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PHOTOIONIZATION EXPERIMENTS IN A SUPersonic MOLECULAR BEAM

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PHOTOIONIZATION EXPERIMENTS IN A SUPersonic Molecular Beam

by

Mark Gregory Liverman

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

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APRIL 1981
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The work described in this thesis was not done by myself alone. Tom Dietz and Mike Duncan worked on all of the photoionization projects. Kudos for the design and construction of the photoionization time-of-flight mass spectrometer and its predecessor, the electron bombardment time-of-flight spectrometer, must go to them. I helped by staying out of their way. Prof. Rick Smalley provided many original ideas. Dr. Steve Beck did the majority of the construction work on the nitrogen laser-pumped dye laser. During his stay, Dr. Dave Monts provided a calming influence in an otherwise hectic environment. Tom and Betty allowed Wendy and I to use their living room floor for a month, and as a result I got this tome written. Finally, I would like to thank my wife, Wendy, for teaching me that there is life beyond science.
ABSTRACT

The uses of resonance enhanced two-photon ionization (R2PI) for studying unimolecular energy redistribution of molecules in a super-sonic molecular beam is explored. The R2PI process relies on initially exciting a molecule to a state that is stable with respect to the up- pumping rate of an ionizing laser field. For such situations, the ion signal produced is proportional to the population of the intermediate state. It can therefore be used in place of the observation of emitted light for measuring the population of an excited state. This is particularly useful for states that do not radiate.

The pulsed valve used to create the molecular beam is described in detail. Several experiments, undertaken to characterize the types of information that might be obtained, are described. From these it was determined that the R2PI technique has a detection efficiency of almost 100%. In addition, at laser fluences less than those required to saturate the first, resonant step, only the parent ion is observed. The technique has been shown to be useful for recording electronic absorption spectra with 1 cm⁻¹ precision, both for molecules with long singlet lifetimes (longer than the 4 nsec laser pulse width) and for molecules with very short singlet lifetimes (up to three orders of magnitude shorter than the laser pulse width). The ionization threshold for a large poly-
atomic molecule, naphthalene, has been determined to a precision greater than previously reported. A two-laser experiment is also described in which the decay of unperturbed singlet and unrelaxed triplet states are observed. This experiment can easily be extended to provide sufficient information, with the addition of a single independently determined quantity, to completely characterize the intramolecular energy redistribution in molecules.
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CHAPTER 1

INTRODUCTION

Chemists have been interested in the applications of lasers to chemistry ever since their inception in the 1960s. The high intensity monochromatic radiation from these devices has enabled many advances in optical spectroscopy. The idea of using photons, available in large quantities and a dazzling array of colors, as a chemical reagent has fascinated chemists. Photochemistry, previously dependant on low power, multiline arc lamps, can now be pursued using the exact wavelength needed to achieve the optimum yield. Unfortunately, these exact wavelengths are largely unknown.

This information will probably have to be obtained by the well-known hit-or-miss technique. However, the yield of this method can be greatly increased by the foreknowledge of detailed information about the nature of the molecular excited states created by the absorption of light.

Spectroscopic studies, observing either the absorption or emission of light, have mapped the excited electronic states of a huge number of chemically interesting molecules /1/. Many of these studies have been done at a resolution sufficient to reveal vibrational structure and a few have even shown rotational structure. Other studies have shown that these optically accessible states live for a very short period of time,
on the order of several hundred nanoseconds at most for such molecules as benzene /2/, toluene /3/, acetone /4/, naphthalene /5/, and aniline /6/. It is also known that the number of photons emitted by these molecules does not equal the number of photons absorbed, that is, the quantum yield is less than unity.

The question of what happens to the molecule after it absorbs a photon has occupied a number of investigators for several years. Several review articles and papers on this subject have recently appeared in the literature /7/. Figure 1-1 shows a simple molecular energy level diagram that illustrates the gross energy transfer processes that can occur in a molecule.
FIG. 1-1 Simple molecular energy level diagram illustrating general energy transfer processes.
\[ \begin{align*}
S_0^+ & \xrightarrow{k_{TS}} \quad S_0 \quad \xrightarrow{T_1} \quad T_1^+ \quad \xrightarrow{k_{P}} \quad T_1 \quad \xrightarrow{k_{f}} \quad S_0^+ \\
S_1 & \quad \xrightarrow{k_{ST}} \quad \xrightarrow{k_{IC}} \quad S_0 \\
\end{align*} \]
The initially excited singlet state, \( S_1 \), can emit a photon and decay to the ground state, \( S_0 \); it can, without absorbing or emitting a photon, undergo intersystem crossing to an isoenergetic, vibrationally excited triplet state, \( T_1^\text{T} \), or it can undergo internal conversion, another relationless, isoenergetic process, to form the ground electronic state with a vast excess of vibrational energy, \( S_0^\text{T} \). The triplet state, via intersystem crossing, can be converted into the ground state, \( S_0^* \), or it can radiatively decay to the ground state, \( S_0 \), via a process known as phosphorescence. The likelihood of these events occurring is measured by the rate at which they occur. Each of these processes can occur in an isolated molecule. In the presence of collisions, the whole picture becomes more complicated. If an excited molecule undergoes a collision it can transform substantial amounts of vibrational and rotational energy into kinetic energy of the collision partners. For example, the vibrationally excited triplet \( T_1^\text{T} \), would be relaxed by collisions to the vibrationless triplet level, \( T_1 \). The rate constant for the intersystem crossing from \( T_1^\text{T} \) is not necessarily the same as the rate from \( T_1 \).

If the rates change as a function of vibrational energy, then it is important to have a detailed picture of the molecular energy levels. For many large molecules this has been impossible in the past because of the large number of ground state vibrational levels that are populated at room temperature. The application of supersonic expansions to molecular spectroscopy has eliminated this spectral confusion.

Of the rates shown in Fig. 1-1 only \( k_f \) and \( k_{ST} \) are known to any reasonable degree of accuracy for most molecules. Triplet decay rates for many molecules have been obtained in the solid and liquid phases /8/. However, due to collisional perturbations or lattice effects, these rates are quite different from those observed in the low pressure gas phase /9/. The knowledge of these rates, \( k_f \), \( k_{ST} \), \( k_{TS} \) and \( K_{IC} \), is crucial to the understanding of what excited state chemistry can occur.

Detection of excited molecular state is another difficulty. In the
gas phase, particularly at such densities where collisions do not occur on the time scale of the experiment, emission is observed only from singlet states. In some cases, these singlet states undergo radiationless transitions so quickly that the quantum yield for fluorescence is too small for efficient observation. In order to overcome this difficulty a new method of detection must be found, one that does not depend on observation of light.

This thesis is a description of several years of work spent on developing a detection technique that overcomes the problems described above. The result is a multi-use instrument that can be used to detect fluorescing and non-fluorescing singlet states, vibrationally excited triplet states, and the dynamic intersystem crossing process that forms and destroys them.

Molecules are introduced into this machine by means of a supersonic expansion, which is skimmed to form a molecular beam, allowing their study in a truly collisionless environment. Excited states are created by irradiation of this beam with the output from high power, tunable lasers. The excited states are detected by ionizing these excited molecules with another high power laser and detecting the ions with a simple ion multiplier after time-of-flight mass analysis. The supersonic molecular beam ensures that the molecules are initially in the lowest possible vibrational state and one of the lowest possible rotational states.

1.0 SUPersonic jets

There have been a great many articles published on the properties of supersonic jet expansions /10/; however, the details that are germane to this thesis will be briefly reviewed.

A supersonic expansion is simply realized. Gas at a high pressure
is allowed to pass through a small orifice into an evacuated region. As the gas passes into the vacuum, it becomes progressively less dense and finally reaches a point where there are essentially no more collisions between gas particles. In the nozzle itself and in a region close to the nozzle, each gas particle undergoes a large number of collisions. These collisions serve to transform random kinetic motion, and internal motion if the gas is multi-atomic, into directed mass flow along streamlines emanating from the nozzle orifice. The gas intensity follows a \( \cos^2 \theta \) distribution about the orifice axis /10a/.

The effect of this expansion is to narrow the distribution of particle velocities, not only in the direction parallel to the nozzle axis, but also in directions perpendicular to the nozzle axis /10a/. It is also true that the magnitude of the velocity components perpendicular to the nozzle axis are small. Fitting these distributions to the Boltzmann equation yields a temperature of only a few Kelvin. If the internal degrees of freedom of a multi-atomic gas are treated in a similar fashion, rotational and vibrational temperatures are also found to be quite low. Since the speed of sound in an ideal gas is proportional to the square root of the temperature and if we use the temperature obtained from the Boltzmann fit of the velocities in the direction parallel to the nozzle axis, the gas can be said to be travelling faster than the speed of sound, i.e., it is supersonic.

The properties of such an expansion that are important to this work are the amount of cooling, the amount of complex formation and the gas intensity. It has been found that these quantities can be related to the physical dimensions of the nozzle /10a/.

\[
\text{Temperature} \propto (Pd)^{-1} \\
\text{Complex formation} \propto P^2 d \\
\text{Intensity} \propto Pd^2
\]
In order to study molecules of general chemical interest, a
gas mixture consisting of a small percentage, usually no more than
0.1 to 1%, of the molecule in helium is prepared. This mixture is
then used as the expansion gas. Helium is used as the buffer gas since
it provides a good degree of cooling of the sample gas, does not di-
merize to any appreciable extent and forms complexes with the sample
gas in only moderate amounts. The utility of such expansions for spec-
troscopic study of molecules has been amply demonstrated /11/. Vast
simplification of complicated spectra is realized since only a very few
vibrational and rotational states are populated. This has been most dra-
matically illustrated by the work of Smalley, et al. on NO$_2$ /11b/.

2.0 PULSED NOZZLE

Continuously operating nozzles, such as those used in the referen-
ces cited above, usually have a very small orifice diameter (10 to
100 $\mu$m) and are operated at a very high pressure (~10 to 100 atm) in
order to achieve the required level of cooling and to keep the through-
put to a level than can be handled by a vacuum system of a reasonable
size. Condensation, i.e., the formation of clusters of molecules or van
der Waals complexes, can be a significant problem in these expansions.
In order to minimize the condensation and maximize the expansion inten-
sity and cooling, the diameter of the nozzle should be made larger and
the pressure made smaller. Since the gas throughput is equal to the pro-
duce of the nozzle duty factor and the intensity, the only way a larger
orifice diameter can be used is to reduce the nozzle duty factor. This
is accomplished by using a pulsed expansion. By using a nozzle that can
be opened for only a few hundred microseconds and operated at a repeti-
tion rate of 5 to 10 Hz, the duty cycle can be reduced to the point
where a very modest pumping system can accommodate a nozzle whose dia-
meter is ~1 mm and which operates at a pressure of only a few atmosphe-
res. The crucial problem then becomes the design of a nozzle that yields
an expansion during its "on" time that is identical to a similar expan-
sion operating at 100% duty cycle. The advantages of a pulsed nozzle are immediately obvious. Consider, as an example, a comparison between the characteristics of a 100% duty cycle nozzle with a 50 μm diameter orifice and operating at 50 atm and a pulsed nozzle with a 1 mm diameter orifice, a 500 μsec pulse width operating at 4 atm pressure at 5 Hz.

\[
\frac{T_p}{T_c} = \frac{P_{c}}{P_{p}} \frac{d_{c}}{d_{p}} = 0.625 \quad \frac{I_p}{I_c} = \frac{P_{p}}{P_{c}} \frac{d_{p}^2}{d_{c}^2} = 32
\]

\[
\frac{C_p}{C_c} = \frac{P_{p}^2}{P_{c}^2} \frac{d_{p}}{d_{c}} = 0.125 \quad \frac{M_p}{M_c} = \frac{I_p}{I_c} \times \frac{DF_p}{DF_c} = 0.08
\]

Such clear advantages of pulsed expansions dictated the design and construction of the pulsed supersonic nozzle used in this work.

3.0 Photoionization

Electronically excited molecules are usually detected by either the absorption or the emission of light. For gas phase studies, the latter is preferred. The detection of fluorescence or phosphorescence can be quite difficult in cases where the quantum yield is low. The detection limit for the technique, using phototubes and other equipment currently available, is a quantum yield of about $1 \times 10^{-4}$. Therefore, the singlet states of carbonyl molecules, with quantum yields on the
order of $1 \times 10^{-3}$, can barely be observed, but the singlet states of other molecules, such as bromobenzene ($\Phi_s < 1 \times 10^{-4}$) cannot be observed at all. Phosphorescence from molecules in a low pressure gas is usually so weak that triplet states are unobservable.

Photoionization offers an alternative to fluorescence detection. The technique has received a considerable amount of study during the past few years, and several different schemes have been investigated /12,13/. It is basically similar to fluorescence in that it is, in its simplest incarnation, a two-photon technique as shown in Fig. 1-2. The molecule absorbs
FIG. 1-2 Simple two-photon ionization schematic. State 2 can be the same as state 1.
a photon and is promoted to an excited state, 1. The molecule is then caused to absorb a second photon, not necessarily of the same wavelength as the first, which removes an electron. The figure illustrates a case where the molecule undergoes a radiationless transition before the absorption of the second, ionizing photon. State 2 can be identical to state 1. The advantages of the technique are that non-emitting "dark" states may now be detected, the efficiency of detection can approach 100% and temporal information about radiationless processes can easily be obtained by delaying the ionizing photon with respect to the pump photon.

Fig. 1-3 shows a more realistic picture of a photoionization scheme.
FIG. 1-3  Two-photon ionization schematic showing radiative and radiationless decay processes that can compete with ionization.
The molecule, once excited to a singlet state can either emit a photon or undergo a radiationless transition to a triplet state. There is no spin selection rule for ionization, since the electron that is formed by the process can have whatever spin is necessary to make the transition allowed. However, the Franck-Condon principle must be obeyed in the ionization process: the positions of the nuclei must be the same before and after the ionization. Therefore, in order to form an ion it is not sufficient for the sum of $\omega_1$ and $\omega_2$ to merely equal the ionization potential unless the intermediate state is vibrationless. If the intermediate state is vibrationally excited than $\omega_2$ must have enough energy to access that same vibration in the ground state ion. Any excess energy can be carried off as translational energy by the electron. Since the triplet state that is populated by intersystem crossing will have more vibrational energy than its singlet predecessor an ionizing photon with energy $\omega_2$ that is able to ionize the singlet will usually not be able to ionize the triplet because of poor Franck-Condon factors.

Even if $\omega_2$ is large enough to promote the molecule to an ion state with good overlap, it is not necessarily true that an ion will be formed. If the up-pumping rate, $k_p$ (a function of the absorption cross section for that transition and the laser flux), is smaller than the decay rate (the sum of $k_r$ and $k_{nr}$), then ions will not be formed efficiently. If the lifetime of state 1 is longer than the laser pulse width, then the magnitude of the total decay rate can be neglected.

This scheme of photoionization is different from other multi-photon ionization schemes /12a/ in that only two photons are used and there is real intermediate state. This process has therefore been dubbed Resonance-enhanced 2-Photon Ionization (R2PI) /13/. The R2PI process is preferred over other, higher-order processes in situations where the study of two-photon allowed intermediate states is not the purpose of the experiment since it affords the maximum ion signal. Multi-photon ionization schemes that rely on one or more virtual intermediate states necessitate the use
of higher laser powers than does R2PI. At these high laser fluences, ion fragmentation occurs quite readily /12b, 14/. In constrast, the R2PI process is gently enough to yield only the parent ion.

Most previous photoionization work has employed a plate ion detector /12a/. Such a device has limited gain and no mass selectivity. The work described here was done using a time-of-flight mass analyzer. This has the advantage of being able to eliminate signals from background gas ions and uses a high gain (1 x 10^6) ion multiplier.

4.0 OVERVIEW

The next chapter is a description of the apparatus including the vacuum system, lasers, and data acquisition equipment. A detailed description of the pulsed supersonic beam source is also given along with the results of spectroscopic tests designed to fully characterize the expansion.

The third chapter contains a description of a number of photoionization experiments undertaken to fulfill the intent of this thesis: the characterization of this technique as a general purpose tool for the investigation of isolated excited state molecules.
CHAPTER 2

EXPERIMENTAL

This section will describe the apparatus used during the experiments discussed later. The equipment consists of a large molecular beam system composed of five separate medium and high vacuum chambers, one or more lasers, two time-of-flight mass spectrometers, and one or more digital computers with associated peripherals and software. Each of these will be discussed in some detail; however, the specific configuration of this equipment as used during the experiments will be discussed in later sections since this configuration is in general different for every experiment.

5.0 VACUUM SYSTEM

The all metal vacuum system is shown in Fig. 2-1. The first
FIG. 2-1 Diagram of the vacuum system. There are time-of-flight mass spectrometers in chambers "B" and "C".
chamber (M) is the free jet expansion chamber. It is a stainless steel cylinder 91.4 cm high by 91.4 cm in diameter and is fitted with four 25.4 cm diameter flanges mounted on nipples around its circumference. The top of the cylinder is sealed with an aluminum cover plate on which a phototube, lenses and filters have been mounted. The bottom of the cylinder is open into a 50.8 cm diameter diffusion pump (Varian HS-20). This pump is backed by a forepump system composed of a Roots-type pump (Leybold-Heraeus WA-500) and a single-stage rotary-piston mechanical pump (Leybold-Heraeus E-150). This pump combination is capable of achieving a maximum pumping speed of 20,000 l sec$^{-1}$ for helium. An aluminum "table" sits over the bottom hole of the cylinder to block backstreaming diffusion pump oil. The pulsed nozzle is mounted on the left hand flange (as shown in the figure) by means of a tri-directional translation stage. This translation stage allows movement of the nozzle by approximately 2.5 cm in any direction perpendicular and 60 cm in any direction parallel to the beam machine axis. A 3 mm diameter nickel skimmer /15/ is mounted on an aluminum cone on the inside face of the opposite flange such that the skimmer edge is positioned 15 cm downstream from the center of the chamber. The other face of this flange mates to a 4 in. gate valve which separates this chamber from the next one (A). The two other flanges are sealed with aluminum cover plates fitted with rotatable, Brewster-angle, quartz windows. Typically, a laser beam is directed through the Brewster windows such that it crosses the gas emitted from the nozzle. Light emitted by the excited molecules may then be detected by the light collection system on the top of the chamber.

The other chambers (A-D) are stainless steel 30.5 cm cubes. Except for chamber C, each is evacuated by a 15.2 cm diffusion pump (Varian VHS-6) and each has a smaller version of the "table" in the main expansion chamber that blocks the backstreaming oil. All three small diffusion pumps are connected to the same foreline which is pumped by a single stage mechanical pump (Welch 1397). All four of these chambers are fitted with liquid nitrogen cryotraps mounted on the top flange.
Each trap holds approximately 10 l of cryogen. These shields are basically boxes with holes cut in them for passage of laser beams and the molecular beam. This insures that the central portion of each box, where the molecular beam and laser beams intersect, is completely surrounded by cold surfaces. With liquid nitrogen in the traps, the diffusion pumps can maintain a pressure of approximately $1 \times 10^{-8}$ torr in these chambers.

The second chamber (A) is used only as a buffer chamber between the expansion chamber and the first mass spectrometer chamber (B). However, 3.8 cm flat quartz windows are mounted in the two side flanges for the admission of a laser beam. A 1.5 mm diameter skimmer, identical in construction to the first, is mounted on an aluminum cone in this chamber such that its leading edge is positioned at the center of the box.

The third chamber (B) houses a time-of-flight mass spectrometer. The details of this spectrometer are discussed later. The side flanges of this chamber are also fitted with 3.8 cm flat quartz windows. A third skimmer, identical to the one in the "A" chamber, is mounted on the downstream wall of this chamber and extends 5 cm into the box.

The fourth chamber (C) houses a second time-of-flight mass spectrometer, also discussed below. It differs from the other chambers of its size in that all the flanges are sealed with conflat high vacuum flanges. In addition, this chamber can be isolated from the rest of the system by means of conflat bellows valves. Instead of a diffusion pump, an 20.3 cm ion/titanium sublimation pump (Granville Phillips Series 220), mounted on a side flange, is used to maintain a $1 \times 10^{-10}$ average background pressure. This background gas is composed of light gases such as $\text{H}_2$, $\text{He}$, $\text{CO}_2$, $\text{N}_2$, etc. that are not pumped efficiently by the ion pump. The opposite flange is fitted with a titanium sublimation source which is used to place a layer of fresh titanium on the interior of the mass spectrometer. There are no windows in this chamber. The chamber is baked to approximately $350^\circ\text{C}$ by means of electric stove heating elements pla-
ced around the outside of the box. An aluminum shroud outside these heaters provides a measure of insulation from the room during bakeout.

The fifth chamber (D) is used solely to cath the molecular beam. It is fitted with one rotatable Brewster window on the downstream wall so that a laser beam may be admitted to the system parallel to the molecular beam axis.

6.0 LASERS

Much of the work done used a commercial dye laser (Quanta Ray PDL-1) pumped by either the second or third harmonic of the output of a ND:YAG laser (DCR-1A). This laser has a linewidth of less than 1 cm\(^{-1}\) throughout its operable frequency range. The peak output power and the pulse duration for the Nd:YAG fundamental and harmonics are given below.

<table>
<thead>
<tr>
<th>Harmonic</th>
<th>Wavelength (nm)</th>
<th>Pulse Duration (ns)</th>
<th>Peak Energy (mJ)</th>
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</thead>
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<tr>
<td>Fundamental</td>
<td>1064</td>
<td>8-9</td>
<td>700</td>
</tr>
<tr>
<td>2nd Harmonic</td>
<td>532</td>
<td>6-7</td>
<td>200</td>
</tr>
<tr>
<td>3rd Harmonic</td>
<td>355</td>
<td>5-6</td>
<td>100</td>
</tr>
<tr>
<td>4th Harmonic</td>
<td>266</td>
<td>4-5</td>
<td>50</td>
</tr>
</tbody>
</table>

The dye laser is equipped with a stepper motor drive for remote control of the laser wavelength. The output of the dye laser is usually doubled to provide radiation in the ultraviolet in the vicinity of 250 to 320 nm. This is accomplished using a KDP crystal which is angle-tuned by hand.

Another Nd:YAG pumped dye laser was used during one experiment. It was built in the laboratory using the same optical configuration as the DCR-1A.
A rare gas halide laser (Lumonics 861) was used to provide high power monochromatic radiation in the far ultraviolet during some of the later photoionization experiments. A variety of gases can be used in this laser providing radiation at a number of wavelengths from the near infrared to the vacuum ultraviolet. The laser was only operated as an ArF excimer laser for these experiments. As such it produced a 10 nsec output pulse with a peak energy of 200 mJ at 193 nm. The manufacturer's recommended gas mixture of Ar, F\textsubscript{2} and He was used.

The dye laser used in the earliest work was built in the laboratory. It is pumped by a 600 kW nitrogen laser (NRG 0.5-5-150) and employs a modified Hänisch-type oscillator /16/ (Fig. 2-2).
Fig. 2-2 Schematic of the nitrogen laser-pumped Hänisch-type dye laser. A. Air-spaced etalon; B. Grating; C. Pressure tuning box; D. 5x beam expander; E. Oscillator quartz dye cuvette; F. Optical flat; G. Flat mirror; H. 25x beam expander; I. Grating; J. Pressure-tuning box; K. Spatial filter; L. Glass plano-convex lens; M. First amplifier quartz dye cuvette; N. Spatial filter; O. Glass plano-convex lens; P. Second amplifier quartz dye cuvette; Q. Spatial filter; and R. Frequency doubling crystal in aluminum housing. Heavy arrows indicate nitrogen laser pump.
Wavelength selection is achieved in the oscillator section by means of a 28 GHz free-spectral-range (FSR) etalon (A) and a 2400 groove mm\(^{-1}\) holographic grating (B) (J-Y Optical 5H), both of which are housed in an aluminum pressure-tuning box (C). The oscillator output contains about 10 modes spaced by the etalon FSR. Mode selection is performed by a 25% beam expanding telescope (H) and a 316 groove mm\(^{-1}\) eschelle grating (I) (PTR Optics UR-0316-6326-7) which are housed in a second aluminum pressure tuning box. Further mode selection is accomplished spatially using a pinhole (K). The two pressure boxes are connected to the same gas manifold so that they may be scanned synchronously.

The dye laser wavelength decreases by approximately 1.33 angstroms per one atmosphere pressure decrease. The dye laser amplifiers (M and P) are pumped by the same nitrogen laser pulse that pumped the oscillator, delayed by the appropriate time so that the dye laser pulse and the pump pulse coincide. All the dye cells are stirred magnetically. The output of the second amplifier (P) is spatially filtered with a pinhole (Q) and passed through a KDP frequency doubling crystal which is housed in a sealed aluminum mount (R) fitted with quartz entrance and exit windows set at Brewster's angle. The peak power of the ultraviolet laser beam is about 1 MW and it has a linewidth of about 1 GHz (FWHM).

The relative dye laser frequency is monitored by recording the transmission maxima of a solid quartz etalon. This etalon was initially calibrated by displaying both the etalon transmission maxima and the fluorescence excitation spectrum of the 13-0 band of the \(^{13} \Sigma_g^+ \rightarrow \chi^3 \Pi_g\) transition of iodine on a strip chart and calculating a frequency calibration using the molecular constants of iodine obtained by Wei and Tellinghuisen /17/. This procedure determined a free spectral range of 0.2324 cm\(^{-1}\) at 616.2 nm. It was noticed in other work in our laboratory /18/ that this calibration resulted in a small systematic error. However, the original calibration was used for the oxalyl fluoride work which will be discussed later. The etalon was recalibrated by counting the number of maxima that occurred between the Ne 607.43377 and 614.30626 nm lines /19/. At 611.0 nm, the etalon FSR is 0.22913 \(\pm\) 0.0002 cm\(^{-1}\) /18/.
The change in the FSR as a function of wavelength was calculated from the wavelength dependence of the index of refraction of fused quartz.

7.0 MASS SPECTROMETERS

Two time-of-flight mass spectrometers are built into the supersonic molecular beam machine. One, in chamber "C", uses the conventional electron beam technique to ionize molecules in the beam. The other, in chamber "B", contains no electron gun; ions must be created by photoionization. Time-of-flight spectrometers were chosen over quadrupole mass analyzers because the entire mass spectrum of the beam could be obtained every laser shot.

The two mass spectrometers are quite similar in design and operation. Fig. 2-3 shows a detailed cross-section of the photoionization time-of-flight
Fig. 2-3  A detailed vertical cross section of the photoionization time-of-flight mass spectrometer. The heavy black arrow indicated the molecular beam path. The laser beam propagates in the direction normal to the plane of the figure. 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; and I. Ion multiplier. The grids and plates are spaced as follows: A-B = 2.54 cm; B-C = 1.27 cm; and C-I = 112 cm.
device. The ions formed in the ionization region by photoionization are pushed onto 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 counteract the translational energy of the molecular beam. The ions are detected by an ion multiplier (Johnson MM-1) whose output is then amplified by two ten-fold fast amplifiers (LeCroy VV100B).

The mass spectrometer materials are either stainless steel or ceramic with the exception of the Teflon insulation on the lead wires and the copper cryotrap shield. The grids are 70 lines inch⁻¹, 90% trans-mission stainless steel mesh (Buckbee Mears).

In normal operation, the following voltages are applied to the grids and plates:

- Repeller Plate + 3100 volts
- Draw Out Grid + 2660 volts
- Flight Tube Grid 0 volts
- Flight Tube 0 volts
- Deflection Plates 100 volts

The electron bombardment mass spectrometer differs from the photoionization instrument in several ways. First, the entire device is inverted, i.e., the flight tube extends downwards. Second, there is a second ionization region, including a second draw-out grid, located between grids "B" and "C" (see Fig. 2-3). This second ionization region is designed to detect photofragments that are ejected out of the molecular beam by a fragmentation event upstream of the mass spectrometer. Third, each ionization region is equipped with two electron guns situated above and below the plane of Fig. 2-3. Only one gun in one
region is in use at any given time. The spacings between the grids and plates and the flight tube length on this instrument differ only slightly from those of the photoionization mass spectrometer.

The total resolution of the photoionization time-of-flight mass spectrometer, including the signal processing equipment, was found to be about 175 as illustrated by Fig. 2-4 which shows the mass spectrum of
Fig. 2-4  Resonance enhanced two-photon mass spectrum of bromo-benzene. The frequency doubled output of the PDL-1 dye laser was tuned to the origin of the first singlet transition at 36,991.5 cm\(^{-1}\). The peak at m/e = 77 is the \(C_6H_5^+\) fragment and the peak at m/e = 128 is the \(C_{10}H_8^+\) parent ion of naphthalene. Naphthalene was a contaminant in the gas handling system.
bromobenzene. The two forms of the molecule, due to the two isotopes of bromine, are clearly discernible in the figure. This resolution is affected by the mass spectrometer design (flight tube length, grid spacing, etc.), the voltages on the grids and plates, the diameter of the laser or electron beam, the velocity distribution of the gas in the ionization region, the transit time dispersion of the ion multiplier and the amplifiers, and the time resolution of the signal detection electronics /20/. The first four items determine how well a packet of simultaneously-ionized ions is focussed onto the ion multiplier and therefore determines the resolution of the mass analyzer. Since the molecules to be ionized are all in a molecular beam, their velocity distribution is small. In addition, their velocity components perpendicular to the molecular beam axis are also small. In conventional mass spectrometers, the large velocity distribution of the room temperature gas molecules is the limiting resolution factor; however, because of the supersonic beam used in this instrument, the velocity distribution is so small that it can be ignored.

The electron bombardment mass spectrometer was used only to observe the temporal profile of the pulsed molecular beam because helium, the major component of the beam, can easily be ionized in this instrument. The photoionization mass spectrometer was used to obtain the majority of the results in this thesis.

8.0 DATA ACQUISITION SYSTEM

8.1 Computer Hardware

The two computers used primarily for the data acquisition and real-time data analysis are both Digital Equipment Corp. LSI-11/2 minicomputers. The CPU boards are mounted in boxes that contain a serial interface board (for communication with a terminal) and an
interface to a CAMAC crate /21/. This packaged system is available from Standard Engineering Corp. and is called a MIK-11/2. Each of the MIK-11/2 units is mounted in a separate crate and addresses 32 kwords (1 kword = 1024 words, 16 bits per word) of random access semiconductor memory (RAM). They communicated via an 8 kword block of shared memory, included in the 32 kword total of each. Fig. 2-5 shows the connection of the two computers. The
FIG. 2-5  Dual processor computer configuration showing the interconnection between the processors and the connection of the peripherals.
master computer also was connected to three other serial I/O ports and a dual double-density floppy disk system (DSD-440). The serial I/O ports were used to communicate with a custom Laboratory Interface system, a serial line printer, and a PDP-11/70 located almost a quarter of a mile away.

8.2 Laboratory Interface

The Laboratory Interface was designed and built to interface a variety of experiments to a computer. Communication with the computer is accomplished using an asynchronous, bit-serial protocol exactly like that used by conventional computer terminals. This method was chosen since most computers support a terminal interface in one form or another and software development is simplified.

The Laboratory Interface is composed of:

1. A 16-channel, 8-bit multiplexed analog-to-digital converter capable of several modes of operation, including interrupt control.

2. Four independent computer-controlled pulse generators.

3. Four independent 8-bit digital-to-analog converters with 0-10 volt outputs.

4. Four independent digital panel meters for displaying digital information.

5. Two independent RS-232-C/RS-422-A converters for driving long communications cables.

A block diagram of the Laboratory Interface is shown in Fig. 2-6.
FIG. 2-6  Block diagram of the Laboratory Interface. The area inside the dashed-line box is a rear-panel connector that can be used to disconnect the Interface from the UART if a direct, high-speed, parallel connection with a computer is desired.
Communication with the computer over a serial line is controlled by the Universal Asynchronous Receiver and Transmitter (UART). Information from the computer is interpreted either as an address or data. These two types of information are distinguished from one another only by the fact that the address is sent first and the data for that address, one word only, follows immediately. Decoding circuitry connected to the receiver translates the 8-bit address into a strobe on one of 256 possible address lines. Table 2-1 summarizes the address assignments in the
<table>
<thead>
<tr>
<th>Address</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Analog-to-digital converter</td>
</tr>
<tr>
<td>1</td>
<td>Interrupt latches</td>
</tr>
<tr>
<td>2</td>
<td>Pulse Generators</td>
</tr>
<tr>
<td>3</td>
<td>Digital-to-analog converter 1</td>
</tr>
<tr>
<td>4</td>
<td>Digital-to-analog converter 2</td>
</tr>
<tr>
<td>5</td>
<td>Digital-to-analog converter 3</td>
</tr>
<tr>
<td>6</td>
<td>Digital-to-analog converter 4</td>
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<tr>
<td>7</td>
<td>Not used</td>
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<tr>
<td>8</td>
<td>Digital panel meter 1</td>
</tr>
<tr>
<td>9</td>
<td>Digital panel meter 2</td>
</tr>
<tr>
<td>10</td>
<td>Digital panel meter 3</td>
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<tr>
<td>11</td>
<td>Digital panel meter 4</td>
</tr>
<tr>
<td>12-255</td>
<td>Not Used</td>
</tr>
</tbody>
</table>
Laboratory Interface. Control of the transmitter section of the UART is delegated by the computer. As currently implemented, only the analog-to-digital converter and the interrupt sections are the transmitter. Rear panel connectors are available for the user to extend either the transmitter or receiver parallel bus outside of the Laboratory Interface enclosure. The UART may be isolated from the rest of the Interface by disconnecting a ribbon cable from the rear of the Interface. A parallel connection to the computer may then be substituted if higher data rates are desired.

8.3 Computer Configurations

8.3.1 Distributed Processor Configuration - As shown in Fig. 2-5, the slave computer has one CAMAC module in its crate, a LeCroy 2256S Transient Digitizer. This unit is used to detect the output of the ion multiplier on the mass spectrometer in use during an experiment. The transient digitizer samples an incoming analog waveform at 50 nsec intervals, performs an 8-bit analog-to-digital conversion, and stores the digitized value in a high speed 1024-word RAM that may later be read out through the CAMAC dataway into the main computer memory. In operation, a program is "down loaded" to the slave computer from the main computer. This program accepts waveforms from the transient recorder, computes the sum of a predetermined number of waveforms and makes this sum available to the master program via the shared memory. It also plots the composite waveform on a graphics terminal. The program running on the master computer calculates the average signal over preselected channels of the composite waveform and stores this average in a file on the floppy disk. The master program also accepts digital data from the Laboratory Interface via one of the serial I/O ports and stores this in the file, too. This data is typically the output from an 8-bit analog-to-digital converter (ADC) whose inputs are usually connected to phototubes or photodiodes which monitor the laser power(s).
Digital data is also sent to the Laboratory Interface for display on one of the digital panel meters, for conversion to an analog signal by one of the 8-bit digital-to-analog converters or for activating one or more of the pulse generators. This system is capable of handling data rates in excess of 10 laser shots per second.

8.3.2 Single Processor Configuration - Fig. 2-7 shows a second configuration used in some of the later
FIG. 2-7  Single processor computer configuration.
experiments which uses only one computer. The custom laboratory interface was replaced with CAMAC modules: a 32-channel, multiplexed, 12-bit ADC (Bi-Ra Model 5301); a 8-channel 12-bit DAC (Kinetic Systems Model 3112); and a 15-channel stepper motor controller (Bi-Ra Model 3101). In addition, the transient digitizer was moved into the same crate. The program used to take data in this configuration is quite similar to the one described above, except that there is only one CPU. This system is capable of handling data rates no greater than 10 laser shots per second. However, it is much simpler to operate.

When entire mass spectra were to be obtained for study, a third mode of operation was used. In this mode, the laser frequency is held constant and a larger number (∼100) waveforms are obtained via the transient digitizer. The program then allows the user to plot the result on the graphics terminal, modify its scale, subtract a background waveform taken previously, obtain a copy of the waveform on an X-Y plotter, or write the entire waveform to a file on the floppy disk for later reference.

The mode that was used for lifetime measurements is similar to the one previously described in that the laser frequency was not changed during the course of the run. A microsecond delay generator (Evans Assoc. Model 4145-2) was interfaced to CAMAC by means of a CAMAC kluge module (Standard Engineering WW-006) and used to control the delay between a pump laser and a probe laser. The signal that is obtained at a given delay between the lasers is proportional to the population in the intermediate state at that time. In order to observe the complete decay of the intermediate state, the delay is incremented by a fixed amount before each laser shot starting at the minimum delay selected by the operator. When the entire delay range has been covered, the data that has been accumulated is displayed on the graphics terminal as a function of time. The process is then repeated until enough measurements have been accumulated to provide a good measure of the true decay. The program is also capable of fitting the data to an exponential
and saving it for later reference in a file.

The delay module can produce delay ranging from 0 to 999.99 μsec in 10 nsec increments with a jitter of approximately 2 nsec. Since the lasers have a jitter of about 2 nsec also, the timing can be known to within ± 10 nsec. With this equipment, lifetimes as short as about 100 nsec can be measured with excellent accuracy.

It is interesting to note how the complexity of the data acquisition equipment increased during the course of the experiments described in this thesis. During the earliest projects, no computer-controlled data acquisition equipment was available. All the data was recorded on strip chart paper and the information was obtained for analysis by measuring distances on the paper with a ruler. This information would then be entered by hand into a computer for such things as a least-squares analysis. The latest experiments discussed in this thesis, the triplet lifetime experiments, were performed using complete computer control of the experiment. The first attempt at a lifetime experiment revealed that computer control was necessary if reliable data was to be obtained in a reasonable amount of time. The computer setup described above is capable of obtaining the data and calculating a lifetime in a matter of a few hours.

9.0 PULSED NOZZLE

9.1 Introduction

The theoretical and experimental history of supersonic expansions with regards to the study of excited molecular species has been reviewed earlier. The rationale for the development of a pulsed supersonic nozzle was also discussed. The following section describes the details of the pulsed nozzle that was used in the experiments des-
Methods for the introduction of short gas pulses into a vacuum have interested experimentalists for the past two decades, resulting in the development of many intriguing valve designs /22/. Most of these valves have found application in plasma research. Some time ago, Hagen and Bier reported the construction of a pulsed valve specifically designed to produce supersonic molecular beams /23/. However, until recently, reliable nozzles for this purpose with pulse widths of less than 1 msec have been unavailable. Gentry and Giese have built a valve that produces repeatable pulses as short as 10 μsec (FWHM), using an extremely simple and elegant design /22h, 24/. The valve discussed here is a modification of this design which, although somewhat slower, generates pulses of an intensity and internal temperature equivalent to that which would be obtained from a continuously operating nozzle of the same dimensions but having no valve mechanism.

9.2 Valve Construction

Fig. 2-8 shows an exploded cross-sectional view of the valve in use.
FIG. 2-8  Pulsed valve detail. A. Stainless steel baseplate, B. Copper return conductor; C. Copper spacer; D. Copper-plated spring steel strip; E. Torr-Seal (Varian Corp.) epoxy insulation coating; F. Viton o-ring; G. Teflon spacer; H. Copper high voltage input lead; I. Plastic clamp bars; and J. Clamping screws.
in our laboratory. As in the Gentry-Giese design, the valve action is accomplished by passing a high energy electrical pulse through two closely spaced conductors, generating opposing magnetic fields which force the two conductors apart. These pulses are produced by discharging a capacitor using a thyratron (EG & G HY-1102). The capacitor is charged to 2-3 kV by a high voltage power supply (Hippotronics 804-250) through a diode and inductor.

The nozzle orifice is sealed by the spring steel strip and an o-ring. This trip is 380 μm thick, has an active length (the length between the clamps) of 3.8 cm and a width of 0.2 cm. The side facing the o-ring is electroplated with copper to a depth of approximately 125 μm in order to reduce heating and to bring the current flow through the strip as close as possible to the return conductor, thereby maximizing the interaction of the magnetic fields. This return conductor is a 250 μm thick copper strip having the same width as the spring steel strip, except in the region of the o-ring where it is wider to accommodate a hole drilled through it for the placement of the o-ring. In construction, this return strip is epoxied to the Torr-Seal epoxy insulation layer, the o-ring is epoxied in its seat to prevent slippage, and the assembly is firmly clamped to the base plate so as to confine flexure to the central portion of the spring steel strip. The Teflon spacer shown in Fig. 2-8 extends the entire length of the spring steel strip except for the section in contact with the copper spacer. The thickness of both of these spacers is 250 μm.

The original discharge circuit used a 15 μF capacitor and was connected to the valve by a 2 m length of RG-8/U coaxial cable. After the early experiment on oxaly fluorid, the design was changed to lower the overall inductance of the circuit. The 15 μF capacitor was replaced with a 5 μF capacitor and the cable was changed to three 1 m lengths of coax wired in parallel. These changes resulted in a more reliable discharge and more reproducible gas pulse characteristics. The original valve also had a 584 μm diameter orifice and an o-ring.
with an internal diameter of 750 \( \mu \text{m} \). These were changed to a 1 mm diameter orifice and an o-ring with a 1.07 mm diameter inside diameter. These modifications allowed the valve to be operated to a lower pressure while maintaining the same expansion characteristics as the original version.

The valve body is an aluminum cylinder with an inside diameter of 5.4 cm, an outside diameter of 8.9 cm, and a height of 1.9 cm. This gives an internal volume of 43.5 \( \text{cm}^3 \). The valve baseplate is bolted to this body. A brass backplate, with fittings for gas and electrical connections and facilities for mounting the valve in the vacuum chamber, is also bolted to the body. Both the baseplate and the back plate are sealed to the cylinder with o-rings. The maximum safe operating pressure for this particular valve design is \( \sim 20 \text{ atm} \).

The valve body and the gas feed lines are wrapped with coaxial heating elements so that their temperatures can be adjusted above ambient. This is important to keep molecules with low vapor pressures from condensing in the nozzle or the feed line.

9.3 Valve Operation and Tests

This valve is normally operated at a repetition rate of 5 Hz, although rates up to 10 Hz have been tried successfully for short periods. Resistive heating of the steel strip becomes a major design constraint at higher repetition rates and/or longer spring lengths. Shortly before this thesis was prepared, work on this problem was completed by David Powers. The result is a nozzle that is essentially the same design as the one described here, but able to operate for long periods of time at 10 Hz. A superior clamping technique was developed in addition to addressing the problem of carrying away the excess heat from the spring.
The shape of the gas pulse delivered by the valve was examined by placing a nude Bayard-Alpert ionization guage in the expanding gas at various distances from the nozzle. Fig. 2-9 shows oscilloscope traces.
FIG. 2-9  Pulsed free jet intensity measurements using a nude ionization guage 15 cm from the nozzle and a nozzle pressure of 18 atm of helium. The charging voltage is shown in the upper right corner of each trace. Each trace is a superposition of three consecutive nozzle pulses. The ionization guage sensitivity was constant for all three traces.
at three different charging voltages of the capacitor with the ionization gauge placed 15 cm from the nozzle and using a nozzle pressure of 18 atm (helium). The anode of the gauge was connected directly to an oscilloscope through a $\sim$1 m length of RG-58/U coaxial cable. The bandwidth of this detection system was about 300 kHz. Each trace is a superposition of three successive nozzle pulses. The trace at the top of the figure shows a fully formed pulse exhibiting a rise and fall time of about 50 μsec and a flat-topped region in the center of the pulse with a duration of about 150 μsec. The fact that increases in charging voltage beyond about 2300 V result only in a broadening of the gas pulse with no change in the peak pulse intensity leads us to believe that the valve is opened completely during the central, constant intensity portion of the pulse.

There is a delay of nearly 500 μsec from the beginning of the pulse until the onset of jet disturbance due to gas particles reflected from the chamber walls. The pulses produced by our valve have a much shorter duration than this time limit, and we are, therefore, able to realize the full cooling and intensity expected from such an expansion. This absence of background disturbance of the free jet also permits a well collimated molecular beam to be skimmed with good efficiency. The pulse profile, as measured in the skimmed molecular beam using the mass spectrometer is shown in Fig. 2-10.
Fig. 2-10  Pulse profile of the supersonic molecular beam as determined by photoionization of napthalene. The concentration of napthalene in the beam was about 0.1%, the remainder being helium. The ArF laser was used to ionize napthalene. The computer was run in the lifetime mode.
The results of these tests indicate that the design objective for the pulsed nozzle was achieved; that is, during the time the valve is open, the expansion has all the properties of a continuous expansion from a nozzle with the same dimensions. However, it is not sufficient to say that the pulsed nozzle works as well as a continuous nozzle simply because a steady-state flow is reached during its on time. Unknown perturbations could be occurring that would destroy the benefits of such a nozzle. To test the expansion conditions thoroughly, a spectroscopic investigation of oxalyl fluoride in the freely expanding jet was undertaken.

9.4 Spectroscopic Tests - Oxalyl Fluoride

9.4.1 Introduction - Oxalyl fluoride was chosen because of its homologous relationship with glyoxal and its lowest electronic transition is in a region of the spectrum that was easily probed by the dye laser.

The lowest excited singlet electronic state in oxalyl fluoride has been shown to have $A_u$ symmetry ($C_{2v}$) and the origin of the $1A_u(n\pi^*) \rightarrow 1A_g$ transition has been found to occur at 32445.0 cm$^{-1}$ /25/. This excited state is of the same orbital parentage as the lowest singlet state in other, more extensively studied dicarbonyls such as glyoxal /26/, methyl glyoxal /27/, and biacetyl /28/.

Of the oxalyl halides, the least is known about the fluoride. Previous spectroscopic work on this asymmetric rotor consists of infrared and Raman studies /29/, absorption studies of the $1A_u \leftrightarrow 1A_g$ and $3A_u \leftrightarrow 1A_g$ transitions /25/, a lifetime investigation of the vibronic levels of the $1A_u$ state /30/, a photoelectron study /31/, and work on the quenching of phosphorescence from the $3A_u$ state /32/. Therefore, the positions of the lowest singlet and triplet as well as the vibrational frequencies of these states and the ground state are well
known. Oxalyl fluoride is believed to be planar in both the $^1A_u$ and $^1A_g$ states. This hypothesis is supported by comparison with glyoxal /26/, \textit{ab initio} molecular orbital calculations /33/, a normal coordinate analysis of the $^1A_g$ vibrational frequencies /29a/, and a band contour analysis of the $^1A_u \leftarrow ^1A_g (0,0)$ band /25/. The most stable conformer in the gas and liquid phases, and the only form in the solid phase, has been found to be the trans form /29/. Theoretical calculations predict a gas phase \textit{trans/cis} ratio of about three at room temperature /33a/, but conclusive experimental evidence of this has not been produced. Two infrared studies /29b, c/ indicate that there is some amount of the \textit{cis} form in the gas and liquid phases, but the ratio of \textit{trans} to \textit{cis} could not be determined. Other infrared /29a/, as well as absorption /25/, fluorescence excitation /30/ and photoelectron /31/ studies show no evidence of the \textit{cis}-isomer.

A study of single vibronic level lifetimes of the $^1A_u$ state of oxalyl fluoride shows the observed lifetimes to be approximately constant with respect to changes in excitation energy over a 1000 cm$^{-1}$ range above the $^1A_u \leftarrow ^1A_g$ origin and to be about the same as the calculated radiative lifetime /30/. A facile predissociation, presumably to form two FCO fragments, is believed to account for the abrupt break-off in the fluorescence excitation spectrum observed at excitation energies higher than 33,400 cm$^{-1}$.

9.4.2 \textbf{Experimental} - A schematic of part of the apparatus used in this study is shown in Fig. 2-11.
Fig. 2-11  Schematic of the electronic signal detection equipment used in the oxalyl fluoride experiment.
For laser excited fluorescence experiments, the freely expanding pulsed supersonic jet is crossed at a right angle to the jet axis in the large expansion chamber (see Fig. 2-1), by a tunable ultraviolet laser beam. The high resolution nitrogen laser pumped dye laser was used in this study. The fluorescence detection equipment is located above the plane of Fig. 2-11.

Laser excited fluorescence is detected at a right angle to the plane including the jet axis and the laser beam using a single quartz lens to focus the fluorescence onto a 0.5 cm wide slit. This limits the observed full Doppler width to a maximum of 0.01 cm⁻¹. The imaged fluorescence then passes through a colored glass filter (Corning 7-54) and is detected by a cooled photomultiplier tube (RCA 8575). The photomultiplier signal is processed by a photon counting system consisting of a fast preamplifier (Ortec 9301), an amplifier-discriminator (Ortec 9302), a photon counter (Ortec 9315), and a digital-to-analog converter (Ortec 9305). The output is divided in a two-quadrant divider (Analog Devices 934) by the signal from a second photomultiplier that monitors the ultraviolet laser power. The fluorescence excitation spectrum, normalized for laser power fluctuations, is then displayed on a strip chart recorder. Part of the visible dye laser output is directed into a solid quartz marker etalon, monitored by yet another photomultiplier. The output of this detector, after suitable averaging, is also displayed on the strip chart recorder, providing a relative frequency calibration of the spectrum.

Oxalyl fluoride was obtained commercially (Armageddon Chemical Co., Durham, N.C.). The cylinder was placed in liquid nitrogen and evacuated to remove any contaminants with a significant vapor pressure at that temperature. A mixture of 1% oxalyl fluoride in helium with a total pressure of about 35 atm was prepared and used directly as the expansion gas.
9.4.3 Results and Discussion - Figures 2-12 and 2-13 display two examples of fluorescence excitation spectra.
FIG. 2-12 Fluorescence excitation spectrum of the $^1A_u \leftarrow ^1A_g$(0-0) band of oxalyl fluoride seeded in helium at 1% concentration. The total pressure was 18 atm and the laser beam crossed the jet 15 cm from the nozzle. The frequency scale in the figure is relative to the origin of the band at 32445 cm$^{-1}$. The rotational temperature is about 0.17 K.
$P_0 = 18$ atm
$X = 15$ cm
$\nu_0 = 32445.0$ cm$^{-1}$
FIG. 2-12  Fluorescence excitation spectrum of the $^{1}A_u \leftarrow ^{1}A_g (0-0)$ band of oxalyl fluoride. Prominent rotational features are numbered 1 through 7 corresponding to the $3_{21}$ $\leftarrow 2_{11}, 2_{21} \leftarrow 1_{11}, 2_{11} \leftarrow 1_{01}, 1_{10} \leftarrow 0_{00}, 0_{00} \leftarrow 1_{10}, 1_{01} \leftarrow 2_{11}$ and $1_{11} \leftarrow 2_{21}$ transitions, respectively. The features labelled R and Q are each composed of several transitions with $\Delta J = \pm 1$ and $\Delta J = 0$, respectively. The rotational temperature is about 0.6 K. Compare with figure 2-12.
$P_0 = 4.4 \text{ atm}$
$X = 10 \text{ cm}$
$\nu = 32445.0 \text{ cm}^{-1}$
of oxalyl fluoride as observed in the pulsed supersonic free jet. At just a few Kelvin, there are over a hundred observed features in the spectrum of the $^1A_u \leftarrow ^1A_g$ (0-0) band, some of which, like the Q branch at the origin (see Fig. 2-13), could be separated into tens of lines given sufficient resolution. The rotational analysis of such a complex spectrum is rendered straightforward by the cooling of a supersonic jet. Line positions are calculated using estimated rotational constants and the C-type selection rules in oxalyl fluoride. The computer program, which has been used previously /34/, computes rotational energy levels by diagonalization of the rigid rotor Hamiltonian and contains a non-linear least squares procedure for fitting observed line positions to rotational parameters. Using these calculated line positions, the major features of the spectrum in Fig. 2-12 are easily assigned.

By changing the nozzle pressure and the distance of the laser beam from the nozzle, spectra characterized by a higher rotational temperature, such as the one in Fig. 2-13, are obtained. Using the calculated line positions and the assignments made to the cold spectrum in Fig. 2-12, new features are identified. This process was carried out repetitively until all the observed lines could be accounted for. The observed lines were then fit to six rotational constants and $v_0$, the band origin. These constants reproduce the observed line positions to within 0.03 cm$^{-1}$, significantly less than the observed linewidth of 0.05 cm$^{-1}$. Input to the computer program consisted of 107 line positions representing 22 different transitions from 11 different spectral scans. The results of the fit are shown in Table 2-2 and a comparison
TABLE 2.2 Rotational constants for oxalyl fluoride.

<table>
<thead>
<tr>
<th></th>
<th>This work(^a)</th>
<th>Balfour(^b)</th>
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<td></td>
<td>A. Ground State (^1)A(_g)</td>
<td></td>
</tr>
<tr>
<td>(A'' \text{ (cm}^{-1}) )</td>
<td>0.204 ± 0.002</td>
<td>0.1975</td>
</tr>
<tr>
<td>(B'' \text{ (cm}^{-1}) )</td>
<td>0.120 ± 0.001</td>
<td>0.1202</td>
</tr>
<tr>
<td>(C'' \text{ (cm}^{-1}) )</td>
<td>0.074 ± 0.006</td>
<td>0.0747</td>
</tr>
<tr>
<td>(K'')</td>
<td>-0.292 ± 0.004</td>
<td>-0.2590</td>
</tr>
<tr>
<td>(\Delta'' \text{ (amu - } A^2) )</td>
<td>4 ± 18</td>
<td>0.0660</td>
</tr>
<tr>
<td></td>
<td>B. Excited State (^1)A(_u)</td>
<td></td>
</tr>
<tr>
<td>(A' \text{ (cm}^{-1}) )</td>
<td>0.201 ± 0.002</td>
<td>0.1843</td>
</tr>
<tr>
<td>(B' \text{ (cm}^{-1}) )</td>
<td>0.120 ± 0.001</td>
<td>0.1225</td>
</tr>
<tr>
<td>(C' \text{ (cm}^{-1}) )</td>
<td>0.073 ± 0.006</td>
<td>0.0736</td>
</tr>
<tr>
<td>(K')</td>
<td>-0.266 ± 0.004</td>
<td>-0.1165</td>
</tr>
<tr>
<td>(\Delta'' \text{ (amu - } A^2) )</td>
<td>6 ± 19</td>
<td>-0.0360</td>
</tr>
</tbody>
</table>

a. Error limits at 95% confidence level.
b. See Ref. 25.
of the observed and calculated line positions is shown in Table 2-3.
TABLE 2-3  Comparison of observed and calculated line positions from computer fit of 107 measurements of 24 different lines from 11 different scans. All numbers in cm$^{-1}$ relative to band origin at 32445.0 cm$^{-1}$. The standard deviation of the fit is 0.012 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Line</th>
<th>No. of Observations</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Avg. Value</td>
<td>Std. Dev.</td>
</tr>
<tr>
<td>$4_{13}$ $5_{23}$</td>
<td>1</td>
<td>-1.380</td>
<td>-</td>
</tr>
<tr>
<td>$3_{21}$ $4_{31}$</td>
<td>2</td>
<td>-1.301</td>
<td>0.013</td>
</tr>
<tr>
<td>$3_{13}$ $4_{23}$</td>
<td>2</td>
<td>-1.253</td>
<td>0.005</td>
</tr>
<tr>
<td>$2_{12}$ $3_{22}$</td>
<td>1</td>
<td>-0.971</td>
<td>-</td>
</tr>
<tr>
<td>$2_{11}$ $3_{21}$</td>
<td>1</td>
<td>-0.911</td>
<td>-</td>
</tr>
<tr>
<td>$2_{02}$ $3_{12}$</td>
<td>1</td>
<td>-0.839</td>
<td>-</td>
</tr>
<tr>
<td>$1_{11}$ $2_{21}$</td>
<td>8</td>
<td>-0.727</td>
<td>0.014</td>
</tr>
<tr>
<td>$1_{01}$ $2_{11}$</td>
<td>8</td>
<td>-0.568</td>
<td>0.011</td>
</tr>
<tr>
<td>$0_{00}$ $1_{10}$</td>
<td>9</td>
<td>-0.328</td>
<td>0.013</td>
</tr>
<tr>
<td>$2_{11}$ $2_{21}$</td>
<td>5</td>
<td>-0.260</td>
<td>0.015</td>
</tr>
<tr>
<td>$3_{12}$ $3_{22}$</td>
<td>1</td>
<td>-0.227</td>
<td>-</td>
</tr>
<tr>
<td>$1_{01}$ $1_{11}$</td>
<td>4</td>
<td>-0.088</td>
<td>0.016</td>
</tr>
<tr>
<td>$1_{11}$ $1_{01}$</td>
<td>4</td>
<td>0.088</td>
<td>0.012</td>
</tr>
<tr>
<td>$3_{22}$ $3_{12}$</td>
<td>1</td>
<td>0.197</td>
<td>-</td>
</tr>
<tr>
<td>$2_{21}$ $2_{11}$</td>
<td>7</td>
<td>0.237</td>
<td>0.008</td>
</tr>
<tr>
<td>$1_{10}$ $0_{00}$</td>
<td>11</td>
<td>0.320</td>
<td>0</td>
</tr>
<tr>
<td>$2_{11}$ $1_{01}$</td>
<td>10</td>
<td>0.564</td>
<td>0.010</td>
</tr>
<tr>
<td>$2_{20}$ $1_{10}$</td>
<td>1</td>
<td>0.680</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLE 2.3 (continued)

<table>
<thead>
<tr>
<th>Line&lt;sup&gt;a&lt;/sup&gt;</th>
<th>No. of Observations</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2_{21}$ $^1_{11}$</td>
<td>6</td>
<td>0.720</td>
<td>0.721</td>
</tr>
<tr>
<td>$^3_{12}$ $^2_{02}$</td>
<td>7</td>
<td>0.827</td>
<td>0.824</td>
</tr>
<tr>
<td>$^3_{21}$ $^2_{11}$</td>
<td>9</td>
<td>0.887</td>
<td>0.888</td>
</tr>
<tr>
<td>$^3_{22}$ $^2_{12}$</td>
<td>5</td>
<td>0.964</td>
<td>0.958</td>
</tr>
<tr>
<td>$^4_{23}$ $^3_{13}$</td>
<td>2</td>
<td>1.202</td>
<td>1.212</td>
</tr>
<tr>
<td>$^4_{31}$ $^3_{21}$</td>
<td>1</td>
<td>1.263</td>
<td>1.271</td>
</tr>
</tbody>
</table>

<sup>a</sup> The notation here is $J_{K-1}^l K_{+1}^l$, $J_{K-1}^u K_{+1}^u$.

<sup>b</sup> This is the standard deviation of the observed line measurements.
Many of the observed spectral features were found to be blended; the degree of blending varying from some that were superpositions of one strong line and one weak line to some that were superpositions of many strong lines. The badly blended lines were not used in the calculations, although a number of the features consisting of one strong and one weak line were assigned to the strong transition and used. In these instances, the intensity of the strong line was calculated to be at least three times that of the weaker one.

The results of Balfour's band contour study /25/ are also displayed in Table 2-3. Balfour assumed a trans-planar geometry for both electronic states. The agreement is excellent considering the model dependency of the band contour method and the fact that Balfour found his analysis to be insensitive to the exact values of the rotational constants. So long as the inertial defect is kept small, variations in the constants over as much as 0.02 cm⁻¹ yield inconsequential shifts in the calculated line positions and no change in the observed contour.

In this study we are interested in the line intensities only in order to determine the rotational temperature of oxalyl fluoride in the jet. The intensity of a particular rovibronic line is a function of the square of a transition dipole matrix element, a nuclear spin statistical weight, and a Boltzmann distribution function. The rotational temperature is the temperature that characterizes that Boltzmann distribution. In this work, tabulated values of the matrix elements were used /35/. The nuclear spin statistics were calculated from well-known group theoretical procedures /36/. Briefly, the asymmetric rotor nuclear spin weights of individual rotational energy levels vary as a function of the even - or oddness of the two quantum numbers $K_{-1}$ and $K_{+1}$ (the projections of the total angular momentum quantum number, $J$, on the symmetric top axis in the prolate and oblate symmetric top limits, respectively). The only atoms in oxalyl fluoride with nuclear spins are the fluorine atoms, each with spin 1/2; so oxalyl fluoride is expected to have two forms, as does molecular hydrogen. It is found
that when \( K_{-1} \) is odd and \( K_{+1} \) is odd, or \( K_{-1} \) is even and \( K_{+1} \) is odd, the nuclear spin weight is three; and when \( K_{-1} \) is even and \( K_{+1} \) is even, or \( K_{-1} \) is odd and \( K_{+1} \) is even, the nuclear spin weight is one.

Assuming nuclear spins are not relaxed, at a rotational temperature of 0 K there would be only two levels populated in oxalyl fluoride \((0_{00} \text{ and } 1_{01})\) and only three lines would be observed in the spectrum \((1_{10} \leftrightarrow 0_{00}, 1_{11} \leftrightarrow 1_{01}, \text{ and } 2_{11} \leftrightarrow 1_{01})\). Examination of Fig. 2-12 shows only two lines of significant intensity arising from levels other than \(0_{00}\) and \(1_{01}\) \((1_{01} \leftrightarrow 1_{11} \text{ and } 2_{21} \leftrightarrow 1_{11})\). Comparison of the intensities of the \(1_{01} \leftrightarrow 1_{11}\) vs. \(1_{11} \leftrightarrow 1_{01}\) and \(2_{21} \leftrightarrow 1_{11}\) vs. \(2_{11} \leftrightarrow 1_{01}\), results in measured rotational temperatures of 0.17 K and 0.18 K, respectively.

9.4.4 Conclusions - A similar study of the \(6^1\) band of the \(^1\text{B}_2 \leftrightarrow ^1\text{A}_1\) transition in benzene was carried out by a colleague on the same apparatus shortly before this experiment /37/. A rotational temperature of 0.3 K was obtained for benzene from that work.

The rotational temperatures measured during these experiments are lower than those measured spectroscopically for \(s\)-tetrazine in a continuous expansion /34/. This comparison provides unambiguous evidence for the hypothesis that the pulsed nozzle provides the same expansion conditions as a continuous nozzle of the same dimensions. It also proves the assertion that a pulsed nozzle is able to achieve better cooling of polyatomics since the orifice diameter is larger.
CHAPTER 3

PHOTOIONIZATION

10.0 INTRODUCTION

This next section describes the results of a set of photoionization experiments performed using the apparatus that was described in the previous chapter. Photoionization techniques, as applied to the study of transient molecular species, are still in their infancy. Much of the work discussed in this chapter was undertaken in order to elucidate these techniques. In particular, the work focusses on resonance enhanced two-photon ionization (R2PI) and its application as a replacement for the widely used laser induced fluorescence (LIF) method.

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. As described in the introduction, 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 molecule is then allowed to absorb, rather than emit
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 emitted, leaving the molecular ion in a vibrationless or vibrationally excited ground state. 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 /12c/.

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.

It was noted in the introduction that in order to observe a photoion signal, the up-pumping rate from the intermediate state must be greater than the sum of the other decay rates out of that state. If the lifetime of the intermediate state is longer than the laser pulse width, the decay rates do not compete with the laser field in depopulating that state. However, if the lifetime is on the order of or shorter than the laser pulse width, then the relative magnitudes of the two rates, up-pumping and decay, become an important consideration. While it is true that ion signal can be observed for case 2 molecules, it is not necessarily true that ion signal cannot be observed from case 1 molecules.

Molecules in class 1 typically have a very low fluorescence quantum yield due to fast non-radiative 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.

Class 2 molecules usually do have a reasonable quantum yield for fluorescence and many have been extensively studied. A comparison between the results obtained using photoionization and those obtained by LIF will serve to confirm the expectation that R2PI is useful for general purpose spectroscopic investigations.

The rest of this chapter is devoted to the discussion of R2PI experiments. These were undertaken with the goal of clearly demonstrating the application of the R2PI technique to the study of molecules in a molecular beam. In addition to illustrating that this method can be used as a substitute for LIF, they prove that the technique is much more powerful, being able to observe dynamic processes that occur without the emission of radiation.

Briefly, the following experiments were performed.

1. Some of the very first R2PI experiments showed an un-
expected dependence of the ion signal on the laser power. Careful examination of the problem revealed that dimers and higher oligomers formed in the supersonic expansion were undergoing a photoionization and fragmentation process that resulted in an increase in ion signal of the single parent ion.

2. A simple excitation experiment intended to observe the absorption spectrum of the lowest excited singlet states in aniline and naphthalene was performed. Proof of the ability of R2PI to only create parent molecular ions with good signal levels was desired. In addition to expected results, information was obtained about the most efficient way to ionize these excited states with respect to the wavelengths of light that can be used for the ionization step. In particular, the importance of the Franck-Condon principle with regards to the efficiency of making photoions from a resonant intermediate state was graphically illustrated. Further, an elegant method of obtaining the ionization potential of a molecule, which depends on the properties of a supersonic molecular beam, was found.

3. Another excitation experiment was performed on the case 1 molecules bromobenzene to prove that the R2PI scheme can be used to obtain high resolution spectra where LIF cannot. In addition, the results here revealed a method for obtaining an estimate of the singlet lifetime of such molecule.

4. A lifetime experiment was done on benzene illustrating the full power of the supersonic beam-photoionization setup by cleanly observing the decay of the initially excited singlet and the decay of the vibrationally hot triplet
state formed by intersystem crossing.

11.0 PHOTOIONIZATION OF MOLECULAR CLUSTERS

During some preliminary ArF multiphoton ionization studies with benzene, anomalous intensity patterns were observed. These investigations were undertaken to determine that the maximum ArF laser power was that which would yield good two color signals (i.e., the ArF laser would supply the ionizing photon for a benzene molecule previously excited to a resonant intermediate state by a doubled dye laser) without causing too much ionization by itself. In these experiments it was found that the ion signal did not follow the predicted laser power dependence. In an R2PI experiment, the ion signal should be proportional to the product of the pump and probe laser powers. A higher order power dependence was actually observed, implying that more than 2 photons were required to form the product.

Closer investigation of the problem revealed that during these experiments a significant fraction of the molecules were forming dimers and higher oligimers in the expansion. Fig. 3-1 shows a photoionization mass spectrum of benzene. Oligimers up to \((\text{C}_6\text{H}_6)_6\) are observed. The amount of oligimer formation is dependent not only on the nozzle parameters, as discussed in the introduction, but also on the partial pressure of the molecule in the nozzle and the nozzle temperature. Reducing the concentration of the molecule in the nozzle reduces the amount of oligimer formation. For example, at benzene concentrations above 0.1%, oligimers were easily observed in the beam. At concentrations exceeding 2%, the complex formation reached the proportions of Fig. 3-1.
FIG. 3-1  Photoionization mass spectrum of benzene. The benzene concentration was about 1% in He. The excitation source was an ArF laser.
The spectroscopy of these oligomers is certainly not well understood. However, from these results it is apparent that a multiphoton process involving these oligomers occurs which results in the formation of the uncomplexed parent ion as well as smaller oligomer ions. The intermediate state in a two photon oligimer ionization scheme, \( (C_6H_6)_n \), probably has a very large dissociation rate. The products of this dissociation are probably a ground state cluster, \( (C_6H_6)_{n-1} \), and an excited benzene molecule, \( C_6H_6^* \). The latter can then be ionized by the absorption of another ArF photon. The results also indicate that some fraction of the excited oligomers do not fragment but absorb a second photon to form oligimer ions, \( (C_6H_6)_n^+ \).

These findings reveal an entire field of study that has never been investigated. However, pursuing this further would be outside the scope of this thesis. What is important to the work here is that the presence of oligimers in the molecular beam can easily invalidate other photoionization results. For this reason, during the experiments described in the rest of this chapter, care was taken to keep the concentration of the molecules in the beam below the level required for oligimer formation.

12.0 ANILINE

12.1 Introduction

Aniline was chosen for the first R2PI experiment because its 8 nsec fluorescence lifetime /6/ is longer than the laser pulse width and the energy of the origin of the \( S_1 \leftarrow S_0 \left( ^1B_2 \leftarrow ^1A_1 \right) \) transition (34,025 cm\(^{-1}\)) /38/ is more than half the ionization energy (62,100 cm\(^{-1}\) /39/). A single light source, in this case the Quanta-Ray dye laser, can be used to provide the pump and ionizing photons. In addition, the second harmonic output from the Nd:YAG laser (532 nm)
was used to provide the ionizing photons in a second experiment in order to compare the efficiency of a single ionizing photon vs. two sequential ionizing photons.

12.2 Results and Discussion

Figure 3-2 displays a schematic of the laser and molecular beam
FIG. 3-2  Schematic of the supersonic beam/laser beam interaction region in the configuration used for the aniline experiment.
arrangement used in the aniline investigations. The figure shows a top view of the "B" chamber (see Fig. 2-1). The expansion gas consisted of a 0.5% mixture of aniline (Baker reagent grade) in helium. The aniline concentration in the beam was about $1 \times 10^{10}$ molecules cm$^{-3}$.

Figure 3-3 shows the total photoion yield produced as a function
FIG. 3-3 Total ion signal observed as a function of laser frequency in the proximity of the origin of the $^1B_2 \leftrightarrow ^1A_1$ transition of aniline. The laser was focused to a 3 mm diameter waist for these measurements. The laser powers were, from the top, 13, 10, and 0.3 MW cm$^{-2}$. 
of laser frequency at a variety of dye laser fluences. At low laser flux, ion signal is observed only when the laser is tuned to the $S_1 \leftarrow S_0$ resonance. The bandwidth of this transition is approximately that of the dye laser, $1 \text{ cm}^{-1}$ (FWHM). As the laser flux is raised, the width of the transition broadens until at the highest laser power it has increased to almost $5 \text{ cm}^{-1}$ (FWHM). The peak of the resonant signal has also begun to flatten, indicating saturation of the $S_1 \leftarrow S_0$ transition. The figure clearly shows the onset of power broadening of the $S_1 \leftarrow S_0$ transition. The rise in the background signal with the increase in laser power shows the increasing importance of non-resonant, two-photon ionization at high powers. At the highest laser power, this non-resonant channel is approximately 25% efficient.

Brophy and Rettner (13e, f) have reported the detection of aniline by R2PI at low laser fluence. Their investigations have revealed:

1. The ion signal scales as the square of the laser power.

2. The frequency dependence of the ion signal follows that observed for the aniline fluorescence excitation spectrum.

3. The aniline parent ion ($C_6H_5NH_2^+$) is the only ion produced.

The results obtained in this investigation confirm those results. An earlier investigation of photoionization of metal carbonyl molecules in our laboratory determined the absolute detection efficiency of Fe(CO)$_5$ to be greater than 20% /40/. Using Fe(CO)$_5$ as a calibration gas, the peak aniline signal obtained as in Fig. 3-3 was compared with that obtained for the same concentration of Fe(CO)$_5$ in the beam under identical conditions. The aniline signal was found to be slightly greater than that obtained from Fe(CO)$_5$. Due to the uncertainty of the Fe(CO)$_5$ efficiency measurements, that figure is low by a factor of at least 4 /40/. The detection efficiency for aniline therefore
approaches unity. It should also be noted that the aniline parent ion was the most predominant species formed in the ionization process irrespective of the laser power used. Fragment ions at m/e = 28, 39, 54, 66, and 78 are also observed at laser fluences greater than about 10 MW cm\(^{-2}\), but these account for only about 20% of the total ion signal at 20 MW cm\(^{-2}\). Even at the highest laser fluences there was no noticeable difference between the amount of fragment ion signal obtained on or off the \(S_1 \leftarrow S_0\) resonance. The most important results of this work are the facts that aniline can be detected with essentially 100% efficiency and that, for reasonable laser powers, only the parent ion is formed.

Figure 3-4 illustrates the results of the two-color R2PI experiment.
FIG. 3-4 Mass spectrum obtained for one- and two-color R2PI experiments on aniline. In each case the UV laser beam was tuned to resonance with the $0^0$ band of the $^1B_2 \rightarrow ^1A_1$ transition. The mass spectrometer sensitivity was the same for both measurements.
UV = 0.93 MW/cm²

GREEN = 41.0 MW/cm²
outlined in the introduction. A portion of the Nd:YAG second harmonic radiation was superimposed spatially and temporally with the ultra-violet dye laser radiation with the latter tuned to the $S_1 \leftarrow S_0$ resonance. The 293.9 nm laser power has been increased so that the one-color R2PI signal is far from saturation. Regardless of the intensity of the additional green laser beam up to the highest intensity we could use without damage to the quartz optics, the only effect of the green radiation is to decrease the photoion signal. The one photon absorption spectrum of aniline indicates that there is a strong absorption in the vicinity of 52,800 cm$^{-1}$, corresponding to a higher singlet state /38/. This state would be accessed by the absorption of one UV photon and one green photon. The fact that the ion signal decreases when the green light is added indicates this higher singlet state must predissociate at a far greater rate than the up-pumping to ionization by the 532 nm radiation and the products of the dissociation are not ionized by either of the wavelengths present.

13.0 NAPHTHALENE

13.1 Introduction

In order to confirm the results obtained from the study of aniline, the same experiment was performed using naphthalene. Results similar to those found from the aniline experiment were expected for naphthalene since its singlet lifetime is longer than the laser pulse width also /5/. The initial results showed an overall detection efficiency that was significantly lower than that obtained for aniline or the metal carbonyls. The origin of the $S_1 \leftarrow S_0$ ($^{1}B_{3u}(\Pi\pi\pi)$ $\leftarrow^{1}A_{1g}$) transition in naphthalene (32020 cm$^{-1}$ /41/) is less than half the energy of the ionization potential (65653 cm$^{-1}$ /42/), which explains the low ion signals that were observed. In order to efficiently ionize naphthalene, a second laser of a different, higher
frequency must be used to provide the ionizing photons.

13.2 Experimental

The low resolution dye laser was directed down the molecular beam axis and tuned to a resonance in the naphthalene $^1B_{3u} \leftarrow ^1A_{1g}$ band. The PDL-1 dye laser was directed into the "B" chamber perpendicular to the molecular beam. The frequency of this laser was scanned such that the sum of the two laser frequencies changed smoothly from an energy somewhat less than the naphthalene ionization potential to an energy somewhat greater than the ionization potential. The voltages on the repeller plate and the draw out grid were both kept at the normal voltage of the grid until after the lasers had fired. At this point, the repeller plate voltage was increased several hundred volts to its normal operating potential to propell the ions out of the ionization region. In this manner, perturbations due to large electrostatic fields in the ionization region were eliminated.

13.3 Results

The ion signal as a function of the ionizing laser frequency when the pump laser was tuned to the $^5H^1_0$ band is shown in Fig. 3-5.
FIG. 3-5  Ionization threshold of naphthalene observed when pumping the $^1B_{3u} \leftarrow ^1A_{1g} \ 8^1 \ o$ band and scanning the ionizing laser. The frequency in the figure is referenced to the observed ionization potential at 66105 cm$^{-1}$. 
The absolute frequency of the dye laser could be obtained from the absorption features observed in the scan. The frequency of these transitions was obtained from the work of Beck, et al. /43/. From the known frequency of the $S_0 \leftrightarrow S_1$ origin and the calibrated laser frequency, the energy of the onset of the ionization continuum was found. The threshold depicted in Fig. 3-5 was found to be at 66105 cm$^{-1}$.

The ion signal obtained when the pump laser was tuned to the $^1B_{3u} \leftrightarrow ^1A_{1g}$ origin was similar to that shown in Fig. 3-5. However, the position of the threshold observed under these conditions was shifted to the red by 461 cm$^{-1}$. This difference is the energy of the $\bar{v}$ vibration in the naphthalene ion. While pumping the $S_1 \bar{v}_0$ level, the second laser was scanned though the region where the transition to the vibrationless ion was expected to occur. At the expected place, a small change in the signal level: The threshold at 66105 cm$^{-1}$ was at least 30 times larger than the one at 65644 cm$^{-1}$ under these conditions.

13.4. Discussion

These observations clearly illustrate the importance of the Franck-Condon principle for the ionization step of the R2PI process. Good detection efficiency is realized so long as the vibrational quantum numbers do not have to change during the ionization step. For cases where the intermediate state of interest has less than half the ionization energy, a one laser R2PI experiment is not practical. However, by using a second laser tuned to a higher frequency than the first, this difficulty can easily be overcome.

The absolute value of the ionization potential obtained from these measurements must be considered one of the most precise that has been obtained. Crucial to the reliability of these measurements is the cooling afforded by the supersonic molecular beam. Past mea-
surements of the ionization potential by photoionization have been difficult because of broadening of the threshold due to thermal population of ground state rotational and vibrational levels /44/. The direct observation of the threshold with such a good signal-to-noise ratio has obvious advantages over the calculation of the ionization potential from the observed positions of Rydberg bands. The exact position of the Rydberg features is difficult to determine and in any case, usually only four or five bands can be identified /45/. Narrow thresholds as observed in this machine greatly reduce the uncertainty in these measurements. The procedure can of course be easily generalized to any molecule for which this quantity is desired.

14.0 BROMOBENZENE AND IODOBENZENE

14.1 Introduction

Bromobenzene and iodobenzene were chosen for this study because they do not fluoresce. Several workers have attempted to observe fluorescence from the monosubstituted halobenzenes /46 - 49/ and only fluoroobenzene has been shown to have a significant fluorescence quantum yield /48, 49/. The major radiationless decay channel from the lowest excited singlet state (\( \pi^* \)) is believed to be intersystem crossing to a triplet state /50, 51/. The absorption spectra of both bromo- and iodobenzene have been observed /52 - 56/, 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 \( \sigma \leftrightarrow n \) absorption on the C-I bond overlaps the lower part of the \( \pi^* \leftrightarrow \pi \) absorption in the region of 250 nm to 300 nm /56/. This \( \sigma \leftrightarrow n \) transition is believed to have an absorption cross section that is two times greater than the \( \pi^* \leftrightarrow \pi \) cross section /56a/. In the 1-iodoalkanes the \( \sigma \leftrightarrow n \) band extends from 35000 cm\(^{-1}\) to 45000 cm\(^{-1}\), is invariant with respect to the length
of the alkane chain and is completely devoid of structure /57/. The corresponding absorption in the bromoalkanes, and presumably bromobenzene, is displaced some 12000 cm$^{-1}$ to the blue /57/. For both molecules the $^1B_2 \leftrightarrow ^1A_1$ origin /58/ is more than half of the energy of the lowest ionization potential /59/ which allows us to use a single laser for our R2PO experiments.

The first singlet state lifetimes of bromo- and iodobenzene have not been measured. The lifetime 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. We have obtained an upper limit for this lifetime for bromobenzene by performing a delayed two photon experiment. A study of the known monohalobenzene lifetimes and our up-pumping rates allow us to give estimates for the lifetimes of the singlet states of both molecules.

14.2 Results

The R2PI spectrum of the $^1B_2 \leftrightarrow ^1A_1$ transition of bromobenzene from the origin at 36991.5 cm$^{-1}$ to the KDP cutoff at 38580 cm$^{-1}$ is shown in Fig. 3-6.
FIG. 3-6 The resonance enhanced two-photon ionization spectrum of the $^1B_2 \leftrightarrow ^1A_1$ system of bromobenzene. The frequency scale is relative to the origin at 36,991.5 cm$^{-1}$. 
The spectrum is the average of three separate scans, each having been corrected for dye laser power fluctuations. For these corrections we assumed that the R2PI intensity was proportional to the square of the laser power, an assumption that should be valid as it is unlikely that we are saturating the $^1B_2 \leftrightarrow ^1A_1$ transition at the laser powers (4 MW cm$^{-1}$) used in this experiment. The individual scans are composed of data points obtained at 0.0048 mm 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
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$^{-1}$)$^a$</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>$16b_0^2$</td>
</tr>
<tr>
<td>294.1</td>
<td>4</td>
<td>$6a_0^1$</td>
</tr>
<tr>
<td>518.9</td>
<td>69</td>
<td>$6b_0^1$</td>
</tr>
<tr>
<td>535.0</td>
<td>3</td>
<td>$16b_0^2 6a_0^1$</td>
</tr>
<tr>
<td>620.8</td>
<td>8</td>
<td>$1^1_0$</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>$12^1_0$</td>
</tr>
<tr>
<td>960.3</td>
<td>43</td>
<td>$18a_0^1$</td>
</tr>
<tr>
<td>1019.1</td>
<td>23</td>
<td>$9a_0^1$</td>
</tr>
<tr>
<td>1139.7</td>
<td>5</td>
<td>$6b_1^1 1^1_0$</td>
</tr>
<tr>
<td>1146.9</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1172.7</td>
<td>7</td>
<td>$16b_0^2 12^1_0$</td>
</tr>
<tr>
<td>1200.8</td>
<td>4</td>
<td>$16b_0^2 18a_0^1$</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>$6b_0^1 12^1_0$</td>
</tr>
</tbody>
</table>
TABLE 3-1 (continued)

<table>
<thead>
<tr>
<th>Relative Position (cm(^{-1}))(^a)</th>
<th>Relative Intensity(^b)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1467.7</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1477.6</td>
<td>33</td>
<td>6b(^1) 18a(^1)</td>
</tr>
<tr>
<td>1493.1</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>1537.5</td>
<td>22</td>
<td>6b(^1) 9a(^1)</td>
</tr>
<tr>
<td>1552.2</td>
<td>7</td>
<td>1(^1) 12(^1)</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. 55).

b. Relative to the intensity of the origin.
and intensities. The modes are numbered using Wilson's system /60/
and were assigned in accord with other work in our laboratory /61/.
Our observations agree quite well with other observations of the bromo-
benzene $^1B_2 \rightarrow ^1A_1$ system /52 - 54/ except for the absence of a strong
cold band at 234 cm$^{-1}$ reported by Prakash and Singh /52/ and Walerstein
/53/. 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 6b ($b_2$). The combination bands of 6b with the totally symmetric
vibrations 12, 18a, and 9a are also quite prominent. The assignment
of the fundamental band at 1018 cm$^{-1}$ to the 9a 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 ben-
zenes /61a/. The intensities observed in our experiment follow the same
general pattern observed in the absorption experiments /52, 53/, but
the absence of quantitative intensity information from the older work
prohibits a detailed 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 har-
monic of a second Nd:YAG laser was time delayed to probe triplets formed
upon intersystem crossing. The intensities of the two lasers were ad-
justed such that the R2PI signal obtained from both lasers was greater
than that obtained from either individually. A definite two-laser sig-
nal was obtained only when the two lasers were temporally overlapped.
The minimum delay for which the pulses were not overlapped was approxi-
mately 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
$^1B_2 (\pi\pi^\ast)$ lifetime.
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 triplets formed upon intersystem crossing. 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 then 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 $^1B_2 (n^*n^*)$ lifetime.

The lifetime of iodobenzene is expected to be shorter than that of bromobenzene and observation of the $^1B_2 \leftarrow ^1A_1$ 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$^{-1}$. The gain of the ion detection system was also increased by a factor of five. 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 /56/ for the $^1B_2 \leftarrow ^1A_1$ absorption (36760 to 38580 cm$^{-1}$).

14.3 Discussion

The most important aspect of the bromobenzene data is that it demonstrates the ease with which the R2PI technique detects a non-fluo-
rescent molecular species with high sensitivity. The results of the
delayed two photon experiment allow us to place a upper limit of
10 nsec on the bromobenzene singlet lifetime. The absence of vibro-
nic linewidths larger than the laser linewidth allow us to place a
lower limit on that lifetime of about 2.5 psec. Fluorobenzene is the
only monohalobenzene for which lifetime and quantum yield measure-
ments are available /48, 49/. Fruitless attempts to observe fluo-
scence from chlorobenzene have placed an upper limit of 1 x 10^{-4}
on the quantum yield of that molecule /46,47/. The integrated oscilla-
tor strength of chlorobenzene is of the same order of magnitude, but
slightly larger, than that for benzene /56a/. We can therefore use
the radiative lifetime of benzene (500 nsec /62/) to obtain an upper
limit for the overall lifetime at chlorobenzene of 50 psec. Investi-
gations of monohalonaphthalenes in solid solution indicate a reduc-
tion by a factor of 36 in the fluorescence lifetime in going from chlo-
ronaphthalene to bromonaphthalene /63/. 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 psec.

It should be noted that any bromobenzene triplet states formed by
intersystem crossing could not be observed in the one color or two co-
lor R2PI experiments because of poor Franck-Condon factors for the io-
nization step. Even the 37594 cm⁻¹ delayed photon, when added to the
36991 cm⁻¹ pump photon, would produce an ion with only 2163 cm⁻¹ of
excess energy. The Franck-Condon factors for the ionization of a trip-
let state would be poor if the triplet origin were more than 2163 cm⁻¹
below the singlet origin. The lowest bromobenzene triplet state is
known to be almost 8000 cm⁻¹ below the singlet /64/. In order to effi-
ciently ionize these triplets, a more energetic photon is necessary.
One such experiment is described in the next section.

Based on the estimated bromobenzene \(^1\text{B}_2\) (\(\pi\pi^*\)) lifetime and the
enhanced sensitivity used during the iodobenzene experiment it can be
inferred that we should have been able to observe the $^1B_2$ iodobenzene singlet even if its lifetime were as short as 0.02 psec. Since we were unable to see any iodobenzene ions, 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, Yang and Bersohn /51/. 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 psec. 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 which is consistent with all known data is that the $^1B_2 (\pi\pi^*)$ state is so strongly coupled to the underlying dissociative continuum of the $\sigma\pi$ 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 $\sigma\leftrightarrow \pi$ 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.

15.0 TRIPLET LIFETIME OF BENZENE

15.1 Introduction
The last section indicated the possibility of detecting molecular triplet states formed by intersystem crossing, by photoionization. In order to do this efficiently, an ionizing laser energy sufficient to create the molecular ion with roughly 8000 cm\(^{-1}\) of vibrational energy is needed. The ArF laser was therefore used as the ionizing laser. Fig. 3-7 shows
FIG. 3-7  Schematic of the laser beam / molecular beam interaction region in the configuration used during the benzene triplet lifetime experiment.
the ionization region of the time-of-flight mass spectrometer and depicts the interaction of the lasers and the molecular beam.

Benzene was chosen for the first triplet lifetime study because of its importance chemically and its popularity in the study of molecular spectroscopy, radiationless transitions and lifetime investigations. The results will indicate, however, that the technique described here is perfectly general and can be applied to any molecule that can be introduced into a supersonic molecular beam.

The triplet lifetime of benzene has been the subject of a number of studies /65/, the most recent being a quenching experiment using cis-2-butene as the quenching gas /91/. The quenching gas selectively absorbs energy only from triplet benzene molecules. From this experiment the relaxed triplet lifetime of benzene was found to be 0.5 msec. In the a crystal lattice, the lifetime of benzene triplets has been determined to be 15 sec /8a - c/. The vast difference in gas phase and solid phase triplet lifetimes reflect the difference in intersystem crossing rates in these media from the triplet manifold to the ground state singlet. Large amplitude vibrational motion is known to promote this conversion /7/, and since vibrational energy is most efficiently absorbed by a crystal lattice, the solid state measurement reflects the completely relaxed benzene triplet lifetime. The gas phase quenching measurements give a shorter lifetime because the vibrational energy has not been completely dissipated. In order to obtain the true lifetime of the vibrationally hot benzene triplet, measurements must be made in a collisionless environment.

Figure 3-8 is an illustration of the benzene energy levels that are
FIG. 3-8  An energy level diagram relevant to the triplet photoionization process for benzene. Dye laser radiation at 295 nm (4.8 eV) excited the cold benzene molecules to the $^1_{0}$ vibrational level of $S_{1}$ which then decays by intersystem crossing (at the rate $k_{ST}$) into isoenergetic levels of the triplet manifold. The resultant vibrationally hot triplet, $T_{1}^{\ddagger}$, then decays (at a slower rate, $k_{TS}$) into very highly vibrationally excited ground state levels, $S_{0}$. Franck-Condon factors for photoionizing transitions in benzene are vanishingly small unless the resultant $C_{6}H_{6}^{+}$ ion has the same vibrational excitation as the molecular state to be ionized. Thus, for the $T_{1}^{\ddagger}$ triplet, only ArF excimer laser radiation (6.4 eV) can produce efficient ion formation by exciting above the first ionization threshold ($IP_{1}$) which can produce $C_{6}H_{6}^{+}$ with 1.1 eV of vibrational energy.
$\text{IP}_1^+$ \rightarrow C_6H_6^+ (E_V = 4.8 \text{ eV})$

$\text{IP}_1^+$ \rightarrow C_6H_6^+ (E_V = 1.1 \text{ eV})$

$\text{IP}_1$ \rightarrow 9.2 \text{ eV} \rightarrow C_6H_6^+ (E_V = 0)$

$S_i$ \rightarrow 6' \rightarrow k_{ST} \rightarrow T_1 \rightarrow 6.4 \text{ eV} \rightarrow k_{TS} \rightarrow S_0^+$

$k_r$ \rightarrow 4.8 \text{ eV} \rightarrow T_1 \rightarrow 3.7 \text{ eV} \rightarrow S_0$
important in the process that will be probed in the experiment. The level, \( \text{IP}_1^+ \), is the level which must be accessed by the ionizing laser in order to form ions with the same amount of vibrational energy as the triplet precursor. \( \text{IP}_1 \) is the vibrationless ion ground state. As shown in the figure, only the 6.4 eV ArF photon has enough energy to ionize both the singlet and the triplet.

15.2 Results and Discussion

Figure 3-9 shows the results of the benzene triplet lifetime study.
FIG. 3-9 Photoion signal due to benzene $S_1$ singlets and $T_{1}^{\dagger}$ triplets in a supersonic beam. The horizontal axis is the delay between the 259 nm pump laser and the 193 nm probe laser.
The data shown here is the result of 1000 scans across the entire delay (see section 2.5.3). The ion signal due to either the pump laser or the probe laser alone was insignificant on the scale of this figure. The decay is bi-exponential, the early decay having a 470 $\pm$ 50 nanoseconds. Approximately 70 to 80% of the intensity decays with the longer lifetime. Since the singlet 6b level of benzene is known to have an 80 nsec lifetime /2/, the fast component probably corresponds to depopulation of this singlet state. The longer lifetime is the decay of the triplet state into highly vibrationally excited ground state singlet molecules.

The accepted value for the fluorescence quantum yield from the $^1\text{B}_{2u}^1\text{a}_0^1$ level is 0.2 /2/ and results of cis-2-butene triplet quenching experiments indicate that the remaining 80% of the initial population is converted to triplets by intersystem crossing /9/. If the singlet and triplet states have the same ion quantum yield for irradiation at 193 nm, then careful study of the decay curve will yield the singlet lifetime, the triplet lifetime and the intersystem crossing quantum yield. The latter can be obtained by extrapolating the long-lifetime decay curve to the time origin and noting height of that curve at that point. If the fluorescence quantum yield or the radiative lifetime is known from other, independent measurements, then the rate and quantum yield of internal conversion from $S_1$ to $S_0$ can be calculated. Any uncertainty in the relative ionization efficiencies for the singlet and triplet can be eliminated by increasing the ArF laser flux to the point where both the singlet and triplet ionization transitions are saturated. Accurate deconvolution of the singlet and triplet decays can be achieved by measuring the singlet decay using a lower energy photon sufficient to ionize the singlet but not the triplet.
CHAPTER 4

CONCLUSION

The experiments described in the last chapter have yielded a number of important results. These are reviewed below.

1. It has been shown that the R2PI technique can be used to obtain optical spectra of the same resolution obtainable by laser induced fluorescence. In addition, R2PI can be used in cases, such as bromobenzene, where the fluorescence quantum yield is too low to permit studies using the emission of light to detect excited states. In either case, the detection of ions is far more efficient than the detection of photons.

2. These spectroscopic experiments can be performed using one laser so long as the resonant intermediate states are at least half of the ionization energy. Under circumstances where this is not possible, such as the origin region of naphthalene, a second laser, tuned to a higher frequency can be used to provide the ionizing photons.

3. If the pump laser is fixed on a resonant transition and the probe laser is scanned, the ionization threshold can
can be observed. Due to the Franck-Condon principle, ionization potentials observed using vibrationally hot intermediate states are shifted to the blue, relative to that obtained using the vibrationless level of the intermediate electronic state, by an amount equal to the vibrational frequency in the ion. Therefore, not only can the ionization potential be determined to within a few wavenumbers, but ground state vibrational frequencies in the ion can be obtained.

In R2PI experiments, the shift in the ionization threshold with different vibrational energy in the intermediate state means that ions are most efficiently created only when the vibrational quantum number does not change during the ionization step. For general spectroscopic studies, for instance, this means that the laser wavelengths must be chosen with some care in order to observe the maximum ion signal that can be obtained.

4. Resonance enhanced two photon ionization has been shown to have almost unit detection efficiency for molecules in a supersonic beam. In addition, at powers that are below the saturation level of the resonant transition, the process yields only the parent ion. This removes any uncertainty surrounding the parentage of an observed mass spectrum. Signals occurring in mass channels other than the parent channel can be definitely dismissed as contaminants.

5. For the first time, the triplet decay of an unperturbed polyatomic molecule, benzene, has been observed. The lifetime of this vibrationally excited triplet has been shown to be many orders of magnitude shorter than the lifetime of the relaxed triplet. The molecular beam environment was crucial to this measurement since it assures that the
lifetime that was measured is unaffected by collisional influences. Through proper analysis of the observed decay, intersystem crossing, and possibly internal conversion, quantum yields can be calculated.

It is obvious that the experiments described in this thesis are just the first of many that can be performed using the combined supersonic molecular beam and photoionization methods. Further high resolution spectroscopic investigations on molecules such as bromobenzene can be easily performed. These could be done at a resolution sufficient to observe rotational structure if desired, using a narrow band, relatively low power dye laser to pump the resonant transitions. A higher power fixed frequency laser could then be used to ionize the excited molecules. Because of the high ion detection efficiency of the time-of-flight mass spectrometer, even a few ions per shot would constitute a sufficient signal. The ionization potential of any molecule that can be introduced into or created in a supersonic expansion can be measured with very good accuracy. The problems encountered in room temperature photoionization or Rydberg measurements of this quantity are eliminated by the cooling afforded by the supersonic expansion. Lifetime measurements of singlet and triplet states can be made almost automatically under computer control. Such measurements are unprejudiced by collisions or other perturbations.

The goal of this work was to describe the construction and operation of a new instrument designed to yield new information about the nature of internal energy transfer in excited molecules. This has been done. The use of resonance enhanced two-photon ionization to elucidate the mysteries of unimolecular photophysical processes in a molecular beam shows great promise as evidenced by the results of the experiments described therein. Not only have the techniques been proven effective, but new, significant information has been obtained about these processes.
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