorobenzene have placed an upper limit 1x10\(^{-4}\) on the quantum yield of that molecule.\textsuperscript{26,27} The integrated oscillator strength of chlorobenzene is of the same order of magnitude, but slightly larger, than that for benzene.\textsuperscript{36a} Using the radiative lifetime of benzene (500 nsec)\textsuperscript{42}, an upper limit for the overall lifetime of chlorobenzene of 50 picoseconds is obtained. Investigations of monohalonaphthalenes in solid solution indicate a reduction by a factor of 36 in the fluorescence lifetime in going from chloronaphthalene to bromonaphthalene.\textsuperscript{43} Assuming that the
difference in lifetimes between chlorobenzene and bromobenzene is of the same order of magnitude as the naphthalene derivatives, we can estimate the bromobenzene lifetime to be about 5 picoseconds.

It should be noted that any bromobenzene triplet states formed by intersystem crossing could not be observed in the one color or two color R2PI experiments because of poor Franck-Condon factors for the ionization step. Even the $37,5994 \text{ cm}^{-1}$ delayed photon, when we added to the $36,991 \text{ cm}^{-1}$ pump photon, would produce an ion with only $2163 \text{ cm}^{-1}$ excess energy. The Franck-Condon factors for the ionization of a triplet state would be poor if the triplet state origin were more than $2163 \text{ cm}^{-1}$ below the singlet origin (assuming similar intermediate and ionic state geometries). The lowest bromobenzene triplet state is known to be almost $8000 \text{ cm}^{-1}$ below the singlet. Unless a massive change in geometry occurs upon crossing to triplet state levels, the poor FCF overlap will result in an extremely poor transition probability for the formation of photoions out of this state in a one color experiment.

Based on the estimated bromobenzene $1B_2 (\pi\pi^*)$ lifetime and the enhanced sensitivity used during the iodobenzene experiment, it can be inferred that it should have been possible to observe the $1B_2$ iodobenzene singlet even if its lifetime were as short as 0.02 picoseconds. Since no iodobenzene ions were observed, this figure constitutes an upper limit for the $1B_2$ lifetime.

The only previous estimate of the lifetime of this state is the photofragment anisotropy measurement of Dzvonik et al. Using a
high-pressure mercury arc light source, they observed a fragmentation pattern that was somewhat more isotropic than that expected for an instantaneous dissociation, assuming the optical transition was polarized parallel to the phenyl–iodine bond. Believing the lowered anisotropy was due to rotation prior to dissociation, they estimated the $1B_2 (\pi\pi^*)$ lifetime to be 0.5 picoseconds. Such a long-lived $\pi\pi^*$ state is inconsistent with our failure to observe it by the R2PI technique and with the known absence of structure in the absorption spectrum of iodobenzene.

An interpretation that is consistent with all known data is that the $1B_2 (\pi\pi^*)$ state is so strongly coupled to the underlying continuum of the $n\sigma^*$ state on the carbon–iodine bond that it is impossible to selectively excite the $\pi\pi^*$ state. Since the $1B_2 (\pi\pi^*) \leftrightarrow 1A_1$ transition is polarized perpendicular to the phenyl–iodine bond while the $\sigma^* \leftrightarrow n$ transition is parallel polarized, absorption in this spectral region will be of mixed polarization. Even instantaneous fragmentation resulting from optical excitation of this mixed polarization absorption will produce the reduced anisotropy pattern observed by Dzvonik et al.31
3.3 Metal Carbonyls

3.3.1 Introduction

The case of bromobenzene illustrates that short-lived states can be detected by R2PI, but in certain respects it represents an ideal case. The predominance of parent ions in the mass spectrum indicates that the fast decay channel does not result in photofragment species which can further absorb pump photons. In many instances, fast decay channels will result in fragment molecules with similar absorption spectra to their precursors. Analysis of the MPI mass spectral data will aid in the understanding of details of these photofragmentation channels and their implications with respect to the R2PI technique.

Transition metal carbonyls, M(CO)ₓ, are typical of a large set of inorganic molecules for which traditional high resolution spectral techniques have proved ineffective in probing excited state structure or dynamics. Extensive molecular orbital calculations reveal the low-lying electronic states to involve both metal centered (d–d) and metal–ligand charge transfer (CT) excitations. All of these states lie above the dissociation threshold which leads to the production of Fe(CO)₄ and smaller Fe(CO)ₓ fragments with high efficiencies. Absorption spectra in gas phase, solutions, or frozen matrices reveal broad ill-defined bands of uncertain assignment. A central question is whether these bands are intrinsically diffuse or trivially broadened by hot rotational and vibrational structure and/or matrix perturbations. Attempts to address this problem using laser
spectroscopy in supersonic molecular beams have been limited by the fact that these $M(\text{CO})_x$ compounds do not fluoresce. However, multiphoton ionization offers the sensitive detection which permits supersonic beam laser spectroscopy to be extended to this wide range of non-fluorescent species.

Multiphoton ionization has been used to monitor the high resolution absorption spectra of Fe(\text{CO})_5, Cr(\text{CO})_6 and Mo(\text{CO})_6 cooled in the pulsed supersonic beam. When exciting in the region of the strong CT absorptions near 2800 Å, the dye laser-induced MPI of these carbonyls is found to be nearly 100% efficient at relatively mild laser fluence. Mass analysis of the ions thus produced reveals that extensive fragmentation occurs. Even near the laser power threshold for ion production, the $M^+$ metal ion is observed to be the dominant ion. The known appearance potential for this ion from electron bombardment of the $M(\text{CO})_x$ parent neutral indicates that the principle photoionization process involves the absorption of at least four laser photons.

Direct observation of the neutral photofragments is also reported below for the Fe(\text{CO})_5 case. Here, we find evidence of the lowest order photon processes (Fe(\text{CO})_5 \rightarrow \text{Fe(\text{CO})}_{5-n} + n\text{CO}) even at higher laser fluences. High resolution spectral scans of both the photoion and neutral photofragment production indicate the absorption spectrum in the 2700–3100 Å region for ultracold, collision-free Fe(\text{CO})_5 is intrinsically diffuse. Similar results are found for the spectral dependence of photoion production in the cases of Mo(\text{CO})_6 and Cr(\text{CO})_6.
This diffuseness and efficient photoion production may be a general characteristic of laser excitation in the region of charge transfer transitions of a wide variety of metal-centered inorganic complexes.

3.3.2 Results

The results presented in this section were obtained with an apparatus that varies from the design presented in Chapter 2. The original apparatus included two additional small chambers. An ultrahigh vacuum chamber situated upstream of the photoionization mass spectrometer contained an electron beam source time of flight mass spectrometer where both photoionization or photofragmentation studies could be performed. The pulsed beam, further collimated by a third nickel skimmer, transited the bakeable ultrahigh vacuum chamber. The fourth vacuum chamber pumped to $10^{-8}$ torr by a 6" diffusion pump (Varian VHS-6) served to catch the residual molecular beam molecules. Background pressure in the detection chamber was maintained at $<10^{-10}$ torr by a Granville Phillips Electroion pump and by liquid nitrogen cooled copper shrouds plated with fresh layers of titanium deposited by a Varian 'Mini Ti-Ball' sublimation source. As shown in Figure 3.3, the beam was made to pass through the ionization region of the time of flight mass spectrometer. A second region 1.0 cm below the molecular beam detected neutral photofragments ejected from the molecular beam by electron impact ionization.

Figs. 3.4, 3.5, and 3.6 present the measured laser energy dependence of the photoion signal from Fe(CO)$_5$, Cr(CO)$_6$, and Mo(CO)$_6$. 
FIG. 3.3 Schematic representation of the photofragment mass spectrometer. The laser beam is overlapped with the molecular beam and ejected photofragments are detected in the lower ionization region.
PHOTOFRAGMENT
IONIZATION

TUNABLE DYE LASER

SUPersonic
MOLECULAR
BEAM

DETECTOR
respectively. As shown in the figures, the $M^+$ ion dominates the photoion production at all charted laser energies. Photoion signals in the range below 0.5 on the scale used in these figures are subject to considerable uncertainty due to statistical counting noise. $Cr^+$ was the only measurable photoion observed from $Cr(CO)_6$ irradiation. For all carbylons, $M(CO)_x^+$, it was possible to observe the full range of photoions $M(CO)_y^+$, where $y = x - 1, x - 2, \ldots, 0$ only near the laser power threshold and even then, except for the charted ions, the ion signal never corresponded to more than one detected ion every 10 laser shots. At higher laser energies these weak ion signals disappeared entirely.

Photoionization efficiency was estimated by the following procedure. Total ion signal produced from the $M(CO)_x$ beam by electron-bombardment ionization was measured and compared with the photoion signal obtained under identical circumstances. The electron beam source utilized an oxide-coated cathode mounted in a 200 G axial magnetic field to produce a uniform, collimated electron beam of cross-section $1.5 \times 0.4$ cm. By measuring the electron beam current and assuming ionization cross-sections of $2.8 \times 10^{-15}$, $2.8 \times 10^{-15}$ and $5.2 \times 10^{-15}$ cm$^2$ for $Fe(CO)_5$, $Cr(CO)_6$ and $Mo(CO)_6$, respectively, the overall electron-bombardment ionization efficiency could be estimated. Comparison with the photoion signals produced at the highest laser energies charted in Figs. 3.4–3.6 indicated the photoionization efficiency was greater than 20% for all three metal carbylons. Due primarily to uncertainty in the effective overlap between the laser and
FIG. 3.4 Photoion signal dependence upon laser pulse energy. All points refer to laser excitation of cold Fe(CO)$_5$ in the pulsed beam at 2833 Å.
Fe\((CO)_5\) PHOTOIONIZATION

![Graph showing ion signal vs laser energy (mj/pulse) with data points for Fe\(^+\) and FeCO\(^+\)]
FIG. 3.5 Photoion signal energy dependence for Cr(CO)$_6$ excited at 2833 Å.
Cr(CO)$_6$ PHOTOIONIZATION

![Graph showing the relationship between laser energy and ion signal. The x-axis represents laser energy (mj/pulse) ranging from 0.01 to 10, and the y-axis represents ion signal ranging from 0.1 to 10,000. The graph shows a gradual increase in ion signal with increasing laser energy.](image-url)
FIG. 3.6 Photoion signal energy dependence for Mo(CO)₆ excited at 2833 Å.
Mo(CO)$_6$ PHOTIONIZATION

![Graph showing ion signal vs laser energy](image)

- **Mo$^+$**
- **Mo(CO)$_3^+$**

**Y-axis:** ion signal

**X-axis:** laser energy (mJ/pulse)
the molecular beam, this estimate may be low by as much as a factor of five.

In the case of Fe(CO)$_5$, neutral photofragments were easily detected by electron-bombardment ionization in the lower ionization region of the TOF mass spectrometer shown in Fig. 3.3. The neutral photofragment signal was observed to increase monotonically with laser energy up to the highest laser energy used (4 mJ). Since the laser focus for these measurements was about twice the diameter used in the photoion work, the maximum laser fluence used for photofragments corresponded to only about one-fourth the maximum charted in Figs. 3.4-3.6 for this laser energy. The maximum observed photofragment signal corresponded to 0.01 to 0.1% of the Fe(CO)$_5$ density originally present in the molecular beam. The actual distribution of Fe(CO)$_x$ photofragments detected in this experiment is difficult to determine, as the electron impact ionization is expected to cause wholesale fragmentation. The mass spectral signals that we observed probably have contributions from several photofragment species. This would be consistent with the results of Yardley et al. 47

All photoproduct signals, whether from neutral photofragments or photoions, were found to give rise to smooth, unstructured excitation spectra throughout the 2700 to 3100 A region when recorded with 0.5 cm$^{-1}$ resolution. Our current data is based on many spot checks and 10 to 50 A scans randomly scattered throughout the 400 A region centered around 2900 A. In every region that has been checked, the spectrum appears completely diffuse, and it seems most likely that a complete
spectral scan of this region will appear roughly as broad and featureless as that seen for simple direct absorption in a room temperature vapor sample.

3.3.3 Discussion

The most intriguing aspect of these results is the high photoionization efficiency coupled with the fact that for all metal carbonyls studied the M⁺ photoion fragment dominates even near the threshold. The appearance potential for Fe⁺ from electron bombardment of Fe(CO)₅ has been measured by a number of independent techniques to lie in the range of 14.7 to 16.1 eV.⁵⁰–⁵³ The 2833 A laser photons used in the photoion energy dependence studies of Fig. 3.4 contribute 4.38 eV each to the absorbing molecule. Therefore the dominant MPI process in the Fe(CO)₅ study requires at least the absorption of four photons. The appearance potential of Fe(CO)₅ is sufficiently low⁵⁴ as to require only two 2833 A photons to generate this parent ion. Yet, even near the threshold laser power, Fe⁺ photoion counts are seen more than ten times as often as Fe(CO)₅⁺. Similar results are found for Cr(CO)₆ and Mo(CO)₆. In the latter case, the Mo⁺ appearance potential⁵² requires this dominant channel to be at least fifth-order in 2833 A photons.

Zandee and Berstein³ observed extensive fragmentation as a result of MPI processes in benzene and 1,3-butadiene. As laser flux was increased, they observed a steady increase in the importance of the smaller fragment ions. At high flux the high appearance potential fragments such as C⁺ predominated over the parent C₆H₆⁺ ion. In both
the benzene and butadiene cases, however, the first step in the MPI was resonant only as a two-photon process. The requisite laser flux was therefore on the order of 10 W/cm². The MPI process involved in our metal carbonyl experiments, on the other hand, utilized a one-photon resonant first step and is therefore observable at much lower flux — $3 \times 10^5$ W/cm² for the lowest point in Fig. 3.4. Extensive fragmentation would be considerably more surprising in these metal carbonyl results.

Rockwood et al.⁴ using a KrF laser observed primarily the $\text{C}_6\text{H}_6^+$ parent ion in an MPI process which was (as $\text{Fe(CO)}_5^+$ would be for our experiments) a one-photon resonant process in a two-photon ionization. This dominance of the parent ion was observed at a laser flux of $4 \times 10^6$ W/cm² — twenty times higher than the minimum flux used for our $\text{Cr(CO)}_6$ MPI experiment still dominated by the Cr four-photon product. These results are also in agreement with the results that have been obtained in other R2PI studies on several other systems studied in this thesis. The predominant production of fragment ions is related to the nature of the resonant intermediate states pumped and not an intrinsic property of the R2PI method. However, understanding the causes of these fragmentation patterns may allow one to largely avoid these paths.

The diffuseness of the excitation spectrum indicates that some intramolecular radiationless process is occurring in the excited state at a very fast rate ($>10^{13}$ sec⁻¹) — almost certainly faster than any possible further optical excitation in this laser field. The fact that
the MPI efficiency shows no structured wavelength dependence indicated that all intermediate states in the ionization process are similarly diffuse. The tendency for all transition metal carbonyl complexes (regardless of the presence of other ligands or their coordination number) to display strong charge transfer transitions in the region of 2800 Å \(46\) suggests this is a uniquely efficient up-pumping wavelength for this class of molecules. Regardless of the nature of the radiationless process responsible for the diffuseness, its product is virtually assured to exhibit a similarly strong charge transfer absorption resonant with the laser field. This will be true even if the result of a previous laser excitation was fragmentation into neutrals. Laser conditions that saturate the first transition are therefore likely to saturate the second and subsequent transitions.

The high ionization efficiency of this multiphoton process at low laser power is understandable, simply as a result of the diffuse nature of the absorption spectra and the high absorption cross-section characteristic of the transition metal carbonyls. Matrix isolated \(\text{Cr(CO)}_6\) for example, has an absorption cross-section of \(2 \times 10^{-17} \text{ cm}^2\) in the region of the CT absorption at 2800 Å. \(46\) Since the absorption spectrum continues to be diffuse for the cold molecule in the beam, this matrix value should be approximately correct for the laser wavelength used to generate the data of Fig. 3.4. Even assuming the excitation laser flux were uniform over the 0.1 cm diameter spot size in the ionization region, the first one-photon resonant transition would be approaching saturation at 0.1 mJ/pulse.
The observation that $M^+$ always dominates over any other photoinon indicates that predissociation dominates over ionization at all but the latest stages of the excitation process (The excited state neutral metal atom photoproduct has been detected\textsuperscript{55}). This in turn indicates the intermediate steps in the up-pumping ladder are valence excitations of more than one electron. Again, this is consistent with a multiple metal-ligand charge transfer up-pumping mechanism. Ionization mechanisms, such as described in this section, are likely to be applicable to a wide range of metal centered inorganic complexes. The extensive fragmentation of these molecules indicates that a careful analysis of R2PI data be made in the case where a weakly bond species is to be probed.

3.4 ANILINE\textsuperscript{14}

3.4.1 Introduction

The power of the R2PI technique is most vividly evident in the detection of organic molecular states with lifetimes that are longer than the laser pulse duration. Optimum sensitivity and selectivity is achieved as the decay channels competing with the ionization step are no longer present. Fragmentation in the mass spectra of these molecules is much less common than in the transition metal complexes of the previous section due to the generally stronger bonding and lack of available predissociative decay channels at moderate energies. In this
case, the predominant formation of parent ions is expected.

The R2PI technique should be compared with the laser induced fluorescence technique, as both are excellent detectors of these states. Comparison of the two methods shows that the overall efficiency of detection is potentially and practically greater with R2PI. The R2PI experiment measures the total population of ionizable intermediate states present during the laser pulse, whereas the LIF experiment detects only the subset of molecules which emit before non-radiative decay occurs. This decay limits LIF sensitivity, as the quantum yield of fluorescence is reduced when the initially pumped vibronic levels can couple into other low lying electronic states. A second advantage of R2PI is its high ion collection efficiency. Roughly, 80% of the ions formed can be collected and detected by the mass spectrometer, while a fluorescence experiment has large losses due to the inefficiency of collection optics and phototubes, reducing the overall efficiency by several orders of magnitude.

The R2PI method yields complementary information to that gathered by fluorescence methods. As ionization methods monitor the population of ionizable species in the beam during the laser pulse duration, a direct analog of the true absorption spectra results whenever the singlet state lifetime is longer than the laser pulse duration. Fluorescence, on the other hand, measures the fraction of molecules which emit before they move out of the field of view of the optics or are quenched by collisional processes. Emission excitation spectra are modulated by the quantum yield for each state, and hence intensities
are not directly comparable to the absorption spectrum. Nevertheless, wavelength resolved emission studies are extremely valuable due to the information that they provide about ground state vibrations.

Results

The high sensitivity and selectivity of R2PI is illustrated in the study of the \(^1B_2 (\pi\pi^*) \rightarrow ^1A_1\) transition of aniline. The features exhibited by the R2PI spectra of this molecule are can be generalized to a large set of molecules studied in our laboratory. Fig. 3.7 shows the total photoion yield produced as a function of laser frequency at a variety of values of the laser flux in the spectral region surrounding the 0 band of the \(^1B_2 (\pi\pi^*) \rightarrow ^1A_1\) transition of aniline.\(^{56}\) As shown in Fig. 3.7, at low laser fluence the only observed ion signal originates when the laser is resonant with the \(S_1 \leftrightarrow S_0\) transition. The \(S_1\) state populated in this transition is known to have a lifetime of 8 ns\(^{57}\) and is therefore a stable state over the laser pulse duration (\(\sim 4\) ns). The energy of this vibrationless level of the \(S_1\) state (34,025 cm\(^{-1}\)) is more than half the energy of the first ionization threshold (62,100 cm\(^{-1}\)). At this low laser flux the bandwidth of the ionization resonance is approximately that of the laser (1.0 cm\(^{-1}\) fwhm). However, as the laser flux is raised the profile of this resonance begins to broaden and, at very high laser intensities, a nonresonant, largely wavelength independent MPI signal is also observed. As shown in Fig. 3.7, the peak of the resonant MPI feature begins to flatten at highest laser flux, and the width of the resonance
FIG. 3.7 Total ion signal observed as a function of laser frequency in the vicinity of the $^1$O$_0^0$ band of the $^1$B$_2 (\pi\pi^*) \leftrightarrow ^1A_1$ transition of aniline. The laser was focused to a 3 mm diameter waist for these experiments. Laser powers were, from top to bottom, 13, 10, and 0.3 MW cm$^{-2}$. 
has broadened to $5 \text{ cm}^{-1}$. All these MPI signals are due to cold aniline in the pulsed molecular beam — no signals are observed under these conditions without the beam.

Sensitive detection of aniline by MPI has been reported previously by Brophy and Rettner \(^1\) where, as in the current experiments, the $S_1 \leftarrow S_0$ one-photon resonance was used in an overall R2PI scheme. Their experiments demonstrated (a) the $I^2$ dependence expected for this process at low laser power, (b) that the MPI signal frequency dependence follows that known for the $S_1 \leftarrow S_0$ fluorescence excitation spectrum, and (c) that the aniline parent ion is the only ion produced. Our data taken at higher laser fluence confirms and extends these results. In the previous section, it was determined that the absolute MPI detection efficiency for Fe(CO)$_5$ in a supersonic beam under intense 2800 A laser irradiation is $>20\%$.\(^{45}\) Using Fe(CO)$_5$ as a calibration gas we have compared the peak MPI signal obtained as in Fig. 3.8 for aniline with that observed for the same concentration of Fe(CO)$_5$ under identical conditions. The aniline photoion signal was slightly higher and therefore also corresponds to an MPI process which is at least 20\% efficient. Secondly, we find that the predominance of the C$_5$H$_6$NH$_2$ parent ion continues through the highest laser intensities we have used. Fragment ions at $m/e = 28, 39, 54, 66$, and 78 are observed at $\text{flux} >10 \text{ MW/cm}^2$, but these account for only 15\% of the ion signal at 20 MW/cm$^2$. At the highest laser fluence there was no observable difference noted in the extent of fragmented ion signal obtained either on or off the $S_1 \leftarrow S_0$ resonance.
FIG. 3.8 Mass spectrum obtained for one- and two-color MPI experiments of aniline. In each case the UV laser beam was tuned to resonance with the $0_0$ band of the $^1B_2 \leftrightarrow ^1A_1$ transition. Mass spectrometer sensitivity was identical for the two experiments.
UV = 0.93 MW/cm²
GREEN = 41.0 MW/cm²
Fig. 3.8 presents the results of a two-color MPI experiment where a portion of the 5320 A YAG second harmonic was superimposed in time and space with the 2939 A dye laser second harmonic beam resonant in the $S_1 \leftrightarrow S_0$ transition. Here the intensity of the 2939 A UV beam has been turned down so that the one-color MPI signal is far from saturation. Regardless of the intensity of the additional green laser beam up to the highest intensity we can use (limited by fear of breaking the quartz input windows on the vacuum chamber) the only effect of the additional laser beam is to decrease the photoion signal. This is true even though the one-photon absorption spectrum indicates the green beam should be resonant with a very strong absorption (from $S_1$) to an upper excited state ($S_{n'}$) of aniline. This state, however, is below the ionization threshold. Absence of a strong, positive two-color MPI signal suggests that this upper state, $S_{n'}$, is predissociative at a far greater rate than the subsequent up-pumping rate in these laser fields, and that the products of this dissociation are also not efficiently laser-ionized.

3.4.3 Discussion

Thus far in our MPI experiments we have encountered two cases of nearly 100% efficient MPI detection, the metal carbonyls and aniline. This high efficiency is not found, however, with a variety of other molecules under strong irradiation in the $S_1 \leftrightarrow S_0$ transition. Naphthalene and benzaldehyde, for example, yield much weaker photoion signals under these conditions in our pulsed beam apparatus. In both
the metal carbonyl and aniline cases the first ionization threshold lies at less than twice the $S_1$ energy, permitting in each case a one-photon resonant, two-photon MPI channel to be open. In aniline the high efficiency is easily understood since the $S_1$ state in this case is stable. The high ionization efficiency at moderate laser fluences for aniline then indicates that the excited electronic state pumped by the second ultraviolet photon ionizes much faster than it predissociates — resulting in a dominance of the parent ion. The metal carbonyl data cautions that such is not always the case: the ionization rate does not always predominate over predissociation. For $\text{Fe(CO)}_5$, $\text{Mo(CO)}_6$, and $\text{Cr(CO)}_6$ the parent ion is never observed to be the dominant ion even at near-threshold laser power. In these metal carbonyl experiments the high efficiency of the MPI process apparently arises from the fact that the photofragments themselves are strongly resonant with the laser field and can therefore not 'escape' readily from the up-pumping process. In contrast, the two-color experiment described above for aniline appears to produce photofragments which are no longer coupled to the laser fields and are therefore lost to the MPI process.

In order to generalize this efficient R2PI detection process to other molecules, the laser excitation will obviously need to be crafted so as to avoid rapidly predissociating states (or to ionize the products of any dissociation). In the common case that the first ionization threshold ($IP_0$) is more than twice the $S_1$ energy, multicolor laser R2PI processes will have to be used which either step directly above $IP_0$, or step on intermediate states below $IP_0$ for which the
predissociation rate is less than the subsequent up-pumping rate. The bromobenzene results also point to the need for two-laser techniques, as the inefficiency in this case is due to a rapid decay to a lower energy (possibly predissociative) triplet manifold. This level is not ionizable by the pump laser field. Higher energy photons that would allow a transition from these levels to those of the ionization continuum would increase the overall ionization efficiency. Therefore it appears that two separately tuneable laser sources are necessary to maximize the utility of the R2PI method.
CHAPTER 4

TWO-COLOR IONIZATION STUDIES

4.1 INTRODUCTION

The multiple advantages that R2PI presents over conventional methods in the efficient and selective detection of large molecules has been illustrated by the previous section. Unfortunately, the method as presented has several short-comings. Up to this point, the restriction that a single frequency be used as the source of both the resonant pumping photon and the second ionization photon, has limited the range of detectable species. For optimum sensitivity and selectivity of the one-color method, the resonant photon must access a stable electronic state at an energy greater than half of the adiabatic ionization potential. In several instances, either the ionization potentials are greater than twice the energy of suitable laser sources or the only stable electronic states are below the requisite energy for this R2PI scheme to be feasible. The use of lower energy photons in larger numbers has been studied in great detail, but generally these MPI methods lack the sensitivity necessary for rarified gases. The cross-sections for three or more photon ionizations are usually very small due to the utilization of non-resonant intermediates (virtual states).
In some instances, it may be possible to circumvent the limitations of one color ionization, by only pumping high energy electronic states, however there are two reasons why this often fails. Photodissociation channels become viable decay mechanisms at higher energies. If dissociation does occur, sensitivity is likely to be lost, unless the photofragments have similar and broad absorption spectra (as in the metal carbonyls). Fragments which cannot absorb additional photons to produce fragment ions may reduce ionization efficiencies to zero. Radiationless transitions to lower electronic surfaces can have similar effects on the total ionization rates. The initial state that is pumped may have sufficient electronic energy for R2PI, but if the non-radiative decay is rapid, as is generally the case, then a large portion of the initial electronic energy is converted to vibrational motions on the lower potential surface, again necessitating higher energy ionization photons.

The lack of sensitivity of one-color R2PI for states with less than half of the ionization energy in electronic degrees of freedom is illustrated by the time evolution of the one-color signals. A timing experiment, where two pulses of the same frequency are temporally displaced, would show for a molecule such as benzene, that the decay characteristics are those of only the $S_1$ state. A triplet electronic level with its origin $8600$ cm$^{-1}$ below the $S_1$ state is primarily responsible for this decay by promoting an intersystem crossing process. The triplet levels populated by this radiationless route are expected to be long-lived and should remain isoenergetic with the
$S_1$ levels, in our beam environment. Energetically, absorption of a single photon by these states would produce a photoion, but unfortunately the probability of such an absorption is very small. It will be shown by several experiments in the following section that the forbidden character of this type of transition is due to vibrational overlap considerations rather than electronic selection rules.

An obvious solution to the problems of one-color R2PI, is to provide a second laser which can provide large per photon energies enabling photoionization from stable intermediate states over a wide range of energies.\textsuperscript{8,59–61} This extends the range of detectable species to most large molecules and overcomes some of the restrictiveness of single frequency ionization. In this section, the applications of two-color R2PI are explored.

Two types of two-color experiments have been completed. Ionization thresholds of both benzene and naphthalene have been probed by two independently tuneable dye lasers.\textsuperscript{59} These studies illustrate the typical behavior in energies near and above the ionization potential, as well as determining the importance of possible ionization routes.

A second set of molecular states that are uniquely detectable by R2PI are triplet states of organic molecules.\textsuperscript{60,61} They have been probed to determine the dynamics of the triplet states formed upon intersystem crossing from optically accessible singlet states. Rates of $T_1 \leftrightarrow S_0$ intersystem crossing for a number of aromatic benzenes and azines have been measured and the comparision of these rates with
previous work points to several interesting results useful to the
general understanding of radiationless processes in large and
intermediate case molecules.

4.2 THRESHOLD EXPERIMENTS \(^{59}\)

4.2.1 Introduction

The first two-color experiments to be examined will be the
two-color threshold ionization studies of benzene and naphthalene.
They address a fundamental issue critical to the understanding of R2PI,
the nature of the structure above the first ionization potential. This
information is necessary to understand the intensities observed in
excitation spectra taken with R2PI. It is also crucial to an
understanding of the nature of ionization in large molecules.

A tunable 'pump' laser is used to excite \(S_1\) vibronic features of
naphthalene and benzene. A second tunable dye laser completes the
ionization. Variation of the frequency of the ionization laser allows
the observation of the onset of ionization as well as any structure due
to direct ionization or autoionization process above the initial
threshold. Different vibronic intermediate states can also be pumped
in order to complete this picture of the ionization thresholds and the
structure above them. The choice of benzene and naphthalene for these
experiments was based on the well known spectroscopy of their
intermediate electronic states.\textsuperscript{62,63} Additionally, both molecules have been the subject of extensive study under supersonic beam conditions in our molecular beam apparatus.\textsuperscript{19,64}

An obvious yet interesting result of this study is the determination of adiabatic ionization potentials for naphthalene and benzene. There have been several recent studies in which laser photoionization has been used to obtain this type of information. DABCO (1,4 diazabicyclo\textsuperscript{2,2,2} octane)\textsuperscript{65} and pyrrole\textsuperscript{66} have been examined in low pressure gases. Schumacher et al.\textsuperscript{9c} have used R2PI to observe the ionization potentials and structure in the ionization continua of alkali metal clusters. However, until now, this experiment has not been performed on large molecules in a supersonic beam. The low internal temperatures of molecules in the supersonic beam allow increased accuracy in the determination of threshold energies, since red shifts due to hot vibrational structure are eliminated.

More importantly, the observation of the electric field dependence of the ionization potential has been measured for both benzene and naphthalene. The draw out voltage in our mass spectrometer induces a shift of the ionization potential to lower energies. A similar effect is well documented in atomic physics, but not for large polyatomic molecules.\textsuperscript{67} The field dependence of the red shift has been determined and can be explained in terms of field ionization of high lying Rydberg states just below the first ionization potential.

Direct ionization, as in a one-photon experiment \textsuperscript{68}, is a transition from the ground state of a molecule to the ground state of
the positive ion. Step functions, that are observed in the wavelength-dependent ionization efficiency are a reflection of the Franck-Condon factors in going from the molecular states to different vibrations in the ground state of the ion. The Franck-Condon overlap is strongly dependent upon geometries and relative displacements of the two states and information regarding these parameters are important to the interpretation of the two-color experiment. Rough estimates of these factors can be easily made. Changes in ionic geometry from that of the neutral depend on the kind of molecular orbital (bonding, non-bonding or antibonding) from which the ejected electron originated. In R2PI experiments, direct ionization occurs from the $S_1$ intermediate state and the important Franck-Condon factors are those between it and the ground state of the ion. Analysis of spectroscopic data can often provide sufficient information for the determination of the excited state geometry.

The energy of the two-photon excitation may promote molecules to discrete neutral states higher in energy than the initial ionization potential. Such highly excited molecules can undergo a radiationless transition from the discrete neutral state to the ionization continuum via the autoionization process. The high energy neutral states are Rydberg states, or vibrational levels within Rydberg states, converging to higher ionization limits of the molecule. The radiationless process can take the vibrational energy of a Rydberg state and convert it by vibrational autoionization to electronic energy to form the molecular ion and an electron with kinetic energy enough to conserve
energy. The one-photon Rydberg states of naphthalene and benzene near the first ionization potential are reasonably well known. If this mechanism is operative the supersonic beam environment ensures that the line profiles will be unperturbed by sequence congestion or line broadening and that the true natural line width measures the lifetimes of autoionizing Rydberg states.

Direct ionization and autoionization are limiting cases to describe the ionization process. In a variety of small molecules, autoionization has been observed to be a significant part of the total ionization (for H₂ there is hardly any direct ionization). Experiments with naphthalene indicate that direct ionization is the dominant process. Observation of threshold steps due to the Franck-Condon factors linking the pumped state to the ground state of the ion, gives a measurement of the frequency of v₈ in the ionic ground state. However in benzene, contributions from both autoionization and direct ionization are present and the autoionization appears to be equal to roughly one-half of the amount of direct ionization. The widths of these autoionizing features indicate that the lifetimes of these states are on the order of 10⁻¹⁴ seconds.

4.2.2 Naphthalene

The initial threshold scans were made in a source with a 1500 V/cm field. A scan done in this configuration appears in figure 4.1 and illustrates the salient features of the threshold studies. In this
FIG. 4.1 Threshold spectrum of naphthalene showing the relative cross-sections for transitions at IP$_0$ ($\tilde{S}^1 - 0_0^+$) and IP$_1$ ($\tilde{S}^1 - \tilde{S}^1_1^+$). All sharp features are due to two-photon absorption of the ionizing laser alone. The main one-laser features (labelled) are known $S_1$ vibronic bands and provide a calibration for the ionizing laser wavelength. Ion source field is 1500 v/cm.
scan, the pump laser was tuned to the $\mathcal{B}^1$ resonance of naphthalene. The labeled sharp features are caused by two-photon absorption of the ionizing laser alone. These vibronic levels are within a single photon absorption of a similar vibrational mode in the ground state of the ion. No one laser signal was observed from the pump laser alone. In the frequency range between $IP_0$ and $IP_1$ there is a low-level signal caused by the combination of pump and probe lasers. At $IP_1$ this two-laser signal rises to a level 20-30 times more intense. After the initial onset, both two laser signal levels are flat and featureless over the range scanned (200 cm$^{-1}$ to the blue of $IP_1$). The onset of the $IP_0$ is quite difficult to discern in the figure, but its position has been measured at a much slower scan rate (500 shots/point). The frequency of the $\mathcal{B}^1$ transition along with the frequencies of the one-color signals are all well known and use of relative frequency markers allows measurement of the threshold positions (taken at the middle of the rise). These values are in Table 4.1. The difficulty in the assignment of the threshold positions arises from the spectral widths of these features as the rise of $IP_1$ is 50 cm$^{-1}$. It appears that this broadness is due to the electric field present in the source of the mass spectrometer (See below). At zero field, the threshold width is essentially the laser bandwidth.

Assignment of the step-like two-laser structure is consistent with direct ionization of naphthalene. There is no evidence of autoionization in these naphthalene spectra. The lowest energy threshold ($IP_0$) is therefore the adiabatic ionization potential (65665
TABLE 4.1

Naphthalene Threshold Positions

<table>
<thead>
<tr>
<th>Ionization Transition</th>
<th>Ionizing Laser Frequency</th>
<th>Total Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8^1 - 0_0^+)</td>
<td>33209 cm(^{-1})</td>
<td>65664 cm(^{-1})</td>
</tr>
<tr>
<td>(0^0 - 0_0^+)</td>
<td>33646 cm(^{-1})</td>
<td>65666 cm(^{-1})</td>
</tr>
<tr>
<td>(8^1 - 8_0^+)</td>
<td>33650 cm(^{-1})</td>
<td>66105 cm(^{-1})</td>
</tr>
</tbody>
</table>

\(a\) Measured at zero field.

\(b\) Assuming \(S_1\) origin = 32020.2 cm\(^{-1}\) and \(\bar{8}^1 = 435\) cm\(^{-1}\).
cm\(^{-1}\) + 10 cm\(^{-1}\)). In the intermediate region between IP\(_0\) and IP\(_1\), vibrationless ions plus an electron with kinetic energy enough to conserve energy are formed. At IP\(_1\), there is enough energy to create a vibrationally excited ion. The transition is \(3^1 \rightarrow 3^1\)\(^+\) (\(\Delta v=0\)). The greater intensity at and above IP\(_1\) reflects the greater Franck-Condon factor for the \(\Delta v = 0\) transition.\(^{72}\) This behavior is consistent with selection rules into the ionization continuum which predict a non-zero Franck-Condon factor when the product \(\Gamma' \cdot x \Gamma\)' is totally symmetric.\(^{70}\) When pumping \(3^1\) \((b_{1g}\) symmetry in \(D_{2h}\)), the favorable transition is to ionic vibrations of \(b_{1g}\) symmetry, hence \(3^1\)'\(^+\).

Adherence to these symmetry conditions indicates that the geometry of the ionic ground state is quite similar to that of the neutral \(S_1\) state. This is borne out by the \(v_8\) frequency that is measured for the ion (IP\(_0 -\) IP\(_1\)) , 440 \(\pm\) 5 cm\(^{-1}\) (compared with 435 cm\(^{-1}\) in \(S_1\)). It is also in accord with the photoelectron spectroscopy observation of the \(v_4\) \((a_{1g})\) vibration in the ion (1371 cm\(^{-1}\) compared to 1390 cm\(^{-1}\) in \(S_1\)).\(^{73}\)

The absence of autoionization features in the naphthalene spectrum is not unexpected. There are no known Rydberg states in this wavelength range. In fact, there are no sharp features of any sort in this vicinity in the optical absorption spectra\(^{73}\) indicating very short-lived states are present at this high energy.

Modification of the mass spectrometer voltages was necessary to observe the electric field dependence of the ionization threshold. In the normal configuration the source region has a constant field of 175
V/cm. The constant field may be varied to higher and lower voltages with a loss in resolution and signal intensity. To obtain a zero field spectrum both backing plate and drawout grid were held at the same potential while a pulse (+200 V, 400 nsec risetime) was supplied to the backing plate after the lasers had been fired. The capacitive coupling of this pulse to the plates at high voltage was sufficiently unstable so that only a limited number of runs could be made. Threshold scans presented in Figure 4.2 (see Table 4.2 for frequencies) show the positions and widths of the $\bar{s}_1 \rightarrow \bar{s}_1^+$ threshold as a function of electric field.

It is well documented in atomic physics that an electric field can distort the potential well of the electron so that it is possible for ionization to occur at lower energy than the adiabatic ionization potential. In fact, the technique of field ionization is commonly used to detect high Rydberg atoms. A test of the field dependence behavior is its consistency with the results of field ionization behavior of atomic systems.

Currently available models for field ionization assume hydrogenic wavefunctions. Since the pertinent states are very near the ionization potential, this is probably a suitable assumption. Even for large organic molecules, states of high $n$ have such large radii that the molecular core resembles an atomic nucleus to the electron. As shown in Figures 4.3a and 4.3b, an electric field distorts the potential well of a highly excited electron. The linear Stark effect, which is most important for high $n$ (Rydberg states) splits a given $n$ state into a
FIG. 4.2 Voltage dependence of the $\Delta v = 0$ ($3^1 - 3^1 +$) ionization threshold. The sharp features are the same as in FIG. 4.1.
TABLE 4.2

Naphthalene $\tilde{g}^1 - \tilde{a}^1_+$ Field Dependence$^a$

<table>
<thead>
<tr>
<th>Field</th>
<th>Threshold Energy</th>
<th>Relative Frequency</th>
<th>Approximate Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500 v/cm</td>
<td>65958 cm$^{-1}$</td>
<td>-147 cm$^{-1}$</td>
<td>50 cm$^{-1}$</td>
</tr>
<tr>
<td>630 v/cm</td>
<td>66007 cm$^{-1}$</td>
<td>-98 cm$^{-1}$</td>
<td>25 cm$^{-1}$</td>
</tr>
<tr>
<td>175 v/cm</td>
<td>66071 cm$^{-1}$</td>
<td>-34 cm$^{-1}$</td>
<td>15 cm$^{-1}$</td>
</tr>
<tr>
<td>0 v/cm</td>
<td>66105 cm$^{-1}$</td>
<td>0 cm$^{-1}$</td>
<td>2 cm$^{-1}$</td>
</tr>
</tbody>
</table>

$^a$Pump laser frequency = 32020 + 435 = 32455 cm$^{-1}$. 
FIG. 4.3 Potential energy of a Rydberg electron in a) the absence and b) the presence of an electric field applied along the z axis. c) The $m_1 = 0$ Stark states for $n = 10$ and $n = 11$. The dashes at the high field end of each state indicate the field range over which the ionization rate goes from $10^7$ to $10^{11}$ sec$^{-1}$. The height of the lowest energy saddle point on the potential curve as a function of the field (classical line) is indicated by Cl.
manifold of \( n^2 \) sublevels (Stark states) spreading out to lower and higher energies (Figure 4.3c). The lower energy states have high probability density near the low side of the potential well and ionize at lower fields. Higher energy Stark states of a given \( n \) manifold require higher fields for ionization since the probability density is toward the higher side of the potential well.

The simplest description of field ionization is the classical model \(^{75}\) which describes quite accurately the behavior of \( m_1 = 0 \) states. This predicts a critical ionizing field of

\[
F_c = 2.665 \times 10^{-2} \, E^2
\]

where \( F_c \) is the field in V/cm and \( E \) is the energy below the IP in cm\(^{-1}\) and the constant \( 2.665 \times 10^{-2} \) accounting for units of conversion. The classical line (a) of Figure 4.4 is calculated from this expression and represents the field dependence for \( m_1 = 0 \) states. Since \( m_1 = 0 \) states generally ionize at lowest field for a given \( n \), this classical line is a good lower bound for possible field ionization. A recent model by Damburg and Kolsov \(^{76}\) describes the field dependence of the upper Stark states which ionize at highest field for a given \( n \) manifold. This gives the upper bound for field ionization (b). As shown in Figure 4.4, the field dependence falls within the bonds for field ionization and follows the same general curvature as the boundary lines. At higher fields the energy range spanned by the boundary lines becomes larger. This is because more overlapping Stark manifolds are split to a greater extent, so that at a given field there is a broader range over which ionization is possible. This qualitatively accounts for the
FIG. 4.4 Boundary lines for field ionization which enclose the data.

a) Classical line for $m_4 = 0$ (lowest Stark states) for an ionization rate of $10^9$ sec$^{-1}$ (see ref. 75).
field dependence of the threshold widths.

In this picture, observation of a red shift in the ionization potential is caused by field ionization of Rydberg states just below the field-free ionization threshold. Although the oscillator strength of these Rydberg states becomes weaker as the series limit is approached, the density of these states becomes quite large. There are vibrational Rydbergs converging to each vibrational state of the ion and the field ionization effect is expected for both the $8^1 \rightarrow 0^+_0$ and $0^+_0 \rightarrow 0^+_p$ thresholds. The variation from hydrogenic wavefunctions at higher $n$ should not be very different for other similar compounds (e.g., benzene).

A threshold study was also conducted for naphthalene when pumping the $S_1$ origin (3132.2A). Again single step-like two-laser features are observed superimposed upon one-color features. The field behavior of this threshold at 175 and 100 V/cm fields is very similar to the dependence observed for the $8^1$ level. Extrapolating this dependence to zero field yields the value of the adiabatic ionization energy of 65666 + 5 cm$^{-1}$. This compares to the literature value of 65600 cm$^{-1}$ from the convergence of Rydberg series. It is not surprising that our value is somewhat higher, as the supersonic beam environment eliminates hot vibrational structure which would cause a red shift in the Rydberg value.
4.2.3 Benzene

The threshold ionization spectrum of benzene is pictured in Figure 4.5. The pump laser was tuned to the $6^1$ resonance (2590.1 Å) of the $S_1$ state, and the ionization laser was tuned between 2700 – 2800 Å. The field dependence of the thresholds are found to be very similar to that of naphthalene. Higher energy features are broad and their field dependence is less certain. After the initial threshold there are two other features in the threshold spectra. The nature of these features are quite different from those observed in the naphthalene. It is not clear whether these are threshold steps or if they are merely very broad features. The first step above the initial onset has a much sharper rise than the second step and is $335 + 20 \text{ cm}^{-1}$ above the initial onset. The second feature has a slower more gradual rise and it reaches a maximum at $860 + 20 \text{ cm}^{-1}$ above the initial onset. This level is at least 15 times the intensity of the $335 \text{ cm}^{-1}$ level and at the lowest laser powers used, it is the only level observed. This data is summarized in Table 4.3. The features observed do not appear to be completely explainable by direct ionization and we will consider both direct and autoionization in this system.

Consideration of direct ionization in benzene requires a knowledge of the ionic ground state. The benzene ion is expected to be distorted with respect to the neutral, whereas the naphthalene ion has a similar geometry to the $S_1$ state. The removal of the outermost π electron from benzene produces a $^2E_{1g}$ ionic state which is subject to Jahn-Teller
FIG. 4.6 Threshold ionization spectrum of benzene with the pump laser tuned to the $g^1$ resonance in $S_1$ (38608 cm$^{-1}$). The lower trace was done at low resolution. The high resolution inset shows the first and second autoionizing features. The third feature is less obvious at the onset of the highest level under low resolution (it is assigned to autoionization by its position, not by its 'peak-like' character).
TABLE 4.3
Benzeno Threshold Structure

<table>
<thead>
<tr>
<th>Feature</th>
<th>Total Energy(^a)</th>
<th>Relative Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Threshold</td>
<td>74528 cm(^{-1})</td>
<td>0</td>
</tr>
<tr>
<td>1st Autoionizing Feature</td>
<td>74568 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>2nd Autoionizing Feature</td>
<td>74861 cm(^{-1})</td>
<td>335 cm(^{-1})</td>
</tr>
<tr>
<td>3rd Autoionizing Feature</td>
<td>75388 cm(^{-1})</td>
<td>860 cm(^{-1})</td>
</tr>
</tbody>
</table>

\(^a\)Pump laser frequency = 38608 cm\(^{-1}\).
distortions through $e_{2g}$ vibrations. Therefore, $\Delta v = 0$ transitions, which were most favorable for the direct ionization of naphthalene, will not necessarily have optimum overlap for benzene.

The photoelectron spectroscopy (PES) of Asbrink and co-workers on benzene has resolved the vibrational structure in the ground state of the ion, indicating the extent of the Jahn-Teller distortion. The $^{2}E_{1g}$ ($D_{2h}$) ionic ground state is distorted to produce the $^{2}B_{1g}$ and $^{2}B_{2g}$ states of the $D_{2h}$ ion. As the ejected electron ($1\,e_{1g}$) is essentially non-bonding in benzene, the Jahn-Teller splitting is small. The double minimum on the potential surface is spanned by the zero-point energy contribution of the $e_{2g}$ vibrations with the result that the vibrational frequencies in the ground state ion are not very different from the neutral ground state. See 63 The vibrations $v_{6a}$ (686 cm$^{-1}$), $v_{1}$ (984 cm$^{-1}$), $v_{9a}$ (1291 cm$^{-1}$), $v_{8a}$ (1589 cm$^{-1}$) are observed. Normally, in an allowed PES transition, only totally symmetric vibrations will be observed ($\Gamma_{\nu} \otimes \Gamma_{\gamma}$ must be totally symmetric for non-zero transition moments, and the neutral ground state is usually $a_{g}$). When the vibrations are considered in the reduced $D_{2h}$ symmetry rather than $D_{6h}$, these selection rules are met, as each of the observed vibrations have an $a_{g}$ component in $D_{2h}$.

Comparison of the PES results is quite useful in evaluating the degree of direct ionization present in our spectra. The total energy of the two photon at the zero field threshold (initial onset $= 74,528$ cm$^{-1} + 12$ cm$^{-1}$) agrees well with the PES origin (74,538 cm$^{-1}$). The feature observed 335 cm$^{-1}$ to the blue does not correspond to any of the
vibrations in the PES work. The 860 cm\(^{-1}\) spacing of the higher energy feature is close, but somewhat lower in energy than the \(v_1\) vibration (984 cm\(^{-1}\)). By analogy to the PES case, the strongest transitions in the two-photon ionization will be those with totally symmetric products \(\Gamma_{ij} \times \Gamma_{v_6}\). In the \(D_{2h}\) representation vibrations with symmetry of \(a_g\) or \(b_{3g}\) fulfill this requirement and in benzene these modes are 1, 2, 3, 6, 7, 8, 9. Of these, only \(v_6\) and \(v_1\) are in the frequency range of interest. \(v_6\) would fall between the 355 cm\(^{-1}\) and 860 cm\(^{-1}\) features and \(v_1\) lies just above the 860 cm\(^{-1}\) peak. Direct ionization can explain the initial threshold and a slow rise to a level around 900 cm\(^{-1}\), but it is unable to explain the 355 cm\(^{-1}\) feature in the spectra.

Autoionization is the second possibility that will be considered. For autoionization to be observed, there must be Rydberg states above the initial ionization potential converging to vibrational states of the ion. These levels which are characterized by a highly excited electron and an ion-like core must be stable enough with respect to all decay processes (dissociation, ionization, etc.) to yield a measureable linewidth in the spectrum. The rate of ionization must also dominate over all of these decay processes (i.e., dissociation). For large polyatomic molecules at these high energies, these restrictions may be rather exclusive requirements.

The one-photon optical absorption spectra of benzene \(^78\) indicates that there are resonably sharp Rydberg states in the spectral region of interest. The \(n = 3 (e_{1u})\) member of the Rydberg series converging at 11.49 ev (\(\delta = 0.47\)) falls here and has resolved vibrational structure.
Transitions to this state from the $S_1$ level ($6^1$) will be allowed through $a_{2u}$ or $e_{1u}$ vibrations ($v_{11}$, $v_{18}$, $v_{19}$, $v_{20}$). The ground state frequencies of $v_{11}$ (671 cm$^{-1}$), $v_{18}$ (1035 cm$^{-1}$), $v_{19}$ (1485 cm$^{-1}$) are easily within range of the region scanned, using the known ($e_{1u}$) Rydberg state (9.16 ev), and allowing for small vibrational frequency changes in the Rydberg compared to the ground state (this is consistent with vibrational spacings observed in lower energy Rydberg states). Based on the known origin of a Rydberg state in this vicinity, it is possible to assign the broad structure to vibrational autoionization of states to which there would be allowed transitions. The likelihood or intensity of these transitions are not known. The vibrational autoionization cannot be due to the same vibrational features observed in one-photon absorption because these transitions would be forbidden by two photon transitions. It is likely that an electronic symmetry Rydberg state exists in this same vicinity, and it could be accessed by our pumping scheme. Autoionization of these vibrations would account for the observed structure.

The structure that is observed is quite broad and difficult to discern from the underlying direct ionization background. The measured widths of all of these features are approximately 100 cm$^{-1}$. From these widths, the decay rate out of these states must be $2 \times 10^{14}$ sec$^{-1}$ and the lifetimes of these levels must be approximately $5 \times 10^{-14}$ seconds. The autoionization rate of these initially excited levels must be comparative with the total decay rate or else these features would not be detected by ion signals. That ionization is a dominant decay route
is not surprising as Rydberg states are not well coupled to the molecular core and hence, are not as likely to decay by dissociation as valence states at the same energy. The effect of the source electric field on the widths of these features has been also considered. It appears that the linelengths do not depend upon the field (over the range of this study), nor do the positions of the features. Electric field is not expected to have a large effect on autoionization features since they would be in low n states and the linear Stark effect is important for low fields only at high n.

Due to the failure of direct ionization arguments to account for the observed structure, and since it is reasonable to expect that suitable Rydberg states are present, the structure in our spectra is probably due to vibrational autoionization. This observation is significant in terms of understanding ionization processes in large molecules. Benzene, which has Rydberg structure that is quite sharp in one-photon studies, has autoionization features which are very broad under high resolution conditions. It appears that similar autoionization features will be difficult to observe for molecules of comparable or greater complexity.

In conclusion, the R2PI spectra of naphthalene and benzene has been observed at and just above the ionization potential. For naphthalene we observe only direct ionization as exhibited by the wavelength-dependent step functions in ionization efficiency. The intensities of these steps reflect the Franck-Condon factors for transitions from our pump state to the ground state ion, while their
spacings yield the vibrational frequencies in the ionic state. The data is illustrative of the nature of highly excited states and the ionization processes in large molecules. In both molecules direct ionization is the predominant process, while autoionization is observed for benzene. The importance of the direct ionization process underscores the necessity for two-color experiments. Vibrational overlap between the intermediate state and the ion must be obtained before high ionization yields will be observed as the naphthalene $H^1$ experiments have illustrated. Such information on the nature of these ionization cross-sections is necessary to the general understanding of the R2PI technique.
4.3 TRIPLET STATE DYNAMICS

4.3.1 Introduction

A large body of data has been gathered on the spectroscopy and decay mechanisms of single quantum states of the first excited singlet states ($S_1$) of aromatic molecules. The majority of this data has been obtained by fluorescence techniques, and therefore is normally limited to the lowest singlet states. The wealth of information available on $S_1$ properties is contrasted by the virtual inavailability of similar data on the nature of dark states, such as low-lying triplet electronic states. A major obstacle in probes of triplet state populations has been the inability to excite or detect triplet states by optical methods. Generally, the absorption cross sections for $T_1 \leftrightarrow S_0$ transitions will be extremely small, due to spin selection rules. Even with high power pulsed laser sources, production of an appreciable population of triplet states molecules is only feasible in a small number of cases, where spin orbit coupling is unusually large. A more efficient population method is formation of triplet state upon intersystem crossing from isoenergetic levels of the $S_1$ state. The efficiency of this process can approach unity for many molecules (e.g., aromatics and carbonyls) but, due to generally poor radiative coupling to the ground state, these triplets must be probed via indirect methods.

Two-color photoionization provides a direct measurement of triplet
state populations (as well as singlet populations) and removes several uncertainties associated with previous studies of triplet state dynamics. Indirect techniques rely on the transfer of triplet electronic energy via an intermolecular process to another species whose excited state can be detected by conventional methods. The time evolution of the sensitized species and quantum yields of formation are obtained for the probe molecule and this data is related to the corresponding triplet state properties. The most widely utilized of these indirect methods are biacetyl triplet sensitization and cis-2-butene isomerization. Although quite informative, these experiments must be viewed cautiously, as the data is affected by collisional quenching and intermolecular vibrational relaxation. A major advantage of the molecular beam multiphoton ionization method is freedom from collisional quenching. The lifetimes measured by this method are obtained directly, without involving complicated kinetic schemes to deconvolute the non-radiative rate from artifacts of the experimental technique.

The purpose of this section is to present the details of the two-color resonant photoionization method for measurement of excited state populations and application to the study of excited state dynamics. Now in a single experiment, the time evolution of both the singlet and triplet states can be measured, yielding the population decay of both states and providing useful quantum yield data. The results of triplet decay measurements can be applied to the interesting question of energy dependence of non-radiative decay channels, an area
which cannot be probed by conventional methods. Much of the confusion surrounding experimental determinations of triplet decay rates in the literature can be explained by the neglect of this dependence.

Although, the data presented in this thesis has been obtained in a collision-free molecular beam environment, it should noted that it is possible to study collisionally perturbed excited state dynamics with the photoionization technique. In high pressure gas phase samples the mass selectivity of the technique is lost, but the spectral selectivity of this laser method will allow species selective studies. Thus, given the appropriate laser sources, intermediate electronic state detection, as described here, is applicable to virtually any gas phase molecular species under a wide variety of experimental conditions.

4.3.2 Substituted Benzenes and Benzene

4.3.2a Results

Substituted benzenes and benzene cooled in supersonic expansions of helium were pumped by a dye laser into single vibronic bands of the $S_1(1^B_2) \leftarrow S_0(1^A_1)$ ($1^B_{2u} \leftrightarrow 1^A_1$ for benzene) electronic transition. The cold excitation spectra of each of these $S_1$ states has been reported in previous works $^{19,41a,89}$ under similar conditions, and the vibrational frequencies and assignments from those papers have been used. Triplet molecules are produced via intersystem crossing from low-lying vibronic
bands of the $S_1$ state. The triplet molecules, having been produced by a laser co-axial with the molecular beam, are allowed to drift into the source of the time-of-flight mass spectrometer. At this point, they are crossed by an ArF excimer laser, which produces the corresponding parent ion. The photoions were collected and dispersed by a TOF mass spectrometer and subsequently detected by a Johnston Labs MM-1 electron multiplier. By recording this photoion signal as a function of the time between the $S_1$ pump laser and the ArF ionization laser, the decay behavior of triplets from $S_1$ singlets and ultimate coupling into the $S_0$ ground states was measured without collisional or migration effects.

The laser timing was controlled via a computer-driven digital delay generator (Evans Model 4145-2). The pump to probe laser delay was sequentially incremented until the appropriate delay range had been sampled. This process was repeated and the new data summed together with the previous scans until sufficient statistics were obtained. The complete delay range was sampled approximately every 10-15 seconds and thus the effects of long term drifts in experimental conditions, such as laser beam alignment and molecular beam intensities were removed. As an additional precaution, the ionizing laser was adjusted to probe the molecular beam at a fixed delay from the nozzle firing, in order to remove possible distortions due to systematic fluctuations of the molecular beam intensity during the nozzle pulse.

In the photoionization region of the TOF mass spectrometer the density of helium in the pulsed beam was approximately $10^{11}$ atoms/cm$^{-3}$. Triplet states produced in this beam are therefore not expected to be
effected by collisional processes with cross sections of less than $10^6 \text{ A}^2$. Since the seed molecules travel with the velocity of the helium carrier gas (1.8 x $10^5$ m/sec), triplet state lifetimes of 500 $\mu$sec can be measured without collisional perturbation. Measurement of longer lifetimes would require the utilization of a heavier carrier gas to provide a longer flight time.

The nozzle conditions are conducive to the formation of large populations of molecular dimers and oligimers, as a result of three-body collision processes. Considerable efforts were made to ensure that our results were not affected by the presence of dimer or oligimers of the seed gas. Oligimer species generally are not detected as parent oligomer ions, as weak van der Waals bonds are easily broken in the ionization process. Thus, as will be discussed later, ions with the mass of monomeric species can be generated from not only monomers, but higher oligimers as well. The concentration of complexed species can be minimized by keeping the source concentrations of seed molecules small. Below concentrations of 500 ppm of seed gas, no evidence of complex formation could be observed. All triplet lifetime measurements were conducted under this constraint.

Two typical excited state decay patterns are presented in Figures 4.6 and 4.7 for toluene pumped to the vibronic origin of the $S_1$ state. This decay behavior will be discussed specifically for the case of toluene, however the results obtained for toluene can be generalized to all of the other benzenes studied by the R2PI method. The signal arriving at the time-of-flight corresponding to the toluene parent ion
FIG. 4.6 Triplet Decay. The time evolution of the triplet levels formed by intersystem crossing from the \(0^0\) level of the \(S_1\) state is determined by scanning the time delay between the dye laser pump and ArF ionization laser pulse. The \(\text{C}_7\text{H}_8^+\) photoionization signal is plotted here as a function of this delay.
FIG. 4.7 Biexponential Fit. The photoionization signal arising from the population of T↑ and S1 intermediate states has been fit to a biexponential. The fast component corresponds to the S1 decay, while the slow component is due to T↑ decay. The solid line is the fit obtained from the model described in the text.
(mass = 92 amu) is plotted as a function of the time delay between the pump and ionization lasers. The resulting time decay shows a clear biexponential behavior due to the sequential decay of the $S_1$ and $T^\pi$ states.

4.3.2b Kinetic Model

The biexponential decay of the ion signal can be modeled as the sum of the transient excited state population $S_1 + T$ as a function of laser time delay. Expressions (1) and (2) represent these time dependent populations.

\begin{align*}
(1) \quad \frac{d[S_1]}{dt} &= -(k_r + k_{IC} + k_{isc})[S_1] \\
(2) \quad \frac{d[T^\pi]}{dt} &= k_{isc}[S_1] - k_T[T^\pi]
\end{align*}

where $k_r$, $k_{IC}$, $k_{isc}$, and $k_T$ are the rate constants for $S_1$ radiative decay, $S_1 \rightarrow S_0$ internal conversion, $S_1 \rightarrow T^\pi$ intersystem crossing, and $T^\pi \rightarrow S_0$ triplet decay. These coupled differential equations can be solved to yield the time dependent sum of $S_1$ and $T$ population in (3).

\[
[T + S_1](t) = S_1(t) + k_s - k_T \left[ (k_s - k_{isc}) - k_T \right] e^{-k_s t} + k_{isc} e^{-k_t}
\]

where the possible $S_1$ decay channels have been grouped into $k_s$, the total singlet decay rate. Our photoionization data has been fit to
equation (3) with a non-linear least squares computer analysis. As the experimental value of $k_s$ is subject to considerable uncertainty due to the limited data at short laser delays, the literature value of $k_s$ has been adopted for the calculation of $k_{isc}$ and $k_T$. The values of the fitted rate constants, and the quantum yield of intersystem crossing have been tabulated along with previous measurements in Table 4.4. The resulting fit of the data is presented in figure 4.7.

In principle, the value of $k_s$ could also be determined in this experiment. This would require shorter pulse duration lasers and faster electronics. The source of the uncertainty in $k_s$ in our experiment arises from the minimum delay interval (10 nsec) and the long pulse width of the excimer laser (10 nsec). With increased timing resolution this one experiment provides a considerable amount of dynamic information under collision free conditions.

The determination of $k_{isc}$ allows calculation of the quantum yield for intersystem crossing by equation (4).

\[ Q_{isc} = \frac{k_{isc}}{k_s} \]

The use of this value along with measured quantum yields of fluorescence allow the quantum yield for internal conversion to $S_0^*$ to be estimated. The value determined in this manner is consistent with higher pressure studies that have estimated that this decay channel is unimportant at low $S_1$ energies. The determination of intersystem crossing yields in this manner can be generalized to all molecules.
## TABLE 4.4

**Toluene Excited State Decay Parameters**

<table>
<thead>
<tr>
<th></th>
<th>This Work&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Previous Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_S$</td>
<td>$\ldots$</td>
<td>$1.32 \times 10^7$ sec&lt;sup&gt;-1&lt;/sup&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>$k_{isc}$</td>
<td>$8.5 (\pm 0.2) \times 10^6$ sec&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>$8.3 \times 10^6$ sec&lt;sup&gt;-1&lt;/sup&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>$k_T$</td>
<td>$3.45 (\pm 0.3) \times 10^5$ sec&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>$&lt; 10^3$ sec&lt;sup&gt;-1&lt;/sup&gt;&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>$Q_{isc}$</td>
<td>$0.64 \pm 0.05$</td>
<td>$0.70 \pm 0.01$&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>All values refer to the excited state produced by pumping the 0<sup>0</sup> band of the $S_1 \leftrightarrow S_0$ transition.

<sup>b</sup>The value of $1.32 \times 10^7$ sec<sup>-1</sup> was used in the least squares procedure to determine the other parameters. This number is not well determined by this experiment due to the jitter and widths of the lasers.

<sup>c</sup>Reference 91

<sup>d</sup>Reference 92

<sup>e</sup>Reference 44
detectable by the R2PI method and, coupled with fluorescence yield data, can measure absolute internal conversion quantum yields, which are difficult to determine otherwise. In the case of toluene, the fluorescence quantum yield has been measured to be $0.30 \pm 0.07$. Together with our value of the intersystem crossing quantum yield ($0.64 \pm 0.05$, see Table 4.4), these two channels account for $94 \pm 12\%$ of the decay from the $S_1$ state. Internal conversion therefore appears to be relatively unimportant for these low singlet levels of toluene.

Critical to the estimation of quantum yields is the presumption that the efficiency of ionization will be equivalent for both of the $S_1$ and $T$ intermediate levels. This assumption, while valid for toluene, is not completely general. For example, the absorption cross-section for the transition into the ionization continuum will be markedly different for the $S_1$ and $T^*$ states near the ionization threshold. Since there is very little change in the geometry of the parent ion from that of either of the intermediate states in toluene, the Franck-Condon factors will favor $\Delta v = 0$ transitions. For the vibrationless $S_1$ state, the ionization threshold will exhibit a sharp step-function behavior at the energy corresponding to the adiabatic ionization potential, $I_{P0}$ (see Figure 4.8). Excitation above this threshold is expected to produce (with relatively constant efficiency) photoions with very little vibrational energy, the excess energy of the ionizing photon being largely removed as kinetic energy of the ejected electron. In the case of the vibrationally hot $T$ state, however, roughly $1.1$ eV of the $4.6$ eV of the excitation originally present in
FIG. 4.8 Energy Levels of Toluene. The energy levels pertinent to the photoionization of toluene are represented above. The initial pumped singlet state can either fluoresce or cross into isoenergetic $T^\dagger$ states. $S_1$ states are ionized by absorption of a second photon to ionic states above $IP_0$. $T^\dagger$ states are also ionized if the ionization photon energy is as large as the gap between the origin of $T_1$ and the adiabatic ionization potential $IP_0$. For the $T^\dagger$ levels isoenergetic with the $S_1$ origin, the effective ionization potential for these triplets is $IP$, as good vibrational overlap is required for efficient ionization.
the parent \( S_1 \) level has degraded into vibrational energy distributed over many of the possible vibrational degrees of freedom. The Franck-Condon factors will still favor \( \Delta v = 0 \) transitions and the effective ionization potential becomes \( I_{P+} \) rather than \( I_{P0} \). IP corresponds to the threshold for producing a parent ion of toluene with 1.1 eV of vibrational energy. The purpose of using the ArF excimer laser is to ensure that the photoionizing transition is made far above these different threshold regions for both intermediate states. As shown in figure 4.8, the ArF photon will reach 2.3 eV above \( I_{P0} \) and 1.2 eV above IP. At such large energies above the threshold regions, Franck-Condon factors are no longer expected to affect the absorption cross-sections. However, since the photoionizing transition does excite effectively 1.1 eV higher into the \( S_1 \) ionization continuum than it does for the \( T^+ \) state, the relevant absorption cross-sections could be a bit different even neglecting vibrational overlap. However, for most large polyatomic molecules the photoionization efficiency is a rather slowly varying function of excitation energy, and the 1.1 eV difference in \( S_1 \) and \( T^+ \) ionization processes will have a minimal effect.

It should be noted that in some cases an apparent difference in photoionization efficiency would occur if only parent ions were being detected. The parent ion from the \( T^+ \) state may have enough internal energy to fragment whereas that produced from the \( S_1 \) state does not. In fact, this process has been observed in the higher alkylbenzenes.\(^{72}\) For cases such as toluene, where the complications mentioned above are
not severe, the assumption of equal ionization efficiencies is excepted to be fairly good. However, this situation must be examined carefully for each molecular system probed.

4.3.2c Vibrational Energy Dependence of Triplet Decay Rates

The triplet decay rates for benzene, toluene, several alkylbenzenes, and aniline are reported at an energy corresponding to the singlet origin pump wavelength. Higher energy vibronic states in the S₁ spectra have also been accessed by our laser, resulting in increased vibrational excitation of the isoenergetic triplet states. This excess energy dependence of the triplet decay in toluene, n-propylbenzene, and aniline has been examined over the output range of the available dye lasers. The absolute triplet decay rates for all of the benzenes studied at various Trolley vibrational energies are listed in Table 4.5.

All of the triplet decay rates listed in Table 4.5 are considerably faster than rates measured by previous workers at higher pressures. The majority of these previous values have been obtained by indirect methods and the data reflects the collisional perturbations inherent in these methods and environments. The relatively slow decay rate of excited T⁺ levels requires very low gas pressures to ensure the absence of collision relaxation processes. In the presence of collisions, the initial vibronic energy will be relaxed and, as the energy content of the triplet molecule is decreased, the
## Table 4.5

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Excitation Band</th>
<th>T Vibrational Energy (cm⁻¹)</th>
<th>k_T (x 10^5 sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>6^1</td>
<td>8500^a</td>
<td>21.3 ± 2.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>0^0</td>
<td>8600^b</td>
<td>3.45 ± .30</td>
</tr>
<tr>
<td></td>
<td>6_b^1</td>
<td>9130</td>
<td>4.26 ± .35</td>
</tr>
<tr>
<td></td>
<td>12^1</td>
<td>9533</td>
<td>4.98 ± .40</td>
</tr>
<tr>
<td></td>
<td>18_a^1</td>
<td>9565</td>
<td>5.32 ± .45</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0^0</td>
<td>(c)</td>
<td>2.65 ± .27</td>
</tr>
<tr>
<td>n-propylbenzene</td>
<td>0^0(t)</td>
<td>(c)</td>
<td>5.50 ± .53</td>
</tr>
<tr>
<td></td>
<td>12^0(t)</td>
<td>(c)</td>
<td>9.01 ± 1.53</td>
</tr>
<tr>
<td>tert-butylbenzene</td>
<td>0^0(t)</td>
<td>(c)</td>
<td>2.72 ± .32</td>
</tr>
<tr>
<td>n-pentylbenzene</td>
<td>0^0</td>
<td>(c)</td>
<td>31.8 ± 7.0</td>
</tr>
<tr>
<td>n-hexylbenzene</td>
<td>0^0(t)</td>
<td>(c)</td>
<td>23.6 ± 3.3</td>
</tr>
<tr>
<td>Aniline</td>
<td>0^0</td>
<td>7250^d</td>
<td>1.92 ± .25</td>
</tr>
<tr>
<td></td>
<td>A^1</td>
<td>8426</td>
<td>4.13 ± .68</td>
</tr>
<tr>
<td></td>
<td>1^12^1</td>
<td>8992</td>
<td>4.00 ± .66</td>
</tr>
</tbody>
</table>
aReference 96
bReference 97
cThe precise singlet triplet spacing is has not been measured. It is expected that the value is approximately that of toluene, 8600 cm⁻¹.
dReference 98
non-radiative rate decreases. In the limit of zero vibrational excitation (a good approximation is a low temperature crystal) the lifetime of the triplet state is typically several seconds and phosphorescence becomes the dominant depopulation method. The absence of phosphorescence from aromatics in room temperature studies indicates that the decay rates for thermalized triplets have increased to several orders of magnitude faster than the radiative rate. The collisionless beam results apply only to the isoenergetic triplet states, which contain $8000 - 9000 \text{ cm}^{-1}$ of excess energy, and therefore the observed hundred-fold decreases in the rates upon introduction of collisional relaxation is hardly surprising.

Collisionless triplet metastable lifetimes of benzene, toluene, and aniline have been estimated in molecular beam environments ($P = 10^{-6} \text{ torr}$) on the basis of Auger emission from Cs and Na surfaces. Although these measurements are not affected by collisional relaxation processes, the nature of the excitation source may explain the apparent discrepancy in results. The electron beam excitation source populates $T^\dagger$ states by mechanisms other than $S_1 \rightarrow T^\dagger$ intersystem crossing. The most likely population route is believed to be an exchange excitation, in which an incoming electron exchanges with an electron of reverse spin. As there will be a wide energy distribution of vibrationally excited $T^\dagger$ states populated, we expect that this vibrational distribution must be markedly different than the narrow band of vibrational states excited by our laser method. As the Auger emission experiments do not directly measure state
lifetimes, but only the existence of a long-lived state, it is likely that the triplets detected in these experiments are only those with low vibrational excitation. This is consistent with the excitation conditions.

The aforementioned variance between experimental determinations of triplet state lifetimes has been largely explained in terms of a vibrational energy dependence of the non-radiative rate. Indeed, the theory of radiationless transitions in both collisionally\textsuperscript{93} perturbed and collision-free environments\textsuperscript{99-101} suggests that the excess energy dependence of non-radiative transitions is strong. In the case of the $T^\uparrow \rightarrow S_0$ decay the energy gap is large (30,000 cm$^{-1}$) and the energy dependence is expected to be exponential. Steep exponential behavior has been demonstrated for increasing excitation in high frequency totally symmetric modes such as $v_1$ mode of the triplet state of benzene.\textsuperscript{100a} However, the same work indicates that the decay rate from low frequency modes increases much slower than with excess energy. Because low frequency modes are generally much poorer accepting modes, the total rate of non-radiative decay from a set of levels will be strongly correlated with their exact vibrational character.

The modes initially excited upon intersystem crossing from $S_1$ will be highly excited and the distribution of vibrational energy in the $T^\uparrow$ states will be governed by the path of the $S_1 \rightarrow T^\uparrow$ transition. The modes of best $S_1 \rightarrow T^\uparrow$ accepting character also have the best $T^\uparrow \rightarrow S_0$ accepting character, so the initial $T^\uparrow$ population is likely to be dominated by excitation in high frequency modes. Therefore, if
vibrational redistribution is slow with respect to $T^\dagger \rightarrow S_0$ crossing, then the energy dependence should be exponential and characteristic of these strong accepting modes. However, there exists a high density of $T^\dagger$ vibronic states isoenergetic with the optically pumped $S_1$ states, that can become populated by rapid intramolecular vibrational redistribution. In the limit of complete randomization of vibrational energy, the states populated will be dominated by the statistically more dense low frequency bending and torsional modes. As the relative density of high frequency stretching modes decreases with increasing energy, the resultant state population will have a decreasing portion of decay enhancing character. At high excess energies, the non-radiative decay rates will behave more like that of the low frequency modes and therefore a decrease in the slope of the excess energy dependence would be expected.

The vibrational redistribution that is required to populate the low frequency modes in the triplet manifold has been well documented in several systems at lower vibrational energies than probed in these experiments. The study of vibrational redistribution in the napthalene $S_1$ state suggests that the number of states involved in the redistribution process must be a large portion of those available. As the density of triplet levels is much larger in this system, the rate of randomization of triplet vibrational character is likely to be rapid and extensive.

The measurements of the substituted benzenes decay rates (k_T) as a function of excess energy is the first demonstration of the importance
of IVR for a radiationless transition. Over the range of energies studied, the decay rate was found to behave in the expected exponential manner, but very slowly. The extrapolated values for $k_T$ at the vibrationless levels of the triplet state were all between three and five orders of magnitude larger than the known rate from matrix studies. This slowing down of the excess energy dependence of $k_T$ is just the effect predicted for IVR dilution of good accepting mode character.

Unfortunately, changes in the slope of the excess energy dependence could not be measured over a wide energy range, for most of the benzenes due to experimental limitations. Vibronic states of lower $T_1$ energies are difficult to populate in these aromatics, as the optical $T_1 \leftrightarrow S_0$ transition is extremely spin-forbidden, resulting in miniscule oscillator strength. Triplet levels more energetic than 2590 Å were not studied due to the cutoff of the KD*P doubler. However, due to the generality of the two-photon ionization method, it is possible to study a great number of molecular triplet states over a wide energy range with presently available laser sources. The azines and carbonyls have been studied so that a broader energy range can be accessed through intersystem crossing from $S_1$ states. It should also be possible to pump triplet states directly, in cases where spin orbit coupling is unusually large, and thus, investigate intersystem crossing in the limit of zero vibrational energy without the external medium effects inherent in a solid state experiment.
4.3.2d Tert-Butyl Benzene: Fragmentation Processes in R2PI

The importance of vibrational energy in the ionization process has been seen previously in the study of ionization potentials of benzene and naphthalene. The ionization of tert-butyl benzene by the two-color R2PI method demonstrates some of the experimental manifestations of this vibrational energy content. Figure 4.9 illustrates the time evolution observed for this molecule when it is pumped to the origin of the $S_1$ state and subsequently ionized by an ArF laser. The two traces were collected for two different ion arrival times, with trace (a) corresponding to parent ion signal and trace (b) for the fragment ion observed with mass 119 (presumably isopropyl benzene radical cation, $C_9H_{11}^+$).

Analysis of the characteristics of the two decay curves allows determination of the intermediate levels which are involved in each ionization process. The parent ion shows the typical decay behavior of the $S_1$ state in the alkylbenzenes. The fast component with an 80 nsec lifetime, corresponds to the depletion of this state, by radiative decay to the ground state as well as intersystem crossing to the triplet state. A second component is observed, with a longer lifetime, but its intensity is much less than would be expected for the true triplet state population (triplet quantum yields for the alkylbenzenes are $\sim .7$). In the fragment ion channel, only the long component decay is observed, and the rise of this component parallels the decay of the parent ion signal.
FIG. 4.9 Time evolution of tert-butylbenzene measured by the two-color ionization method. Trace (a) is the signal observed in the parent mass channel and decays on a time scale characteristic of the $S_1$ state. Trace (b) is the signal observed at mass 119 amu. The longer decay in (b) is due to the triplet parentage of these ions.
The nature of the states accessed in the ionization continuum is responsible for this behavior. Ions produced from the $S_1$ intermediate levels will have primarily low vibrational excitation, as the maximum in the absorption cross-section will occur for transitions to these states. The excess energy of the ionization photon will be then partitioned into translation degrees of freedom of the ejected electron. Ions with triplet parentage will have vibrational motion in ionic states similar to that of the excited triplets molecular levels. The initial vibrational energy content will be much higher than $S_1$ parented ions, and a smaller portion of the excess energy will be partitioned to the ejected electron. This result is in accord with the results of the threshold studies which indicate that Franck-Condon factors control the absorption probability into specific levels of the ionization continuum.

The presence of a facile ionic fragmentation channel at a vibrational energy less than the molecular singlet-triplet energy gap, explains the differing time evolution of the two mass channels. Ions produced from triplet levels must be above the energetic threshold for fragment formation. Parent ions would then only be detected when the rate of predissociation is slow with respect to the flight time to the detector (20 μsec) or if the vibrational excitation is small.

4.3.2e Oligimers

Throughout all of the lifetime experiments the concentration of
seed molecules have been carefully controlled in order to remove the possibility of dimer formation. The motivation behind this precaution is that a strong probability of complex formation has been observed in our beam at high seed gas concentrations. The presence of dimers and higher oligimers has been observed for benzene in our beam, by one-color photoionization with the ArF laser.\textsuperscript{60} Figure 4.10 illustrates the mass spectra obtained at benzene concentrations of 1% in helium. The distribution in the figure is distorted by the use of high deflection voltages, but the large cluster sizes detected are indicative of the high probability of formation.

The mechanism of photoionization is believed to be as follows:

\begin{align*}
(5) \quad & (C_6H_6)_n \xrightarrow{\text{hv}} \frac{1930\text{\AA}}{} (C_6H_6)_{n-1} (C_6H_6)^* \\
(6) \quad & (C_6H_6)_{n-1} (C_6H_6)^* \rightarrow (C_6H_6)_{n-1}^* + (C_6H_6) \\
(7) \quad & (C_6H_6)_{n-1}^* \xrightarrow{\text{hv}} \frac{1930\text{\AA}}{} (C_6H_6)_{n-1}^+ 
\end{align*}

The oligimer that is initially excited by a 6.4 eV photon will have internal energy greater than the weak dimer bonds, and that energy can cause dissociation (6) during the laser pulse width. In the dimer case (n=2) the dissociation produces an excited state monomer (probably T\textsuperscript{+}) that will have been 'cooled' by the energy released into the translational motion of the fragment molecules. The monomer produced can now absorb another photon in order to produce a photoion. Thus,
FIG. 4.10 Benzene Clusters. Distribution of benzene clusters in the supersonic molecular beam observed and ionized with an ArF laser at 1% benzene seed gas in helium.
the presence of dimer molecules can be detected by the observation of parent ions. For larger oligomers, the electronic excitation will remain within an oligimer fragment and then absorption of a second photon will produce an ion of mass equal to that fragment. Normally, parent ions of benzene are not efficiently detected by the ArF laser, as the 6.4 eV photon produces a benzene intermediate state which is unstable on a time scale of the laser pulse. The benzene predissociates and therefore, is lost to the photoionization scheme. We have seen a similar effect in aniline when pumping to high energy intermediate states. By lowering the toluene concentration, the signal due to the ArF laser can be reduced to a very low level, indicating that no dimer or oligimer species are present.

Presence of the dimer molecules may produce lifetime data which is distorted by a similar mechanism as the dimer photoionization. While this effect is not likely to be important for molecules which exhibit a highly structured absorption spectra, in diffuse spectral regions this factor can severely affect the experimental results. The lifetime could be lengthened by the following mechanism:

\[ (8) \quad (C_6H_6)^2 \xrightarrow{\text{hv}} (C_6H_6) \quad (C_6H_6)(T^+) \]

\[ (9) \quad (C_6H_6) \quad (C_6H_6)(T^+) \xrightarrow{\text{or e-\text{beam}}} (C_6H_6) + (C_6H_6)(T^+) \]

Oligimer molecules that are excited will decay by similar radiationless routes as the monomeric species and thus it is likely that a triplet
oligomer will be formed. The vibrational energy of the triplet can be utilized on a fast time scale to dissociate a weak dimer bond, resulting in a triplet parent molecule with less vibrational energy than the initially excited state. The resultant triplet will have a slower non-radiative rate (due to the steep energy dependence) for conversion into vibrationally hot $S_0$ levels.

4.3.3 Pyrazine and Pyrimidine

4.3.3a Introduction

In order to further elucidate the behavior of large energy gap radiationless decay mechanisms in aromatic molecules, it is necessary to test the results of the benzene $T^+ \rightarrow S_0$ measurements in a case where a much larger range of energy can be accessed. The benzene experiments point to a leveling off of the rate of increase in the energy dependence of these decay rates, but the existence of such an effect is based on only a few rate measurements in a small energy range. The azines provide a system where the energy dependence can be probed over several thousand wavenumbers, as their $\pi^* \rightarrow \pi$ states are generally at lower energies than the corresponding $\pi^*$ levels of the benzenes. Pyrazine and pyrimidine have been studied due to their accessible absorption spectra and small singlet-triplet energy gap.

The dynamics and spectroscopy of both of these azines have been
studied extensively. Pyrazine exhibits a structured absorption spectra in the region of $3200 - 3000 \text{ A}$ in the gas phase, assignable to the $^1B_{2u} \leftrightarrow ^1A_1$ transition.\textsuperscript{103} The spectra has been thoroughly studied by fluorescence techniques\textsuperscript{104-107} and the vibrational assignments and frequencies of the ground and excited state motions are known. Additionally, the $S_2 (\pi\pi^*)$ state absorbs within the frequency range of our lasers, although the vibrational structure has not been assigned due to the intrinsic broadness of this transition. The pyrimidine $S_1$ transition is much more extensive, extending from $3200 - 2800 \text{ A}$. This $^1B_1 \leftrightarrow ^1A_1$ transition is characterized by several long progressions of totally symmetric modes.\textsuperscript{108,109} The vibrational analysis has been made by Knight et al.\textsuperscript{109} and their assignments have been adopted for this work.

In the benzenes, the large singlet-triplet energy gaps ($8000-9000 \text{ cm}^{-1}$) allow the density of states of triplet vibronic levels to become large enough to assure that a statistical limit intersystem process would occur upon the population of singlet state levels. However, the azines have much smaller gaps between the lowest singlet and triplet states and thus radiationless decay processes are not necessarily describable by the statistical limit. Pyrazine and pyrimidine have energy gaps corresponding to 4056 cm$^{-1}$\textsuperscript{110,111} and 1800 cm$^{-1}$\textsuperscript{112}(2545 cm$^{-1}$\textsuperscript{113} respectively. At these small energies the level density of the triplet manifold is rather sparse and uneven. The intersystem crossing process for these molecules has been successfully described by the strong coupling intermediate case.\textsuperscript{114}
Intermediate case behavior has been observed previously for these azines.\textsuperscript{104,115-118} The time evolution of emission is characterized by a bieponential decay. The emission has two components, a prompt fast decay and a slower fluorescent decay. The spectral characteristics are attributable to the singlet state levels, however the long fluorescence has a lifetime which is much longer than the radiative lifetime expected for this state.\textsuperscript{107,116,117} This slow decay corresponds to the incoherent decay of individual mixed eigenstates (having singlet and triplet character) via radiationless processes to the ground state. The short-lived emission is due to a coherent decay process where the initially excited phased array of true molecular eigenstates (the mixed states) lose their initial phase relationships.

A detailed theory has been developed for this strong coupling intermediate case.\textsuperscript{114} The coupling of a single radiative level $s\rangle$ with the manifold of poorly radiative $t\rangle$ levels produced by excitation with a photon with an energy width $\Delta$, can be described by quasistationary states of the form

$$|n\rangle = a_n |s\rangle + \sum_i B_{n i}^t |t\rangle$$

The initial excitation is only coupled to the $|s\rangle$ character of the true eigenstates and thus the initial superposition of levels corresponds to

$$\Psi(t=0) = a_n |n\rangle \langle n |s\rangle = \sum_n A_n |n\rangle$$

The time evolution of the initially excited states decay by the two mechanisms noted above. The fast decay can exhibit recurrences or quantum beats, if the energy distribution of the $|n\rangle$ states is regular and the number of strongly coupled states is a small. Quantum beats
have been observed in methyl glyoxyl and bisacetyl.\textsuperscript{118} However in the azines, this type of coherent effect has not been observed. The slow component is due to incoherent decay of individual eigenstates. As the emissive properties of these levels depend on the square of the coefficients of the $|s\rangle$ wavefunctions ($a^2 \sim 1/N$), the lifetime of this state will be much longer than that of a pure singlet level.

The fast component of the biexponential decay has been measured to be 100 picoseconds\textsuperscript{118} and 2.0 nanoseconds\textsuperscript{116,120} for low lying vibronic bands in the $S_1$ spectra of pyrazine and pyrimidine respectively. The long components, which are extremely pressure sensitive vary from 200 - 400 nanoseconds for the origin of both molecules\textsuperscript{104,107,116,117} The R2PI experiments of this work are only sensitive to the slow component population decay. This is because the ionization method is sensitive to the total excited state population, and not the emissive properties of these states. The fast component observed in fluorescence is only a decay in the overall singlet state character and very little or no real crossing to the ground state occurs during its lifetime. The long decay components can be successfully studied, and when the number of strongly coupled triplets becomes sufficiently large, the overall decay characteristics will be governed by the non-radiative behavior of the triplet character. For all but the lowest energy singlet vibronic bands, this is likely to be true. The excess energy dependence of this decay can be followed over a considerable energy range.
4.3.3b Results and Discussion

The rate of the decay of the slow component for both pyrazine and pyrimidine has been plotted as a function of the triplet state vibrational energy in Figures 4.11 and 4.12. These results are also listed in tables 4.6 and 4.7. The data is consistent with the benzene results of the previous section. Again, the energy dependence appears to have an exponential dependence over the range that was studied, but extrapolation of this curve to zero vibrational energy yields a value for the zero point decay which is several orders of magnitude greater than measured in low temperature crystals (pyrazine\textsuperscript{121} pyrimidine\textsuperscript{122}). The remarkable aspect of the data is that it indicates that the slope of the energy dependence must change at fairly low energies (less than 2000 cm\textsuperscript{-1}).

In both molecules the highest energy accessed is rather uncertain due to the rapid rate of triplet state decay. The 35 nanosecond lifetimes of these two levels are approaching the limit of our timing resolution and therefore these values should be considered upper values of the lifetimes of the triplet levels populated at these energies.

Strictly speaking, the states that are populated in the molecular beam are not true triplet levels due to the intermediate case coupling. Nevertheless it is true that the rate of the non-radiative process to the ground state will be governed by the predominately triplet character of the mixed eigenstates. The radiative properties of the singlet state could also cause a rapid depopulation of the mixed
FIG. 4.11 Decay rates of excited state levels as a function of triplet vibrational energy in pyrazine. The highest energy measurement (pump laser at 266nm) is quite uncertain due to the jitter and pulse widths of the two lasers used to detect these molecules.
TABLE 4.6

Triplet State Decay Rates for Pyrazine

<table>
<thead>
<tr>
<th>Laser Excitation Band</th>
<th>$T_1$ Vibrational Energy (cm$^{-1}$)</th>
<th>$k_T$ ($\times 10^{6}$ sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 $\overset{0}{o}$</td>
<td>4056$^a$</td>
<td>3.41 ± .27</td>
</tr>
<tr>
<td>6 $\overset{1}{a_0}$</td>
<td>4639</td>
<td>4.59 ± .50</td>
</tr>
<tr>
<td>8 $\overset{1}{a_0}$</td>
<td>5439</td>
<td>7.04 ± .74</td>
</tr>
<tr>
<td>6 $\overset{3}{a_0}$</td>
<td>6031</td>
<td>5.00 ± .91</td>
</tr>
<tr>
<td></td>
<td>10774</td>
<td>28.6 ± 16.5</td>
</tr>
</tbody>
</table>

$^a$References 110 - 111.
FIG. 4.12 The rate of decay of the excited state population in pyrimidine is plotted as a function of the energy above the $T_1$ origin. The initially pumped vibronic band in $S_1$ is denoted along side the corresponding data points.
<table>
<thead>
<tr>
<th>Laser Excitation Band</th>
<th>T&lt;sub&gt;i&lt;/sub&gt; Vibrational Energy cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>(x 10&lt;sup&gt;6&lt;/sup&gt;)&lt;sub&gt;sec&lt;/sub&gt;&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0&lt;sup&gt;o&lt;/sup&gt;</td>
<td>1793&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.77 ± 0.21</td>
</tr>
<tr>
<td>6&lt;sup&gt;ao&lt;/sup&gt;</td>
<td>2406</td>
<td>1.41 ± 0.17</td>
</tr>
<tr>
<td>1&lt;sup&gt;o&lt;/sup&gt;</td>
<td>2734</td>
<td>1.21 ± 0.17</td>
</tr>
<tr>
<td>12&lt;sup&gt;o&lt;/sup&gt;</td>
<td>2805</td>
<td>1.39 ± 0.20</td>
</tr>
<tr>
<td>6&lt;sup&gt;ao&lt;/sup&gt; 112&lt;sup&gt;1o&lt;/sup&gt;</td>
<td>3422</td>
<td>2.00 ± 0.28</td>
</tr>
<tr>
<td>12&lt;sup&gt;o&lt;/sup&gt; 2</td>
<td>3818</td>
<td>2.56 ± 0.38</td>
</tr>
<tr>
<td>6&lt;sup&gt;ao&lt;/sup&gt; 112&lt;sup&gt;2o&lt;/sup&gt;</td>
<td>4435</td>
<td>4.22 ± 0.64</td>
</tr>
<tr>
<td>12&lt;sup&gt;o&lt;/sup&gt; 3</td>
<td>4826</td>
<td>5.71 ± 0.91</td>
</tr>
<tr>
<td>12&lt;sup&gt;o&lt;/sup&gt; 316&lt;sup&gt;bo&lt;/sup&gt; 2</td>
<td>5518</td>
<td>7.87 ± 1.55</td>
</tr>
<tr>
<td>——</td>
<td>6396</td>
<td>9.26 ± 2.79</td>
</tr>
<tr>
<td>——</td>
<td>8314</td>
<td>28.6 ± 16.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reference 112
states, but this is likely to occur only at very small $S_1$ vibrational energies, where the number of strongly coupled triplet levels is small. This may be occurring at low energies in pyrimidine. However, the majority of the data is for regions of much higher triplet state densities and therefore will not be affected by this mechanism.

The observation of an increase in the decay rate for pyrimidine at low $S_1$ energies appears to be consistent with the small energy gap and low triplet density. In pyrimidine the energy gap may be as small as 1800 cm$^{-1}$ in the gas phase and at this triplet state energy the density of states is very small and uneven. Indeed, a rough idea of the vibronic level density can be gained through the use of the Harhoff formula. Using the ground state frequencies of Knight et al., this method indicates that at this energy only 1.5 states per wavenumber are present (~8 states/cm$^{-1}$ if the crystal value of the energy gap is used). Addition of rotational states into the state density calculations will increase the overall level density, but in the cold supersonic beam experiments, this would provide only a moderate increase.

The supersonic beam environment may result in an additional factor relevant to the lifetime shortening observed at the pyrimidine origin. It has been observed by Baba et al. that there is a strong rotational dependence of the fluorescence quantum yield for this band. Apparently, the coupling between the singlet and triplet levels is dependent upon the rotational level, with low J values providing the highest emission yields (implying that the number of strongly coupled
triplet levels has decreased). This effect has been confirmed in the study of Jameson et al.,\textsuperscript{118} which indicates that the rate of the slow fluorescence does increase with decreasing $J$. The increasing decay rates of levels below 1000 cm\textsuperscript{-1} in our experiments would be in accord with these results, as in this region the effective singlet character must be rapidly increasing. As only low $J$ rotational levels are populated in the beam, the number of coupled triplet levels would be smaller due to this effect.

An increasing decay rate at low singlet energies was not observed in the low pressure studies of Spears and El-Manguch.\textsuperscript{116} It is not surprising this previous measurement would not have observed this effect, as many higher $J$ levels are populated in these thermal experiments. The resultant decay would be dependent upon the number and nature of $J$ states populated by their laser. The overlap of the decays from this excitation would produce lifetime data which would appear longer than that of the low $J$ states populated in the supersonic beam. Nonetheless, a manifestation of this effect may have been seen by Spears et al., as they mention that the decay of the slow fluorescence of the 0–0 band has 'gradual non-exponential behavior that yields a slowly decreasing decay rate at longer times'.\textsuperscript{116} This is exactly what would be expected if the $J$ state argument applies.

4.3.3c Conclusion

The studies of these two azines has confirmed the previous results obtained for the energy dependence of non-radiative decay channels in
aromatic molecules. The general behavior that is indicated is that a dramatic change of the slope of this dependence occurs at relatively low energies. This result may be an effect of intramolecular vibrational redistribution in the vibronic levels of the triplet manifold, causing a dilution of the strong accepting character of high frequency modes by the higher density, poorer accepting, low frequency bath modes.

In the case of pyrimidine, these cold collision-free experiments indicate that at low $S_1$ energies the number of strongly coupled triplet levels is extremely small. This is seen in the increasing rate of population decay with decreasing $S_1$ energy. That this effect has not been seen in low pressure thermal experiments suggests that this may be due to a rotational state dependence of the singlet-triplet coupling.

4.3.4 Conclusion

The interpretation of data on the dynamics of triplet states has been confused by the neglect of the influence of vibrational energy content upon triplet decay rates. Unlike singlet states, triplets are usually not optically accessible or do not emit on time scales that would enable studies of non-collisionally perturbed states. Therefore, correlation of the results of differing experimental determinations of decay rates requires knowledge of the exact extent of the collisional relaxation. The coupling of multiphoton ionization with a molecular beam allows, for the first time, dynamic studies of isolated molecular
triplet states with high selectivity and sensitivity. For all of the aromatic molecules studied here, the slope of the excess energy dependence for triplet states populated by $S_1 \rightarrow T^+$ intersystem crossing does not extrapolate to the value of non-radiative decay for the lowest $T_1$ level, as measured by low temperature crystal work. As changes in the non-radiative decay rate are strongly correlated to the specific nature of the vibronic states populated, the observed effect appears to be a manifestation of the increasing statistical weight of low frequency poor acceptor modes in conjunction with rapid intramolecular vibrational redistribution. The photoionization method described in this work is capable of extending this knowledge and it is expected that a new body of information will emerge to further test and improve the theories of radiationless transitions in both the collisional and collision-free regimes.
CHAPTER 5

METAL CLUSTERS

5.1 INTRODUCTION

Synthesis and characterization of small metal clusters have become a topic of considerable fascination in the chemical community over the past decade.\textsuperscript{125-134} Aside from the intrinsic interest always expressed in a rich new class of molecules, research in these novel species is particularly intense due to their relevance as models of catalytic activity. The Fischer–Tropsch catalyst,\textsuperscript{135} for example, is composed of microcrystals of transition metals such as Fe supported on a suitably inert surface such as silica. Interest in the Fischer–Tropsch process has skyrocketed lately since it provides an economically realistic path in the conversion of coal to methane and higher hydrocarbon fuels. Metal clusters (particularly iron–sulfur clusters such as Fe\textsubscript{4}S\textsubscript{4}) are also found at the active site of a wide variety of enzymes.\textsuperscript{136}

Detailed spectral investigation of metal cluster molecules has been particularly difficult due to their extremely complex electronic structure, and often fluxional vibrational behavior. The coordinatively unsaturated clusters (including the bare metal clusters themselves) are highly reactive and are easily perturbed by even the most inert support. For these reasons alone any technique which would permit metal clusters to be studied in an ultracold collisionless
supersonic beam would have considerable value.

5.2 LASER VAPORIZATION

5.2.1 Method

Supersonic beams of metals and small metal clusters may, in principle, be prepared simply by heating the entire nozzle source above the boiling point of the desired metal. Gole and co-workers have succeeded with such an approach in producing supersonic beams of the copper dimer (and perhaps also the trimer).\textsuperscript{137} Supersonic cluster beams of the alkali metals have also been common for many years and recently the spectroscopy of these beam species has been studied in increasingly impressive detail by Schumacher and co-workers using mass selective multicolor laser photoionization.\textsuperscript{9} These hot oven nozzle sources are limited, however, to relatively low boiling metals and to a rather modest extent of cooling of the internal degrees of freedom.

It has long been recognized that metal vaporization is easily accomplished by irradiation with pulsed high power lasers.\textsuperscript{138} Atomic beams of a variety of metals have been generated by laser irradiation of appropriate targets, and in some circumstances the metal vapor plume initially created was even of sufficient density to produce some cooling upon expansion.\textsuperscript{139–141} However, these mildly supersonic metal vapor beams have not been found to contain a substantial cluster
concentration. In order to provide the requisite extra cooling to form clusters and then cool these clusters to cryogenic temperatures, we have combined this laser vaporization technique with the pulsed supersonic nozzle technology. The laser-driven metal vaporization is then carried out within the supersonic nozzle such that the ejected metal vapor is entrained in the high density helium carrier gas prior to the full supersonic expansion of this gas further downstream. Resonant two-photon ionization provides the detection and the mass selectivity necessary to deconvolute the spectra of the large distribution of cluster species possible in such a molecular beam.

5.2.2 RESULTS AND DISCUSSION

The vaporization of aluminum into the molecular beam was accomplished by focusing the second harmonic from a Nd:YAG laser (80 mJ/pulse) to a 1 mm diameter spot onto an aluminum plug. The vaporization laser counter-propagated the molecular beam, in order to allow the vaporization to occur in the expansion channel of the nozzle. This is illustrated by Figure 5.1. Clusters species formed in the pulsed expansion were probed 1.2 meters downstream by direct photoionization using a 10 mJ/cm$^2$ excimer laser beam at 1570 A.

Figure 5.2 shows the time-of-flight mass spectrum of an aluminum cluster beam produced by the laser vaporization technique. This spectrum was obtained by photoionization using an unfocused eximer laser beam at 1570 A ($F_2$ laser transition, 10 mJ/cm$^2$). Due to the
FIG. 5.1 Nozzle source for aluminum cluster vaporization. The 2nd harmonic of a Nd:YAG laser which was focused onto the aluminum plug located in the expansion channel.
FIG. 5.2 Time-of-flight mass spectrum of a supersonic aluminum cluster beam produced by laser vaporization of an aluminum plug inside a pulsed supersonic nozzle. The vaporization laser beam was the second harmonic from a Nd-Yag laser (80 mJ/pulse focused to a 1 mm diameter spot on the aluminum plug). The labeled peaks correspond to three distributions of metal cluster species.
fact that all metal clusters produced in the nozzle are accelerated to
the same speed by the helium carrier gas (\(~2 \times 10^5\) cm/sec, regardless of
the cluster size), parent ions of these clusters produced by
photoionization have a translational energy along the beam direction
which is linearly proportional to their mass. Electrostatic deflection
plates are used in order to turn the cluster photons, direct them down
the flight tube, and onto the detector. For Fig. 5.2 these plates were
adjusted to produce optimum deflection for mass 200. The apparent
distribution of intensity in the various clusters is therefore somewhat
distorted in this figure. The large signal at the beginning of the
spectrum is electrical noise which accompanied the eximer laser firing.
This noise signal, as well as the signals due to He, Al, and \(\text{Al}_2\), were
far off scale on the sensitivity setting used to obtain the spectrum
shown here.

The Al monomer signal observed in this cluster beam was the most
intense we have ever seen for any species in this molecular beam
apparatus (including the \(\text{FeCO}_5\) signals of section 3.3). A rough
estimate of the Al density in the TOFMS ionization region would be at
least \(10^{10}\) cm\(^{-3}\). The Al dimer was found, under the most severe cooling
conditions we tried, to be approximately 10% of the monomer signal.
The \(\text{Al}_3\) trimer signal which is the first Al cluster to be shown on
scale in the figure is roughly 5% of the dimer intensity. Other peaks
in the mass spectrum of Fig. 5.2 reveal that there was a bit of
acetone impurity in the helium carrier gas. This impurity is
responsible for formation of the acetone-\(\text{Al}_x\) and acetyl-\(\text{Al}_x\) species
seen in the mass spectrum. The first member of the acetyl-\(\text{Al}_x\) series (\(\text{Al}-\text{C}_2\text{H}_3\text{O}\)) is extremely weak due to a facile fragmentation to \(\text{Al}^+ + \text{C}_2\text{H}_3\text{O}\) under the 1570 Å excitation conditions used here. This spectrum demonstrates nicely the ability of this technique to prepare beams of clusters with reactive species attached. It is these species which may be the key to the understanding of fundamental catalytic processes.

In the nozzle used to produce these cluster beams the gas output from the 1 mm diameter, 5 mm long orifice of the standard design, was deflected through a 2 mm diameter tube inclined at a 25° to the original nozzle axis. This slanting tube then opened into a 2 mm diameter, 9 mm long tube directed parallel to (but offset 2 mm from) the axis A. The bottom of this latter tube contained the plug of aluminum to be vaporized by the laser, and the top of the tube served as the true nozzle exit. We suspect that this design was certainly not the optimum, since the flow path for the helium carrier gas was rather tortuous. However, it did permit an easy alignment of the Nd:YAG second harmonic vaporization laser beam down the axis of the molecular beam apparatus without allowing scattered light from this laser to destroy the sealing mechanism of the pulsed valve.

An appealing aspect of this cluster beam generation technique is its great generality. Any metal or mixture of metals may be used and even the most refractory materials are readily vaporized by pulsed Nd:YAG lasers. The doubled, Q-switched volitization laser used here is certainly not the optimum, since it is well recognized in the literature that a fast pulse produces very little vaporization. At
such high intensities (> 10 W/cm²) the metal vapor is efficiently ionized and the resultant plasma becomes optically dense. The result of further irradiation is an extremely hot plasma with very little further vaporization. Normal (non-Q-switched) micro-second time pulses from a Nd:YAG laser at 1.06 µm may be far more effective at vaporization to produce cold metal cluster beams. Mass selective multicolor photoionization spectra of such clusters and their adducts with reactive molecules seem imminently feasible, and could produce useful new insight into the structure and dynamics of these fascinating species.

Further efforts are being presently made in our laboratory to further optimize the conditions of this laser vaporization technique. The ultimate goal of this work is to be able to determine the spectroscopy of these unique molecules. Resonant two-photon ionization will be utilized, as the cluster beams will be characterized by a variety of cluster species. The mass selectivity of the method will be of paramount importance to these studies, as otherwise it would be impossible to deconvolute the overlapping M_x spectra.
5.3 Photoysis of Transition Metal Complexes

5.3.1 Introduction

An alternate method for the preparation of metal cluster species in the molecular beam is the photoysis of volatile organometallic species. It is well known that the bonding interactions in these species are relatively weak and that these molecules are usually sensitive to ultraviolet irradiation. With high intensity laser sources it is possible to strip a organometallic complex to the bare metal atoms (or ions) through a multiple photon absorption process. If a high frequency of molecular collisions can be maintained, it may be possible to form metal complexes upon recombination of the bare atoms.

A second possibility that has been uncovered, while investigating the photoionization behavior of iron pentacarbonyl in a supersonic beam. Apparently, an unique laser photolytic process can occur upon irradiation of this molecule with the light from an ArF excimer laser, whereby microcrystals of Fe(CO)$_5$ are efficiently converted in a single laser shot into Fe$_x$ clusters ($x = 1$ to $30$). This process is remarkable in that it involves wholesale reorganization of the chemical arrangement within a Van der Waals-bound molecular crystallite prior to vaporization of this crystal, and that it occurs in the rarified collision-less environment of the skimmed supersonic beam. Since sublimable carbonyl species are readily available for most of the transition metals, this laser chemistry may offer quite interesting new
possibilities for polynuclear metal cluster synthesis on a macroscopic scale.

One of the oldest preparative techniques for multinuclear metal clusters is simply irradiation by direct sunlight.\textsuperscript{143} In fact this remains a favored technique for the synthesis of Fe\textsubscript{2}(CO)\textsubscript{9} and very recently has been used to produce new cluster species such as \((\eta^5-C_5H_5)Nb_3(CO)\textsubscript{7}\).\textsuperscript{143} In the case of Fe(CO)\textsubscript{5}, the primary photochemical event in the liquid phase is known to be ejection of CO to form Fe(CO)\textsubscript{4}.\textsuperscript{47,144} This radical is then free to participate in further reactions such as cluster formation:

\[
\text{Fe(CO)}_4 + \text{Fe(CO)}_5 \rightarrow \text{Fe}_2(\text{CO})_9.
\]

Addition of more Fe(CO)\textsubscript{4} radicals to produce larger clusters is known to occur, but only when the reaction mixture is heated and then only in small yield. Under normal photolytic conditions the dimer concentration is limited by the fact that metal-metal bond scission is by far the most favored primary process.\textsuperscript{145} Prolonged exposure to light will ultimately lead to the decomposition of Fe(CO)\textsubscript{5} to produce bulk metallic iron and CO gas, so it is clear that some mechanisms do exist for the photolytic production of larger clusters. Under conventional conditions, however, these mechanisms are slow and never result in a substantial yield of metal clusters of intermediate size. The following experiment indicates that a much more favorable situation exists under intense pulsed ArF eximer laser irradiation.
5.3.2 Results and Discussion

A metal carbonyl microcrystal beam was produced by pulsed supersonic expansion of 0.2% Fe(CO)$_5$ in 15 atm helium from a 0.1 cm diameter orifice at 300K. Using an eximer laser operating on the F$_2$ transition at 1570 A, the presence of iron pentacarbonyl microcrystals was readily monitored since all crystals larger than (Fe(CO)$_5$)$_3$ are directly photoionized at this wavelength to produce primarily ions of the type (Fe(CO)$_5$)$_n^+$. A typical mass spectra obtained under these excitation conditions is shown in Figure 5.3.

Drastically different results are observed when the eximer laser is operated on the ArF transition at 1930 A. The resultant photoionization mass spectra is plotted in figure 5.4. The strong mass peaks corresponding to Fe and Fe(CO)$_2$ shown off-scale in this figure are due to multiphoton ionization of Fe(CO)$_5$ monomer in the beam$^{45}$. The strong peaks numbered from 3 up through 14 arise from ArF laser photolysis of the (Fe(CO)$_5$)$_n$ microcrystals and occur in the appropriate mass channels for the bare clusters Fe$_3$ through Fe$_{14}$. Intermediate peaks are observed at 28 amu spacing and are due to complexes containing an odd number of CO attached to the Fe clusters.

The intensity pattern of this mass spectra suggests that the more intense peaks spaced by 56 amu are assignable to the bare metal clusters. The presence of the intermediate peaks allows an estimation of the contribution of the signal occurring at the cluster arrival times from species of the type Fe$_x$CO$_{2n}$$. As there is no intrinsic reason to expect that the Fe$_x$CO$_{2n}$ signals would be favored over the complexes
FIG. 5.3 Iron pentacarbonyl clusters detected by direct ionization with an $F_2$ laser. Relative intensities are distorted by high deflection voltages (see text).
FIG. 5.4 Time-of-flight mass spectrum of ions produced by an ArF laser excitation of a Fe(CO)$_5$ microcrystal beam. Numbered peaks are predominantly due to bare iron clusters.
with odd numbers of CO, the numbered peaks in the spectra are predominately due to Feₓ species. The apparent cluster distribution shown in the figure is also distorted by the fact that only one mass is perfectly focused onto the detector at any one time. Mass spectra optimized for larger clusters show the distribution to extend with measurable intensity out to approximately Fe₃₀.

Generation of these Feₓ clusters was found to be strongly dependent on ArF laser fluence. Halving this fluence from 20 to 10 mj/cm² reduced the Feₓ cluster intensity by a factor of 20. Excitation with the 4th harmonic of a Nd:YAG laser at 2650 Å failed to produce any significant cluster photoion signal other than the very strong Fe and very weak FeCO and Fe(CO)₂ signals expected from Fe(CO)₅ monomer. This remained true for all laser fluences from 0 through 100 mj/cm² (4 nanosecond pulse). Even though the absorption cross section for Fe(CO)₅ at 2650 Å is only about one-half of that at 1930 Å, the fluence range explored with the 2650 Å laser was more than sufficient to achieve equivalent energy deposition.

At 20 mj/cm², a ten nanosecond ArF laser pulse will excite Fe(CO)₅ molecules at a rate of roughly 2 x 10⁸ sec⁻¹. Microcrystals of less than 1000 Fe(CO)₅ molecules are optically thin at this wavelength so this excitation rate applies to all molecules regardless of their position in the microcrystal. Such a rate is sufficient to excite over 80% of the crystal during the laser pulse. At either laser wavelength this degree of excitation is far more than needed to totally vaporize the crystal into separate Fe(CO)₅ molecules, or to completely
reorganize it into an iron cluster plus a rapidly expanding cloud of CO gas. Reorganization is favored in the internal regions of the microcrystal where vaporization is slowed by inertial confinement of the outer layers. Metal cluster growth here competes well with vaporization if the local temperature following absorption of a photon rises above some critical value. For these supersonic microcrystals of Fe(CO)$_5$, such a threshold appears to lie between 2650 and 1930 Å.

Additional experiments have been attempted to produce cooled metal cluster beams by this photolysis. Very little success has been obtained along these lines as an extreme number of collisions are necessary to trap these species into the molecular beam. As the production of the metal clusters by the above mechanism is a result of very high laser fluences the resultant metal species are likely to be very hot translationally. Ion formation will also limit the amount of clusters trapped in the beam, for if the extent of ionization is large, space charge effects will cause the resultant metal species to be ejected from the beam before electron-ion recombination can occur. Based upon the experiments described in this thesis it appears that the laser photolysis method will prove to be far better for the production of cluster beams. In conclusion, the use of molecular beam technology in conjunction with ionization techniques has developed to the point, that metal cluster spectroscopy is imminently possible.
CHAPTER 6

SUMMARY

All of the preceding studies contain the unifying thread of the tandem application of laser ionization and supersonic molecular beam technologies. This work has taught us the advantages and limitations of these methods and how to take the maximum advantage of the information derivable from these experiments. Whereas, there are inherent limitations on the sensitivity and range of one color ionizations, the use of two-color ionization methods can enhance and extend the utility of resonant two-photon ionization, just as the use of resonant intermediate states increases molecular selectivity over that of multiple photon ionizations of earlier workers. The addition of a second laser provides another parameter, the temporal dependence of the intermediate state populations, which provides a rich area for study of excited state decay process. The supersonic molecular beam technology supplies an unique rarified environment, which allows these ionization results to be unaffected by confusion from sources other than the true isolated molecular properties. The experiments in this thesis illustrate many of these points. However, the experiments and methods discussed above are just the precursors to a wider body of work which can be developed on the foundations of these two powerful techniques.
REFERENCES


38. The first \( \pi^* \) state of the monohalobenzenes belongs to the \( B_2 \) irreducible representation of the \( C_4 \) point group. We will take the \( z \) axis to be collinear with the \( C-X(\text{Br, I}) \) bond and the \( y \) axis to be in the same plane of the ring perpendicular to the \( C-X \) bond. It should be noted that our axis and character table convention differs from that used in Refs. 29 and 32–34.


67. In static gas phase experiments at room temperature, collisional ionization of Rydberg states below the ionization potential is a common source of red-tailing in ionization potential measurements. (See Ref. 66).


72. T. G. Dietz, M. A. Duncan, and R. E. Smalley, To be published.


76. R. J. Damburg and V. V. Kolosov, Atomic Molec. Phys. 12, 2637 (1979).


79. There appears to be broadening in the linewidths of lower energy Rydberg states of benzene observed by MPI (P. M. Johnson, J. Chem. Phys. 64, 4143 (1976)). Since this experiment used a room temperature sample at 50 torr pressure, the observed linewidths are due to a variety of complicating factors. In our cold \( T_{\text{vib}} \approx 50 \text{ K} \), collision-free environment, we should observe true natural linewidths.


90. In this paper the symbol T is used to represent the vibrationally excited triplets formed by intersystem crossing from excited S1 singlet states. The symbol S0 is used to represent the highly vibrationally excited ground state species formed by subsequent non-radiative decay of this triplet.


APPENDIX 1

Critical to many of the experiments in this thesis was the need for a computer controlled digital delay generator. The triplet experiments in section 4.3 relied on this hardware as the long term experimental drift in beam intensity and pulse profile can strongly affect our data. Timing precision is also very important in these experiments as the stability of the delay between the two laser pulses will strongly affect the data.

As there was no commercially available CAMAC based delay modules with the requisite precision, several home-built digital delay modules were constructed around an Evans digital delay board (4041-2). The Evans board is programmable, providing delays from 0 – 1 μsec at 10 nsec intervals (with ±1 nsec total jitter between two output pulses). The delay generator requires binary coded decimal data (BCD). Binary data is sent along the CAMAC dataway to the module containing the delay generator. The data is latched by several 'LS175 circuits and this data is then converted into BCD data by a hardware converter (18 'LS185 binary–BCD converters). The output of 5 BCD decades is then inverted to provide the correct polarity for input into the Evans board.

In some cases it was necessary to sample background data in the same sequential manner that was necessary for the lifetime determination. This was accomplished by sending two additional bits of binary data to the delay module. The state of each of these bits determined whether the appropriate delay generator output would be pulsed
(e.g., if the control bit is high, no pulse will be output.). Thus, signal from each laser alone, in a two-laser experiment could be at measured at periodic intervals in the data taking cycle. The control bits were latched along with the other data and used to enable a 'LS221 one shot on the output of the delay generator circuit. The controlled outputs are amplified by fast transitors to 5-20 V, 1 microsecond duration pulses. A second output was also provided and it was not controlled by the computer, in order to allow synchronization of the detection with the appropriate delay for background measurements.