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# INVESTIGATION OF CONCEPT OF EFFICIENT SHORT WAVELENGTH LASER

Quarterly Progress Report

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# ABSTRACT

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~~This report describes progress during the first quarterly period of the subject contract.~~ An experiment has been designed to study the wavelength-selected photolysis of gaseous, covalent azides. The apparatus to be built for these studies is described. The azides are to be photolyzed by light from a doubled dye laser, and the photolysis fragments probed by laser-induced fluorescence (LIF) or by the observation of photon emission. Kinetics of the photolysis fragments may be studied by precisely controlling the time between the pulses from the photolysis and probe lasers. In such a system ~~we shall be able~~ it should be possible to determine the product yields from the photolysis, the kinetics of the electronically excited fragments, and the spectroscopy of the photolysis fragments. The latter measurement is accomplished by scanning the fragment fluorescence spectrum with a monochromator, or by scanning the probe laser over the absorption bands of the fragment molecules. The problems of scattered laser light and techniques to reduce them are discussed in detail.

Calculations have been performed to simulate typical experimental conditions to be expected in studies on the photolysis of $HN_3$. Typical fragment densities are calculated along with the signals expected from the LIF diagnostic. Several experimental problems, such as fluorescence quenching and diffusion, are disucssed in detail. It is concluded that the proposed experimental design will have sufficient sensitivity and flexibility to perform the experiments.

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# I. INTRODUCTION

It is generally recognized that a laser device possessing all of the properties required for a practical fusion reactor does not yet exist. Therefore, a substantial effort is currently underway to find and develop such a laser. Some of the desirable characteristics for a laser-fusion driver are short wavelength ($300 \text{ nm} \le \lambda < 3000 \text{ nm}$), high overall efficiency ($\ge 1\%$), and scalability to large size ($\ge 100$ kJ/pulse). The development of a laser with the above characteristics, together with acceptable cost and reliability, is acknowledged to be a difficult task, and a number of different technical approaches are being pursued in parallel. For example, one effort is concerned with the photolytic production of group VI atoms such as O or S in the metastable singlet state.

Under the present contract PSI is investigating the photolytic decomposition of a class of endoergic molecules--azides. Because these compounds contain substantial chemical energy, they offer a potentially more efficient approach for the production of electronically excited fragments. The goal of the present program is not to demonstrate a laser, but the acquisition of sufficient data and understanding of certain fundamental processes to permit the critical evaluation of this approach for laser development.

Under a previous ERDA contract[1], we reviewed the literature pertaining to the decomposition of azides and concluded that the production of electronically excited species of potential laser interest may be achieved via essentially two major pathways: (i) the photolytic or thermal decomposition of covalent azides to produce electronically excited singlet nitrenes; or (ii) various chemiluminescent reactions of the azide radical. The major task of the present contract is to investigate the first method of electronic-state production, by focussing upon the wavelength-selected photolysis of gaseous covalent azides.

This report summarizes progress during the first quarterly period of this contract. The major effort has been directed toward a detailed design of the experimental apparatus and the development of specifications for the purchase of the major items of equipment. These accomplishments are reviewed in the following section.

## II. EXPERIMENTAL DESIGN

### A. General

The major technical considerations of this experiment are as follows: (i) the primary products of the photolysis must be identified as a function of photolysis wavelength, (ii) detailed spectroscopy of the electronically excited fragments, such as energy levels and life times, must be obtained, and (iii) the kinetics of chemical and energy-transfer reactions of selected electronically excited species must be determined. To perform these measurements a photochemical reactor must be developed in which the wavelength of the photolysis source may be varied, the detection techniques provide high sensitivity with good temporal resolution, and reasonably well defined spectral diagnostics are available. The requirement of a wavelength-tuneable photolysis source may be met with a tuneable dye laser provided it supplies sufficient intensity in the spectral region of interest. Sensitive detection may be achieved either by laser-induced fluorescence (LIF) or by direct observation of photon emission. Good temporal resolution is possible by pulsing the photolysis source and using a gated detection system to monitor species at varying times after the photolytic pulse. Suitable spectral diagnostics may be obtained by the use of interference filters, a fast monochromator, and/or tuning the laser used in the LIF studies over the absorption bands of the species to be studied.

### B. Experiment

The apparatus which we are constructing for this experiment is shown schematically in Fig. 1. It consists of a photolysis cell to contain the azide and an inert buffer gas. A slow flow is used to maintain good gas purity and to control the relative concentrations of the reagents. The azide is photolyzed by pulses from a doubled dye laser operating at a repetition rate

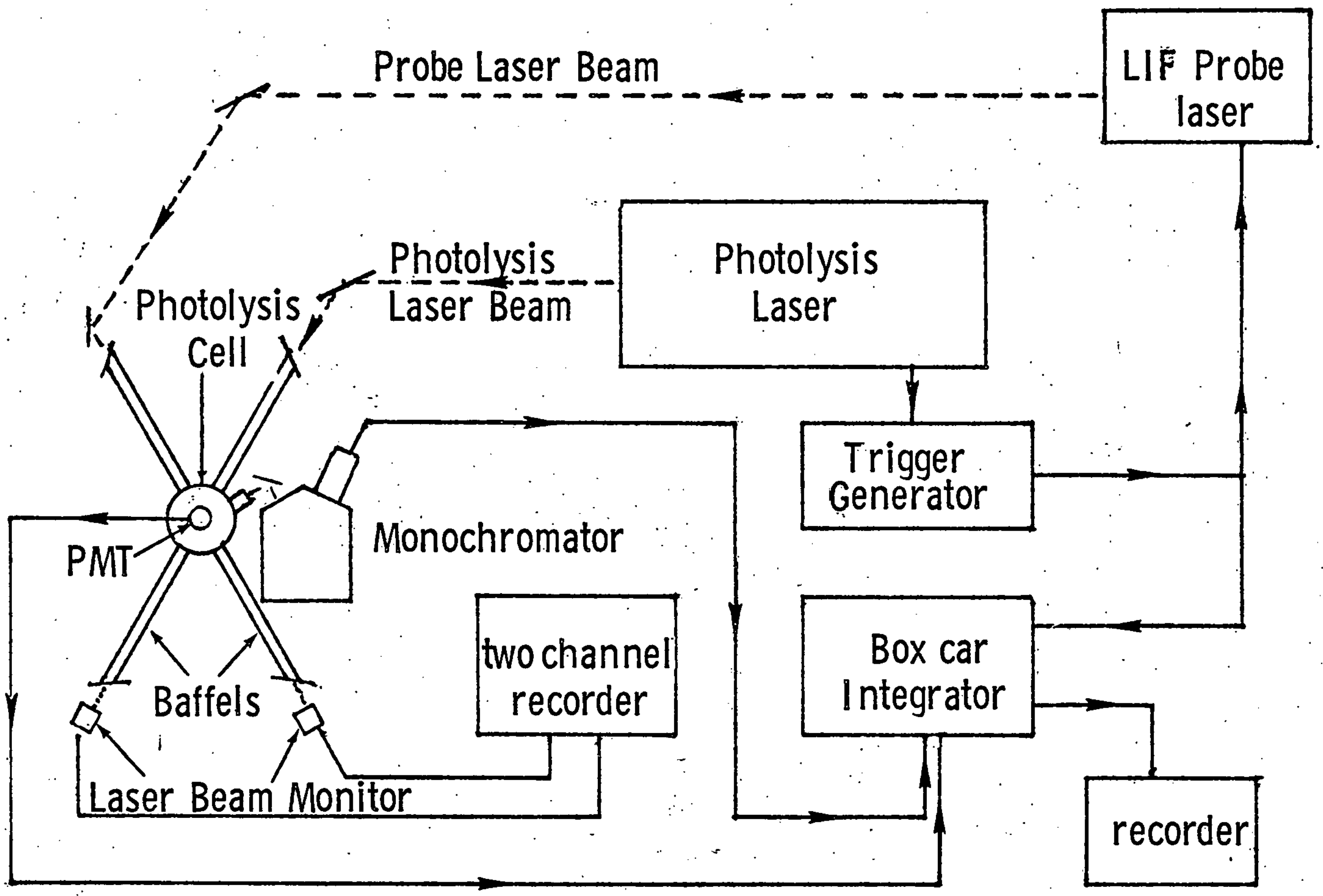

Fig. 1 Schematic of Laser Photolysis Apparatus

of 5-30 Hz. The density of fragements is probed via LIF from pulses from a second dye laser which is triggered off the photolysis laser after a precisely controlled delay. The fluorescence induced from the probe-laser pulse is detected by a photomultiplier placed at right angles to the plane defined by the photolysis and probe lasers. Output from the photomultiplier is fed to a box-car integrator, the gate of which opens shortly after the pulse from the probe laser is off. For studies in which the fragments produced in the photolysis radiate, the box-car integrator will be gated off the photolysis laser, and the probe laser will not be used. In addition, a monochromator will be used to monitor any chemiluminescence emissions. The average intensities of the two lasers will be monitored so that corrections may be made for long term drift. The time resolution of the system is determined essentially by the minimum box-car gate width appropriate to the species under study, or for the short-lived fluorescing species, by the pulse width of the photolysis laser which is 1 μs.

The major requirement of the photolysis laser is that it have a high energy per pulse in the wavelength region of interest. This requirement is most easily met by a flashlamp-pumped dye laser. We have selected the Candela SLL-1 laser which provides about 5 mJ per pulse at 265 nm at 20 Hz in a beam approximately 1 cm square. This recent entry into the commercial-laser market provides more than an order of magnitude increase in output over its competitors with no sacrifice in beam quality. The Candela dye laser has a nominal visible tuning range of 430-730 nm. With temperature-tuned doubling, this range can be extended to cover 255-310 nm in the ultraviolet. By operating at reduced power (~ one half of nominal), where excellent beam quality is claimed, angle tuning can be employed to further extend the wavelength range to 217-360 nm.

The laser to be used for the LIF probe should ideally have high energy per pulse, short pulse width and precise triggering. The high-energy-per-pulse requirement is less important, however, than the other two requirements.

It is useful to have a short pulse width so that one may delay gating on the detection electronics until long after the laser pulse has terminated. This technique reduces significantly interference from scattered laser light. If the laser-pulse time is comparable to or longer than the fluorescence lifetime of the species being probed, then a significant fraction of the signal of interest will decay before the laser pulse has terminated. The pulse width of a nitrogen-pumped dye laser is about 5 ns, significantly shorter than the lifetimes of most allowed molecular transitions. By contrast, the pulse width of most flashlamp-pumped dye lasers is on the order of 1 μs. The short pulse width was the major criterion in our selection of the molectron $N_2$ pumped dye laser (DL-200) for the LIF technique. Calculations (discussed below) indicate that the energy per pulse of these lasers is more than adequate for our applications.

In general, a gated detection system may consist of either a box-car integrator or a photon-counting system. Errors resulting from pulse pile up limit photon-counting systems to effective counting rates less than about 10 MHz, which for a typical 2 μs gate time is only ~ 20 photoelectrons per laser pulse. The box-car integrator is an analog device which is limited primarily by current saturation in the photomultiplier dynode chain. For fast-focussed photomultipliers, peak currents of 100 mA are possible without saturation. This peak current corresponds to approximately $10^5$ photoelectric events per laser pulse for a 2 μs gate time. The box-car integrator should be reasonably sensitive down to less than 5 photoelectric events per laser pulse, so that it is only at very low signal levels that a photon-counting system offers an advantage over a box-car integrator. At such low signal levels, the collection time to obtain good signal-to-noise ratio at the modest repetition rates of the experiment becomes excessively long for either type of detection technique. The calculations (shown below) indicate signal levels several orders of magnitude above the maximum allowable for a photon-counting system, therefore we have decided to detect fluorescence signals with a box-car integrator.

One of the major problems associated with laser-induced fluorescence detection is scattered laser light. The radiation arises not only from scattered photons from the laser beam, but also by fluorescence from cell materials which have been excited by photons scattered from the laser beam. This fluorescence can be an especially severe problem because it is typically of long duration compared to the laser pulse, and cannot readily be avoided by delaying the opening of the box-car gate. Several techniques will be used to minimize this problem. Firstly, photons scattered out of the laser beam will be reduced significantly by having the laser beam enter the cell through very long side arms provided with a series of carefully aligned baffels. Secondly, the reaction cell will be constructed out of chemically blackened metal, anodized stainless steel, rather than glass. This will reduce, but not eliminate, fluorescence from cell materials. Thirdly, the use of appropriate filters or a monochromator between the excitation region and the photomultiplier will further reduce interference from scattered light and materials fluorescence. Finally, scattered light and fluorescence may be reduced by the use of spatial filtering techniques, i.e. the design of a light-collection system which will efficiently collect light emanating from the excitation region, but which will reject light arising from all other regions of the cell. This is accomplished with a series of lenses which image the excitation region on the photocathode of the photomultiplier. The disadvantage of this technique is that the restricted field-of-view resulting from the spatial imaging can degrade temporal information. At low pressures, the time required for a molecule to diffuse from the detector field-of-view can become short compared to molecular fluorescence life times or to chemical reaction times. Diffusion may be slowed to some extent by using an inert buffer gas at high pressures. This approach will work however, only if quenching of the LIF by the buffer gas is not too significant. This is true for most diatomic molecules even at pressures of a few hundred torr; however for polyatomic molecules such as $NH_2(^2A_1)$,[2] the quenching by the bath gas may be more important, so that operation at lower pressures and with a larger field-of-view may be necessary.

# III. SUPPORTING CALCULATIONS

## A. General

Calculations, based upon the photolysis of hydrazoic acid, $HN_3$, were performed to test the feasibility of the experiment. The $HN_3$ system has been studied in sufficient detail that reasonably accurate calculations are possible. These calculations give an indication of the sensitivity and flexibility of the apparatus. The first experiments will be performed on $HN_3$, and these data compared against the calculations will provide a further test of apparatus performance.

McDonald et. al.[3] have claimed that photolysis of $HN_3$ at 266 nm produces $NH(a\,^1\Delta)$ and $N_2(X\,^3\Sigma_g^+)$ in over 99% yield. The $NH(a\,^1\Delta)$ appears to be highly reactive toward $HN_3$ producing $NH_2(^2A_1)$ and presumably $N_3$. McDonald et. al. have not attempted to observe $N_3$ in their system, but others report it as being present as a secondary product of the photolysis.[4-7] The experiments of McDonald et. al. do not preclude the possibility that $N_3$ may also be formed in the primary photolysis as others have suggested,[5-7] nor do they indicate the origin of other states of NH which have been observed by others in photolytic systems.

In the following sections we reproduce the calculations performed to test the experimental concept. First, we compute the density of fragments produced in the photolysis laser beam and the signal level to be expected by probing this fragment density with LIF both in terms of photon flux incident upon the PMT photocathode and the voltages to be measured by the boxcar integrator. In the latter computation we also treat sources of signal noise. Finally, we consider the effects of fluorescence quenching and diffusion upon the expected signals.

## B. Density of Photolysis Products

The density of photolytic fragments produced by the photolysis laser pulse may be calculated using Beer's Law,

$$\frac{N}{V} = \frac{I_o - I}{A\ell} = \frac{I_o}{A\ell}\,(1 - e^{-C\,\sigma_\lambda \ell}) \quad , \tag{1}$$

which in the thin target limit reduces to

$$\frac{N}{V} \approx \frac{C\,\sigma_\lambda}{A}\, I_o \quad . \tag{2}$$

N/V is the fragment density produced by a laser beam of initial intensity $I_o$ and cross sectional area A propagating a distance $\ell$ through $HN_3$ at concentration C. The absorption cross section at wavelength $\lambda$ is given by $\sigma_\lambda$. I is the intensity of the laser beam after it exits the cell. For a typical condition of our experiment, the following values are appropriate:

$C = 10^{14}$ molec $cm^{-3}$,

$\sigma_{265} = 5.75 \times 10^{-20}$ $cm^2$,[8]

$A = 1$ $cm^2$,

$I_o = 5$ mJ $= 6.67 \times 10^{15}$ photons.

This leads to a transient fragment density,

$$\frac{N}{V} = 3.84 \times 10^{10} \text{ molec cm}^{-3} \quad ,$$

which is the density of $NH(a^1\Delta)$ produced in the photolysis before losses due to chemical reaction and/or diffusion have occurred.

## C. LIF Intensity

The NH($a^1\Delta$) is detected by LIF operating upon the $c^1\Pi \Rightarrow a^1\Delta$ transition at 326 nm. The calculation of the signal due to LIF assumes no quenching of the NH($c^1\Pi$) fluorescence and no optical losses due to reflections or absorptions in the collection system. The optical system is designed to have an effective f-number of 1.6 corresponding to collection of 2.5% of the total fluorescence. We also assume a photomultiplier quantum efficiency, $\eta$, of 20%. The probe laser intersects the observation region at right angles to the photolysis laser, thus giving an effective absorption path length for the probe laser of 1 cm. The detector fluorescence signal is then the number of photons absorbed by NH from the probe laser beam multiplied by the collection efficiency of the optical system and the quantum efficiency of the photomultiplier:

$$I_f = (I_o - I) \frac{\Omega}{4\pi} \eta \quad . \tag{3}$$

The absorption of photons in the probe laser beam by the photolysis fragments can be calculated adequately by line-absorption formulae. We assume that the line width of the absorbing NH($a^1\Delta$) is dominated entirely by Doppler broadening at ambient temperature, i.e. 300°K. The Doppler width (FWHM) is given by[9]

$$\Delta\nu_D = \frac{2(2R\ell n2)^{1/2}}{\lambda_o c} \left(\frac{T}{M}\right)^{1/2} \; (\mathrm{cm}^{-1}) \quad , \tag{4}$$

or = 0.1 $\mathrm{cm}^{-1}$ for NH transitions at 326 nm. The probe laser beam can be adequately described as a Gaussian distribution with a width of 0.4 $\mathrm{cm}^{-1}$ (the manufacturer's specifications).[10]

The fractional absorption is given by

$$A_\alpha = \frac{I_o - I}{I_o} = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}\,(k_o\ell)^n}{n!(1+n\alpha^2)^{1/2}} \,, \tag{5}$$

where $k_o\ell$ is the optical depth of the absorbers and $\alpha$ is the ratio of the emission to absorption line widths. In the limit of small optical depth, we need retain only the first term in the sum. Thus, the number of absorbed photons becomes

$$I_{abs} = I_o - I = \frac{k_o\ell\, I_o}{(1+\alpha^2)^{1/2}} \;. \tag{6}$$

The optical depth may be calculated if the absorption oscillator strength of the transistion is known,[9] i.e.

$$k_o\ell = \frac{2}{\Delta\nu_D}\sqrt{\frac{\ell n 2}{\pi}}\,\frac{\pi e^2}{m_e c}\,Nf \;. \tag{7}$$

For a single rotational line we have

$$f^{J''J'}_{v''v'} = \frac{S^{J'}_{J''}}{2J''+1}\, f^{abs}_{v''v'} \;, \tag{8}$$

where $S_{J''}^{J'}$ is the Honl-London factor and $f_{v''v'}^{abs}$ is the band absorption oscillator strength given by[11]

$$f_{v''v'}^{abs} = \frac{m_e c \lambda_0^2}{8\pi^2 e^2} \frac{du}{d_l} A_{v'v''} \quad . \qquad (9)$$

$A_{v'v''}$ is the Einstein coefficient and du and $d_l$ are the electronic degeneracies of the upper and lower states respectively. The transition probability for the transition NH($c^1\pi$, v' = 0) → NH($a^1\Delta$, v'' = 0) is $2.27 \times 10^6$.[12] For the P-branch transition from J'' = 2 we calculate $S_{J''}^{J'} = 3/2$ for each component of the Λ-doublet, or 3 overall.[13] The Λ-doublet splitting for the P(2) transition is only 0.06 $cm^{-1}$,[12] which is less than the Doppler line width. We, therefore, consider the two components as a compound line with an effective Doppler width of 0.12 $cm^{-1}$, i.e. slightly broadened from the single line case due to the Λ-doubling. The oscillator strength is $f_{0,0}^{2,1} = 2.17 \times 10^{-3}$. Using Eq. 7 we find that

$$k_o \ell = 1.53 \times 10^{-14} N_{v''=0}^{J''=2} \ell \quad . \qquad (10)$$

McDonald et. al.[3] have shown that the phytolysis of $HN_3$ yields only NH($a^1\Delta$, v''=0). If we assume a Boltzmann rotational distribution at 300°K, $N_{J''=2}/N_{total} = 0.25$, and $k_o \ell = 1.47 \times 10^{-4}$. From Eq. 6 we calculate $8.45 \times 10^7$ photons are absorbed from the probe laser beam and that $I_f = 4.2 \times 10^5$ photoelectric events per laser pulse. A signal this large would saturate the photomultiplier. The actual signal should be smaller due to losses in the collection system and to losses from the narrow-band interference filters used to reject scattered light. However, the magnitude of the calculated signal indicates that initial experiments should not be signal limited, and that our sensitivity for the detection of fragments should be on the order of $10^6$ to $10^7$ molec $cm^{-3}$.

## D. PMT Signal and Noise

The output from the photomultiplier is a current pulse, which is shunted to ground through a load resistor, $R_L$, and a voltage is detected by the box-car integrator. The value of $R_L$ is made as large as possible to maximize the voltage within limitations imposed by the box-car gate width and the capacitance of the line between the PMT and the input of the box-car. Optimum values of the PMT $R_L C_L$ time constant are between 0.02 and 0.2 times the box-car gate width,[14] e.g., for $\tau_{gate} = 2.0\ \mu s$, 40-400 ns. In order to minimize $C_L$, the cable length between the PMT and the box-car must be kept short. It is easiest to do this if a preamplifier is inserted close to the PMT output. Then, cable lengths of a foot are feasible for which $C_L \sim 30$ pf and $R_L$ will be $\sim 10^4\ \Omega$.

The voltage signal read by the box-car is given by Ohm's Law

$$V_s = I_s R_L \tag{11}$$

where $I_s$ is the average PMT anode current,

$$I_s = \frac{\eta N G e}{\tau_{gate}} . \tag{12}$$

$\eta$ is the PMT quantum efficiency, N is the number of photons incident upon the photocathode, G is the PMT gain and e is the electron charge. For a typical gain of $10^6$, $R_L \sim 10^4\ \Omega$ and $\tau_{gate} = 2\ \mu s$, the voltage will be 0.80 mV per photoelectric event ($\eta N$), or 8.0V for $10^4$ photoelectric events per laser shot.

Sources of signal noise[15] are statistical fluctuations in the signal source itself,

$$V_{SN} = \sqrt{\eta N}\,\frac{Ge\,R_L}{\tau_{gate}} \quad , \tag{13}$$

dark noise generated within the PMT,

$$V_{DN} = (2e\,I_d\,G\Delta f)^{1/2}\;R_L \quad , \tag{14}$$

thermal noise in the load resistor,

$$V_{TN} = 1.29 \times 10^{-10}[R_L\,\Delta f]^{1/2} \quad , \tag{15}$$

and amplifier noise in the box-car or preamplifier (specified by manufacturer). In the above equation $I_d$ is the PMT anode dark current, and $\Delta f$ is the noise band width of the system. The noise band width is 1.57 times the signal band width which is $0.35/\tau_{rise}$ ($\tau_{rise} = R_L C_L$). The total noise is the square root of the sum of squares of the various noise components. The signal noise, the first three noise components, may be reduced by using a photomultiplier of high quantum efficiency, high gain, and low dark current, and by working with a large load resistor. Taking $G = 10^6$, $I_d = 2$ nA, $R_L C_L = 300$ ns, $R_L = 10^4\,\Omega$, and $\tau_{gate} = 2\,\mu s$, we calculate that $V_{SN} = 8 \times 10^{-4}\sqrt{\eta N}$ V, $V_{DN} = 3.42 \times 10^{-4}$V, and $V_{TN} = 1.75 \times 10^{-5}$V. Thus the only important contribution to the noise is the statistical fluctuation in the number of photons emitted per laser shot. This noise may be reduced an arbitrary amount by signal averaging.

## E. LIF Fluorescence Quenching

The reduction of the fluorescence signal by collisional quenching may be calculated from the Stern-Volmer relationship[9]

$$\frac{I}{I_o} = \frac{1}{1 + \tau_{rad} k_q [Q]} \quad . \qquad (16)$$

For NH($c^1\pi$), $\tau_{rad} = 4 \times 10^{-7}$ s.[16] If we assume a quenching rate constant of $1 \times 10^{-10}$ cm$^3$ molec$^{-1}$ s$^{-1}$, then the reduction of fluorescence is less than 10% for quencher concentrations less than $2.5 \times 10^{15}$ molec cm$^{-3}$ or about 100 mtorr. This is not a severe limitation except for the inert buffer gas which will be at higher pressures. However, rate constants for quenching of electronic energy by gases such as helium and argon are generally $\leqslant 1\text{-}5 \times 10^{-16}$ cm$^3$ molec$^{-1}$s$^{-1}$. Thus, buffer-gas pressures of several hundred torr should not significantly reduce fluorescence due to collisional quenching.

## F. Diffusion

There are two problems created by diffusion. First, the molecules excited by the probe laser can diffuse out of the detector field-of-view before fluorescing, thus reducing the LIF detection efficiency and, in addition, render it pressure dependent. Second, the photolysis fragments can diffuse from the excitation region during the time interval between the photolysis and probe pulses, thus complicating the analysis of the temporal behavior. In both cases, the effects of diffusion may be reduced by operating at higher pressure, although one must be careful to strike a balance between the reduction of diffusional effects and the enhancement of quenching.

In the diffusion of electronically excited molecules out of the detector field-of-view prior to fluorescence, we are concerned only with diffusion in the plane defined by the two laser beams. Molecules diffusing in directions normal to this plane remain within the detector field-of-view. The solution of the problem is that for the decay of the on-axis concentration in an infinite cylinder due to radial diffusion. In this case the radius is the effective radius of the detector field-of-view. The decay of photolysis-fragment density due to diffusion out of the region defined by the photolysis beam is also a problem in loss by radial diffusion but not axial diffusion. The LIF laser essentially probes the density along the axis of the cylinder defined by the photolysis laser beam. For this case the solution of the diffusion equation leads to the result[17]

$$\frac{C}{C_o} = 1 - e^{-a^2 P/4 D_o t} , \qquad (17)$$

where $C_o$ is the initial concentration, a the cylinder radius, P the pressure and $D_o$ the diffusion coefficient.

Combining a first-order loss process such as radiation or chemical reaction with the diffusive losses, we obtain[17]

$$\frac{C}{C_o} = e^{-t/\tau} \left\{ 1 - e^{-a^2 P/4 D_o t} \right\} , \qquad (18)$$

where $\tau$ is the first-order decay time, i.e. $\tau_{rad}$ for radiation or $(k[Q])^{-1}$ for a bimolecular reaction under pseudo first-order conditions. The diffusion coefficient of most gases in argon is about 160 $cm^2 s^{-1}$ at 1 torr. For the radius a = 0.5 cm, which is essentially the radius of the photolysis laser beam as well as the diameter of the detector field-of-view, we conclude that the reduction in concentration is less than 10% if

$$t < 1.7 \times 10^{-4} P. \quad , \tag{19}$$

for t in seconds and P in torr. Thus, even at 1 torr diffusional losses will be negligible during typical molecular decay times of less than a few microseconds. Chemical reaction times in our reactor will be more typically on the order of hundreds of microseconds so that losses due to diffusion of the photolysis fragments will compete in importance with reaction losses at a bath gas pressure of 1 torr. However, operation at pressures of 10 to 100 torr will alleviate this problem.

## IV. CONCLUSIONS

The major features of the planned experiment have been defined and approximate experimental conditions have been calculated. These calculations indicate that the experiment to study the wavelength photolysis of gaseous azides is feasible and that the apparatus has considerable flexibility as designed. This information has been used to define the required specifications for the major equipment necessary to perform the experiment. The major components of the experiment have been purchased under the capital budget of the contract. During the next reporting period the major efforts will be the detailed design and construction of the apparatus, the purchase of the necessary peripheral equipment and supplies, and the completion of a laboratory area to house and perform the experiments.

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