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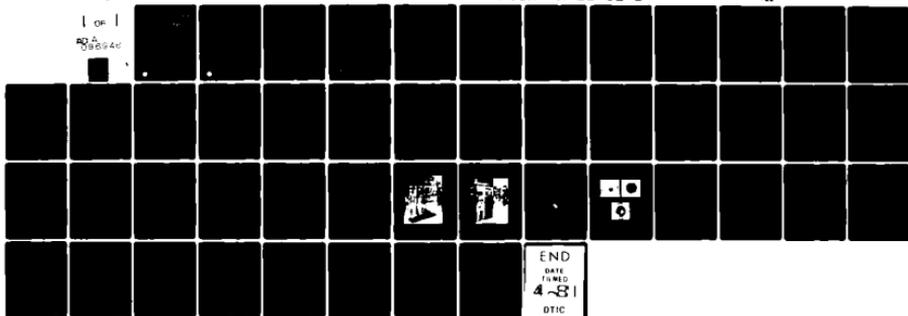
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PROGRAM TO INVESTIGATE LASER INDUCED
SYNTHESIS OF CHEMICAL MATERIALS

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P. M. Castle
Principal Investigator

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Final Technical Report
For Period July 1, 1978 to June 30, 1980

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November 1980

Air Force Office of Scientific Research
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This Final Technical Report describes the work specifically directed toward the use of lasers to synthesize highly reactive fluorine containing species as well as related work carried out under Westinghouse support related to the general use of lasers for chemistry. The original objectives concerning the synthesis of NF_4BF_4 and related compounds were not achieved. It is not felt, however, that this lack of success lies as much in the lack of validity in the techniques but, rather, inexperience in the area of fluorine chemistry.		

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AFOSR Research Program F49620-78-C-0113

PROGRAM TO INVESTIGATE LASER INDUCED SYNTHESIS OF CHEMICAL MATERIALS

P. M. Castle

Westinghouse Research and Development Center

Pittsburgh, Pennsylvania 15235

1. PROGRAM OBJECTIVES

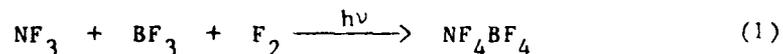
The overall objective of this program was the study and evaluation of lasers as applied to the synthesis of chemicals, with highly reactive species being of particular interest. The more specific objectives, as can be seen in Figure 1, deal with the chemistry of fluorine compounds. The program was designed with several stages of experimentation. In the initial phases the feasibility was to be proven via the synthesis of a model compound, NF_4BF_4 . This compound had been previously produced by standard UV photochemical techniques and would serve as a benchmark indicating the probable success or failure of additional experimentation. The rest of the program was designed as an extension of that which was learned in the synthesis of NF_4BF_4 . Augmenting the technical objectives was the exchange of information discovered in the course of studies in the general area of laser induced chemistry which were funded separately by the Westinghouse Research & Development Center.

2. STATUS

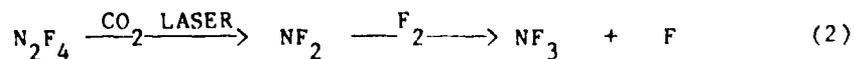
The progress made during the course of this program was minimal. The objectives concerning the demonstration of the applicability of lasers to this type of chemistry were not achieved. However, this failure was not necessarily due to the scientific principles involved but more probably caused by unfamiliarity with the practical aspects of fluorine chemistry and handling. Significantly more information was generated in parallel studies of the gas phase, laser induced chemistry of less reactive species. These studies were internally funded by Westinghouse.

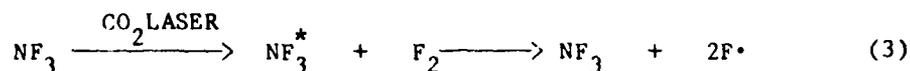
2.1 Synthesis of NF_4BF_4

The goal of this portion of the program was the demonstration of the use of infrared laser photochemistry to produce the molecule tetrafluoroammonium tetrafluoroborate (NF_4BF_4). This molecule had been prepared by standard UV photolysis techniques as well as by chemical methods.⁽¹⁻³⁾ In the UV photochemical method the following overall reaction occurs:



The initiating step in the reaction has been postulated to be the liberation of the fluorine atom radical by the fluorine molecule upon the absorption of a UV photon. It was felt fluorine atoms could be produced in several different ways using infrared radiation from a CO_2 laser:





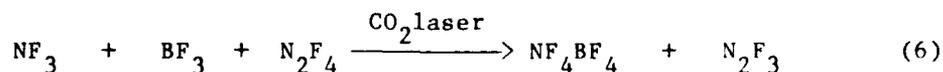
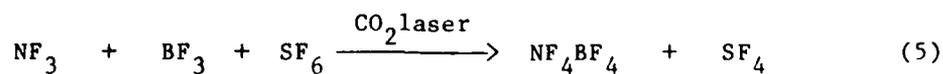
There was the additional possibility of the simple dissociation of F_2 utilizing the UV radiation available from a laser such as the excimer ArF.

The barriers to successful completion of this task lay in the difficulties experienced in the construction and maintenance of the gas handling and irradiation facilities. Delays in the delivery of a number of the components of the vacuum system put the program behind schedule by nine months or more. The biggest problem, however, was the maintenance of the transmissive windows in the aggressive environment of the experiment. Figures 2-4 show the schematic for the gas handling system and photographs of the completed setup. The system was constructed to be portable in order to allow interfacing with more than one laser. The leak rate for the total system was $1.73 \times 10^{-3} \text{ cm}^3\text{-torr/sec}$, or in terms of pressure rise, $1.16 \times 10^{-6} \text{ torr/sec}$.

The sample cell which is shown in Figure 5 was designed to allow radiation and spectroscopic monitoring simultaneously at right angles. The cell is also equipped with a cold leg to facilitate in-situ preparation of gas mixtures. For these experiments the cell windows were originally chosen to be KCl with laser grade surface finishes. However, there were difficulties experienced in using these windows in an aggressive environment. The picture of two of the cell windows, shown in Figure 6, indicates the type of damage experienced at the laser beam entrance and exit windows. In order to combat this difficulty the KCl substrates were coated by multiple layers of MgF_2 and BaF_2 in the hope of passivating the surfaces against attack by fluorine and fluorine atoms. While the coating provided antireflection capabilities, it did not enhance the resistance to chemical attack to any great degree. The window damage leads to several problems. As seen in Figure 6, the

damage site is opaque. As such it heats up on absorption of the laser beam. The reactions that occur subsequent to this, within the cell, are no longer homogeneous gas phase reactions driven by the laser beam. Instead they are heterogeneous thermal reactions with the heat source at the cell window. The only positive indication found in this is the likelihood that fluorine atoms were produced. It is possible that the use of a window material such as barium fluoride would resist attack in this environment. However, there is the problem of window heating associated with this material as it is not as transparent at these wavelengths as are the alkali halide crystals.

There has been a CO₂ laser-initiated synthesis of NF₄BF₄ reported in the patent literature⁽⁵⁾ which appeared shortly before the beginning of this program. The reactions are based on initiation by pulsed CO₂ laser radiation. The two patented reactions, (5) and (6), are shown below.



In the case of reaction (5) the SF₆ acts as the primary absorber and the fluorine source. In reaction (6) N₂F₄ performs these functions. The author claims to have isolated product from these reactions. There is, however, no detail on the analysis of these products. These claims should be viewed with caution. A high efficiency is claimed for this gas phase process which is contrary to that which has been observed for the standard UV photolysis reaction.⁽⁴⁾ There is no reason to suspect that the overall mechanism of the UV photolytic reaction and the CO₂ laser induced reaction should be very different, with the exception of the initiating step. Christie et al., conclude that the low yield at room temperature in the gas phase stems from the fact that several of the intermediates in the reaction are thermally unstable. A CO₂ laser

pulse will certainly provide temperatures many hundreds of degrees in excess of room temperature. In addition, the chemistry that is indicated in reaction (6) is apparently predicated on the abstraction of a fluorine atom from N_2F_4 . The primary event observed upon the irradiation of N_2F_4 by a CO_2 laser has been shown by a number of researchers to be the dissociation into two $.NF_2$ radicals.⁽⁶⁾ The production of a stable N_2F_3 molecule or radical cannot be considered. These observations indicate the need for caution in the consideration of this work.

Our lack of success in this area of the program has not provided a valid example from which to judge the utility of laser induced chemistry in the synthesis of high energy compounds. In fact, there have been some successes both in our laboratories and elsewhere. Large quantities of $B_{10}H_{14}$ have been prepared in high yield by the action of a CO_2 laser on B_2H_6 (diborane).⁽⁷⁾ We have been able to prepare dichloroacetylene using a CO_2 laser and sensitizers. This will be discussed in more detail in a later section. It is hoped that in the future laser induced chemical processing will have another opportunity to be evaluated for high energy compound synthesis.

3. PROGRESS IN RELATED WESTINGHOUSE R&D CENTER PROGRAMS

The R&D Center has funded studies in laser induced chemical processes since 1974. We are currently doing research in two broad areas of laser photochemistry, infrared gas phase processes and visible light induced polymerization. Most of our studies in infrared laser induced processes have been concerned with the interaction of CW laser radiation with gas phase absorbers. More specifically, we have been concerned with the differences between normal thermal gas phase chemistry and the "unusual" chemistry that is occasionally observed in systems irradiated by lasers. Our investigations of laser initiated polymer chemistry have encompassed both free radical and charge transfer polymerization reactions. Some of our achievements and directions in these two areas will be discussed in the subsequent sections.

4. CW CO₂ LASER INDUCED PROCESSES

It has been recognized for some time that a laser provides a unique method for the coupling of energy into the gas phase. Much of the early work and a great deal of the current effort in the study of laser induced processing is still directed at the proof or discredit of the idea of "bond specific" laser induced chemistry. Most of the evidence accumulated up to this point seems to indicate that bond specific chemistry is only possible under very specialized sets of conditions. In addition, the conditions which have to be met in order to achieve bond selective chemistry are the types of restrictions that frustrate practical applications, i.e., low pressures, low quantum yield processes, low duty cycle pulsed systems, etc. Our studies of infrared laser induced processes have been directed to other areas. We have been primarily concerned with the chemistry which occurs when a CO₂ laser is used under conditions in which it should only be a source of thermal energy. It is under these conditions that some of the, thus far, unrationalized observations have been made. Our investigations have included attempts to unravel the thermochemistry, the thermal behavior and patterns, and the effects of physical processes such as convection in order to understand more fully the possibilities offered by infrared laser chemistry.

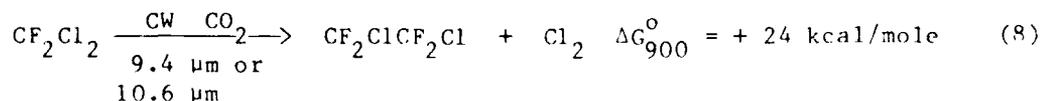
Most of the work we have carried out in this area has been directed toward the understanding of the chemistry of CF₂Cl₂ when excited in the gas phase (at pressures of 5 torr to one atmosphere) by a CO₂ laser. The R branch of the 9.4 μm band of a CO₂ laser strongly overlaps the C-F stretching mode of CF₂Cl₂. The P branch of the 10.6 μm transition of the laser overlaps the C-F bending mode. Both of these spectral features have large absorption coefficients. Despite the fact that the atomic motions involved in these two vibrational modes are

quite different, the chemistry which can be observed, as a result of absorption of laser energy at these two different frequencies, is the same under similar pressure conditions. This would lead one to say that the processes which occur are thermal in nature rather than bond specific chemistry. The additional fact that the chemistry which does occur involves the C-Cl bonds rather than the C-F bonds, which are directly involved in energy absorption by the molecule, supports this idea.

In spite of the above arguments that the chemistry should be governed by thermodynamics, unusual reactions are observed. A calculation of the free energy change for the various possible thermally initiated reactions indicates that reaction (7) would be thermodynamically favored.

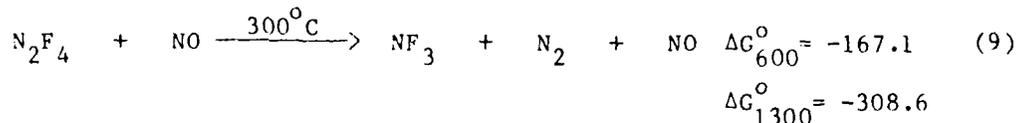


If one heats CF_2Cl_2 to 700°C in a glass tube, this is the distribution of products that is observed. There is also some SiF_4 produced, indicating that the observed reaction is probably heterogeneous, occurring at the tube walls. When CF_2Cl_2 is irradiated by a CO_2 laser at power densities of 7 W/cm^2 or greater, reaction (7) is observed in the range from 10 torr to one atmosphere. However, in the pressure regime from 200-400 torr, with irradiation powers in the range of $4\text{-}6 \text{ W/cm}^2$, there is a large contribution from reaction (8). The stoichiometry for the actual reaction has not yet been accurately determined, but the appearance of a large amount of $\text{CF}_2\text{ClCF}_2\text{Cl}$ is noted.

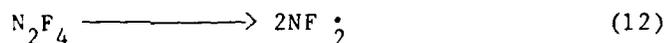


Basov et al.,⁽⁸⁾ have reported several similar occurrences. In the case of reactions (9) and (10), reaction (9) was observed under normal

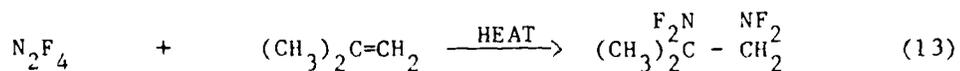
pyrolytic conditions, and (10) occurred during irradiation with a laser. The mechanism for reaction (10) has been altered by a better



understanding of the reaction of N_2F_4 after irradiation. It was thought, at the time, that reaction (11) occurred. It has since been demonstrated (5) that reaction (12) takes place. This is the same primary event that is observed under pyrolytic conditions. On this basis one would predict that the thermal process and the laser induced process should be the same, but they are obviously not.



The same authors⁽⁹⁾ report a reaction between N_2F_4 and isobutylene which takes two different directions depending on whether the mixture is heated or irradiated by a CO_2 laser. Reactions (13) and (14) illustrate these differences.



Again, since the primary step in the pyrolysis reaction and in the laser initiated reaction is the creation of an NF_2 , one should predict that the reactions will be the same, but they are not.

The behavior of these systems is unusual when examined with respect to their thermodynamic parameters. In the case of reactions (7) through (10), for which the equilibrium Gibbs free energy changes are shown, one notes anomalous behavior. Laser irradiation in these cases causes the reaction with the more positive free energy changes to be favored. In the case of the CF_2Cl_2 reactions, a reaction with a positive free energy change appears to be allowed. The problem presented here was approached with the attitude that the laser does not act in any way other than as an averageable energy source with no vibrational mode selectivity. With the knowledge that, in general, thermodynamic principles are obeyed at equilibrium, we have attempted to define the thermal characteristics of the system as it is irradiated. We have tried to obtain information regarding the temperature in the irradiated volume by inserting a very fine thermocouple in the beam path. An infrared imaging camera was employed in order to determine the shape, the size, and the qualitative temperature distribution of the high temperature zone.

Measurements of the absorbance of CF_2Cl_2 as a function of laser power and sample pressure, as well as the absorption cross sections computed from these data, appear in Figures 7 and 8. The variation of the cross section with pressure for a given laser power is suggestive of a large variation in temperature. The apparatus which was used in the temperature measurements was simple and consisted of a cell such as the one shown in Figure 9. The cell was modified in a manner which allowed the insertion of a thermocouple in the beam path near the entrance window.

The temperatures in the beam path were measured with the cell in either a horizontal or vertical position and with the thermocouple at several distances from the beam entrance window. Representative sets of these data are shown in Figures 10 and 11. Since the absorption cross sections plotted in Figure 8 were computed with number densities based on room temperature gas densities, the cross sections were recomputed using the measured temperatures and are displayed in Table 1. From the

behavior of the corrected values of the cross section (no variation with pressure), it is apparent that the measured temperatures show the proper qualitative behavior. The quantitative accuracy of these numbers is, however, suspect. The measured small signal cross section for this molecule is $1.6 \cdot 10^{-18}$, fifty percent larger than the corrected values. This could indicate that the temperatures are in error by as much as 500°K in the higher temperature regions.

TABLE I
Temperature Corrected Absorption
Cross Sections

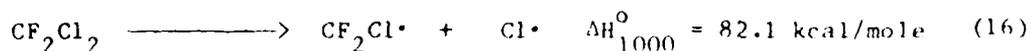
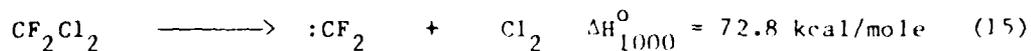
<u>Pressure (torr)</u>	<u>Temperature°K</u>	<u>(Measured)·10⁻¹⁹</u>	<u>(Corrected)·10⁻¹⁸</u>
3	588	5.85	1.14
10	778	4.00	1.03
30	932	3.32	1.04
50	979	3.19	1.07

The existence of these temperature gradients in the irradiation cell could lead to other effects. The laser beam (for most of the work) had a cylindrical cross section which was one eighth that of the cell. The cell walls remained close to room temperature during an irradiation. At the center of the beam, only 0.5 inches away, the temperature was 1000°C or more, a temperature gradient of 2000°C per inch. It was evident that there should be some sort of convective flow in such a system. A BOFORS thermal imaging camera was used to view the high temperature region of the beam/gas interaction volume by monitoring the radiation emitted from the sample in the 1-5 μ m region of the infrared spectrum. Several examples of these images appear in Figures 12 and 13. These images show two important facets of the thermal behavior of a strong absorber in an intense radiation field. The first of these is that optical density is

very important in determining the shape and size of the high temperature region. Also, convection affects not only the shape and the size of the high temperature region but also the position. In both Figures 12 and 13 in the higher pressure samples, the highest temperature regions have been totally isolated from the cell entrance window by convective flow of cooled gas towards the center of the window. This phenomenon is only readily apparent when the cell is irradiated in a vertical position. Figure 14 indicates, schematically, the reasons for this.

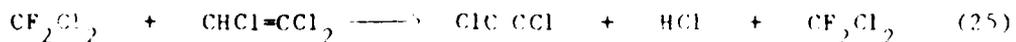
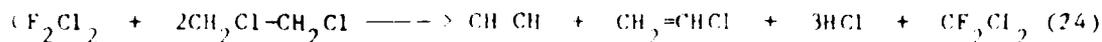
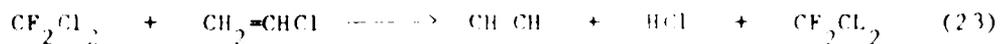
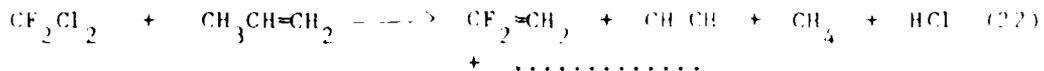
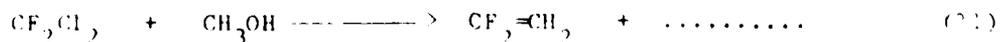
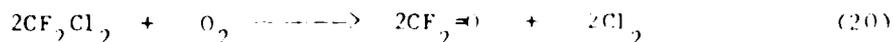
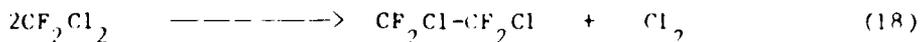
There is now an accumulation of data concerning the fact that temperatures in excess of 1000°C can be reached during the irradiation of an absorbing gas with a CO_2 laser. In addition, the infrared images provide at least qualitative indications of the effects of convection. How does this relate to the chemistry which was reported earlier? One of the most important features to note is that, in isolating the high temperature region completely from the cell walls and windows by convective flow, a high temperature region is created which is completely homogeneous in phase. All heterogeneous reactions, heterogeneous equilibria, and/or catalytic effects are eliminated. In this region gas phase reactions can occur under conditions previously available only in shock tubes. It is interesting to note that the pressure range 200-350 torr and the laser power of 5 W, that are associated with the convective isolation of the high temperature region from the walls, are parameters similar to the pressure and power under which the unexpected production of the $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ molecule was observed. Some simple calculations have been made on the gas velocities which indicate flow rates of 2 meters/second are reached. With flow patterns like the ones indicated in Figure 14, the reactants and products would be subjected to heating and cooling cycles in which the high temperature region would be traversed in 10 milliseconds or less. Conditions such as these could lead to kinetic limits on reactions instead of thermodynamic equilibration.

It would appear that the initial step in most of the CO₂ laser induced chemistry that we have observed in the gas phase of CF₂Cl₂ is the formation of :CF₂ (difluorocarbene):

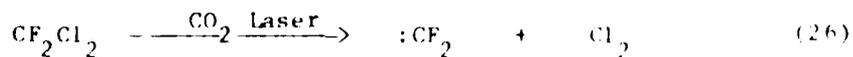


The heats of reaction for the two lowest energy processes, reactions (15) and (16), can be related to the activation energies for these processes. In the case of reaction (16) the heat of reaction is equivalent to the activation energy. This is true as there is no barrier to the recombination of the free radical products. However, there is a recombination barrier in the case of reaction (15) since it is a three center process. The activation energy for the insertion of :CF₂ into HI is 0.68 ± 0.45 kcal/mole.⁽¹⁰⁾ The mechanism for insertion into Cl₂ should be the same, i.e., the insertion of a non-binding pair from chlorine into a vacant pi orbital on the difluorocarbene.⁽¹¹⁾ The activation energy barrier will probably not be much larger, if at all. This small activation energy for the reverse reaction in (15) would probably add no more than 1 kcal/mole to the heat of reaction calculated for the forward reaction. The activation energy (ΔE_a) for reaction (15) is, therefore, somewhere in the vicinity of 74 kcal/mole.

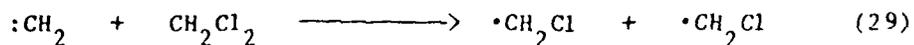
The numbers indicated for activation energies for the above reactions were computed for temperatures of 1000°K. Under the conditions of our experiments the temperatures were probably distributed on either side of 1000°K. But, in all cases, the formation of the difluorocarbene radical is the lowest activation energy channel for a thermal process. The reactions we have observed for CF₂Cl₂ reacting with itself and other molecules indicate the :CF₂ is the predominant initiating species. The list of these reactions is not extensive but is large enough to provide some information.



The reactions (17) through (22) provide the most obvious arguments for the formation of the $:\text{CF}_2$ radical from CF_2Cl_2 . Reaction (18), the thermodynamically unexpected reaction, is, in fact, most easily explained on the basis of reactions initiated by $:\text{CF}_2$ as shown by the following sequence:



The abstraction reaction (27) is analogous to abstraction reactions which are observed⁽¹²⁾ when methylene chloride is attacked by the methylene, $:\text{CH}_2$, radical.



Another strong indication of the possibility of the involvement of $:\text{CF}_2$ in the formation of $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ is that the apparent initial reaction of $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ to irradiation with a CO_2 laser is decomposition into $:\text{CF}_2$ and CF_2Cl_2 .⁽¹³⁾

The reactions (21) through (25) are important in that they illustrate the thermal nature of these processes. In these reactions the CF_2Cl_2 acts as a thermal source or a radical source. The role in which it participates is governed by the lowest activation energy reaction channel in the system. If the molecule with which CF_2Cl_2 is paired in the mixture has a thermal reaction which has a lower activation energy than the elimination of Cl_2 from CF_2Cl_2 , then that reaction will occur with the energy supplied by the photons absorbed in CF_2Cl_2 . If, however, the partner molecule has no low lying thermal dissociation channel, then the subsequent chemistry will be based on the dissociation of CF_2Cl_2 with the attendant production of $:\text{CF}_2$. We have succeeded in producing at least one very reactive molecule, dichloroacetylene, by this technique. Reaction (25) is the means by which this synthesis was carried out. One could extend this elimination type chemistry to higher activation energy processes by using an absorber with a higher thermal dissociation energy such as SiF_4 . This has been the subject of earlier studies.⁽¹⁴⁾

Our understanding of CW CO_2 laser induced chemistry can be summarized as follows:

1. The chemistry is thermal in nature but not necessarily at equilibrium.
2. Phase homogeneity is possible and important.
3. The lowest activation energy channel dominates. Laser chemistry with nonabsorbing molecules is possible by using inert absorbing molecules as partners.

4. Modest laser powers can produce temperatures well in excess of 1000°C.

There is still a great deal of work left to do in this area. Pulsed systems are not likely to be of considerable importance in a chemical production sense in the near future. Therefore, the understanding of the high temperature chemistry induced by CW systems will ultimately determine the laser's usefulness in chemical production applications.

5. LASER INDUCED POLYMERIZATION

Ultraviolet and visible photons are expensive. In terms of cost per pound of processed material, a laser driven reaction with unit quantum efficiency can consume between \$0.05 and \$1.00 of photons. These are large numbers for merely running the reaction. One of the situations in which the expense of these photons is mitigated is that in which one photon can trigger many subsequent reactions. Polymerizations provide such an opportunity. One quantum of energy can produce tens of thousands reactions from a single initiating event. We have been examining a number of reactions in polymer chemistry with the goal of finding initiators that will couple the laser energy into the monomer solution and create suitable propagating free radicals or ions. We have, thus far, investigated free radical reactions in acrylate and methacrylate systems and the possibility of using charge transfer complexes as photoinitiators for ionic polymerization.

5.1 Free Radical Polymerization of Acrylates

The molecule p-benzoquinone (PBQ) has a moderately strong absorption feature which extends from about 330 nm to about 520 nm (see Figure 15). This absorption is attributable to an $n\pi^*$ electronic transition associated with the carbon-oxygen double bond. This absorption spans all of the lasing lines of the argon ion laser, including those in the UV. Wilson and Wunderly⁽¹⁵⁾ had demonstrated that PBQ, when irradiated by an argon ion laser, would react readily with a molecule containing an unsaturation in the presence of oxygen under pressure. The resulting product was a reactive trioxane. The mechanisms involved were postulated to be free radical in nature and based on the PBQ diradical as the initiating species. It was felt that in a monomer system in which the free radical could be propagated, a

polymerization reaction would occur. The mechanism by which the reaction would proceed is shown in Figure 16.

A schematic of the apparatus which was used in these experiments appears in Figure 17. A thermocouple was placed in the solution in order to monitor the temperature rise due to the absorption of laser radiation and to detect the reaction exotherm. The helium-neon laser coupled with the spatial filter was used to monitor the progress of the polymerizations. This was accomplished by measuring the increased amount of scattered light as the polymer chains grew. It was found that the reactions were much more efficient if the system and the solutions were purged with an inert gas such as nitrogen to remove oxygen from the reactants. The laser which was used was a Coherent CR-18 USG, which is capable of delivering 9.0 watts at 488.0 nm. With the proper formulation it was necessary to use only small fractions of this power to carry out the polymerization.

The reaction appears to be extremely efficient. We have calculated quantum yields of 20,000 to 50,000 for a number of the acrylates which we have studied. Molecular weights have been measured, prior to complete gelation, which are as high as $2 \cdot 10^6$. Figure 18 shows the evolution of the molecular weight as a function of time as well as the associated reaction exotherm. The sharp rise in temperature above 50,000 MW is ascribed to the beginning of rapid increase in cross linking between the chains. The temperature rise is not as dramatic as it might appear. The full scale for the temperature axis for most of the molecules studied is in the vicinity of 15°C . Thus, the process is not a thermally triggered free radical process but depends on the electronic excitation by the laser. The concentrations of PBQ that are necessary for initiation and for optimum rate are atypically low. Many of the usual initiators, such as peroxides, are used at concentrations of 1-2%. PBQ works best in the acrylate systems at concentrations 50-100 times less than this. The monomers which have been polymerized using this technique include:

n-Hexylacrylate
2-Ethylhexylacrylate
2-Ethylbutylacrylate
t-Butylacrylate
Propanedioldiacrylate
Hexanedioldiacrylate
Trimethylolpropanetriacrylate
Tetraethyleneglycoldiacrylate
1,3-Propanedioldimethacrylate
2-Ethylhexylmethacrylate
Dicyclopentadiene
N-Vinylcarbazole

The polymerization of the last member of this group, N-vinylcarbazole, may not involve a free radical mechanism as do the rest. There are indications that a possible charge transfer intermediate may be involved.

We are currently trying to generalize this reaction to systems in which the chain extension portion of the free radical reactions is higher in activation energy. The main features of this reaction as they are understood at this time can be summarized as follows:

1. The reaction will occur with irradiation sources operating in the blue-blue/green (420-500 nm), the $n\pi^*$ electronic transition in PBQ.
2. Concentrations of 200-500 ppm of PBQ are sufficient to initiate the reaction.
3. PBQ acts as an inhibitor for thermal free radicals prior to its photoinitiation.
4. The reaction rate appears to be linear with respect to laser output power (prior to the cross linking phase of the reaction).

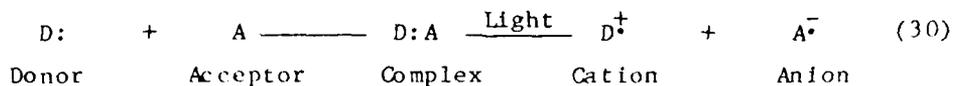
5. Quantum yields between 5000 and 50,000 have been observed, with the variation being dependent on monomer type and PBO concentration.
6. Polymerization to depths greater than two inches has been demonstrated.

While it is probably naive to assume that a process such as this will ever be able to compete with the normal thermal methods for initiating and maintaining polymerization reactions in bulk, there may be appropriate situations in which the speed (a ten watt laser could gel one pound of material in 20 s) or the geometric control will be important. In addition there are no coherent effects in this reaction. As a result, the polymerization could be effected by a more efficient incoherent source operating in the same wavelength region.

5.2 Charge Transfer Initiation of Polymerization

There are, in addition to free radicals, other methods of initiating and propagating chain reactions. Cationic and anionic processes are useful in this application. In contrast to the neutral unpaired electron which is present in the propagating species in free radical processes, there is a formal positive (or negative) charge which propagates with the growing chain. It is this carbonium ion or carbanion which is responsible for the chain growth in these systems. As another part of our study of laser induced polymerization we have been examining the possibilities for the creation of these carbonium ions and carbanions via visible and near UV laser excitation.

In these studies which comprise the most recent efforts in our program, both a pulsed nitrogen laser (337.1 nm) and an argon ion laser (488.0 nm and 350-360 nm) have been used to supply the visible and near UV light for the experiments. The lasers supply the energy to drive the second step in the following reaction:



In this reaction sequence the complex formed is identical to the complex formed between simple Lewis acids and bases. Although these complexes are neutral, they may be highly polarized. In these cases there is a large ionic component to the complex bond, and the donor molecule becomes the more positive end of the complex. If the proper energetics exist, it is possible to cause the complete transfer of an electron from the donor to the acceptor via laser irradiation. In our early work⁽¹⁶⁾ we have adopted a brute force screening technique in which a donor and an acceptor are mixed in solution and irradiated. The solution is subsequently tested for the appearance of polymer. Table II indicates the donors and acceptors which have been tried. About 25 combinations

TABLE II
CHARGE TRANSFER COMPLEX
STARTING MATERIALS

<u>DONOR MONOMERS</u>		<u>ACCEPTOR MONOMERS</u>	
STY	Styrene	TCE	Tetracyanoethylene
VT	Vinyltoluene	CHL	Chloranil
VA	9-Vinylnanthracene	DEF	Diethyl Fumarate
VN	2-Vinylnaphthalene	MA	Maleic Anhydride
t-BS	t-Butylstyrene	MM	Maleimide
HDDA	1,6-Hexanediol Diacrylate	FN	Fumaronitrile
Vl	1-Vinylimidazole		
2MVl	2-Methyl 1-Vinylimidazole		
VC	N-Vinylcarbazole		
 <u>SOLVENTS</u>			
MC	Methylene Chloride		
SUL	Sulfolane (Tetrahydrothiophene-1, 1-dioxide)		

have been screened. Of these 25 possibilities that were screened, only two of these, 2-vinylnaphthalene/fumaronitrile and 9-vinylanthracene/fumaronitrile, gave rise to polymer. The system 2-vinylnaphthalene/fumaronitrile was the only representative to provide consistent, reproducible results. The resulting polymer was shown to be a one to one copolymer. This result is strong evidence for a cationic mechanism based on the ionic decomposition of a charge transfer complex. It was mentioned earlier in the previous discussion of laser polymerization of acrylate that PBQ causes the polymerization of n-vinylcarbazole. It is suspected that this example of PBQ participation is through a cationic or anionic mechanism. In the case of the acrylate polymerizations, if the PBQ concentration is increased beyond a tenth of a percent the reaction is slowed considerably. The rate of the free radical formation and propagation is slowed by high concentrations of this free radical scavenger. However, in the case of N-vinylcarbazole the reaction rate maximizes at a very high concentration of PBQ (20-50% by weight). Additionally, strong color changes (toward the red end of the spectrum) indicate the presence of organic cations. We feel that, with these simple first experiments, we have demonstrated that it is possible to initiate and propagate both anionic and cationic polymerization reactions using charge transfer complexes as the starting materials.

6. LIST OF PUBLICATIONS

There were no publications created concerning the production of NF_4BF_4 . However, related projects supported by Westinghouse have produced several which are published, submitted, or in draft.

LASER POWER DENSITY DEPENDENCE IN ABSORPTION MEASUREMENTS, P. M. Castle, J. Applied Spectroscopy, 34(3), 311 (1980).

LASER INITIATED POLYMERIZATION OF CHARGE-TRANSFER MONOMER SYSTEMS--PART I, M. A. Williamson, J. D. B. Smith, P. M. Castle, and R. N. Kauffman, submitted to Polymer Preprints.

TEMPERATURES AND TEMPERATURE DISTRIBUTIONS IN LASER HEATED GASES, P. M. Castle, under revision for J. Phys. Chem.

LASER INITIATED BULK POLYMERIZATION OF ACRYLATES, P. M. Castle, in draft for J. Polymer Science.

7. PROFESSIONAL PERSONNEL ASSOCIATED WITH THE PROGRAM

P. M. Castle, Principal Investigator

D. C. Phillips, Manager, Chemical Physics

8. INTERACTIONS

Presentations of this work have been given in March of 1979 and 1980 at the AFOSR/AFRPL Meetings in Lancaster, CA.

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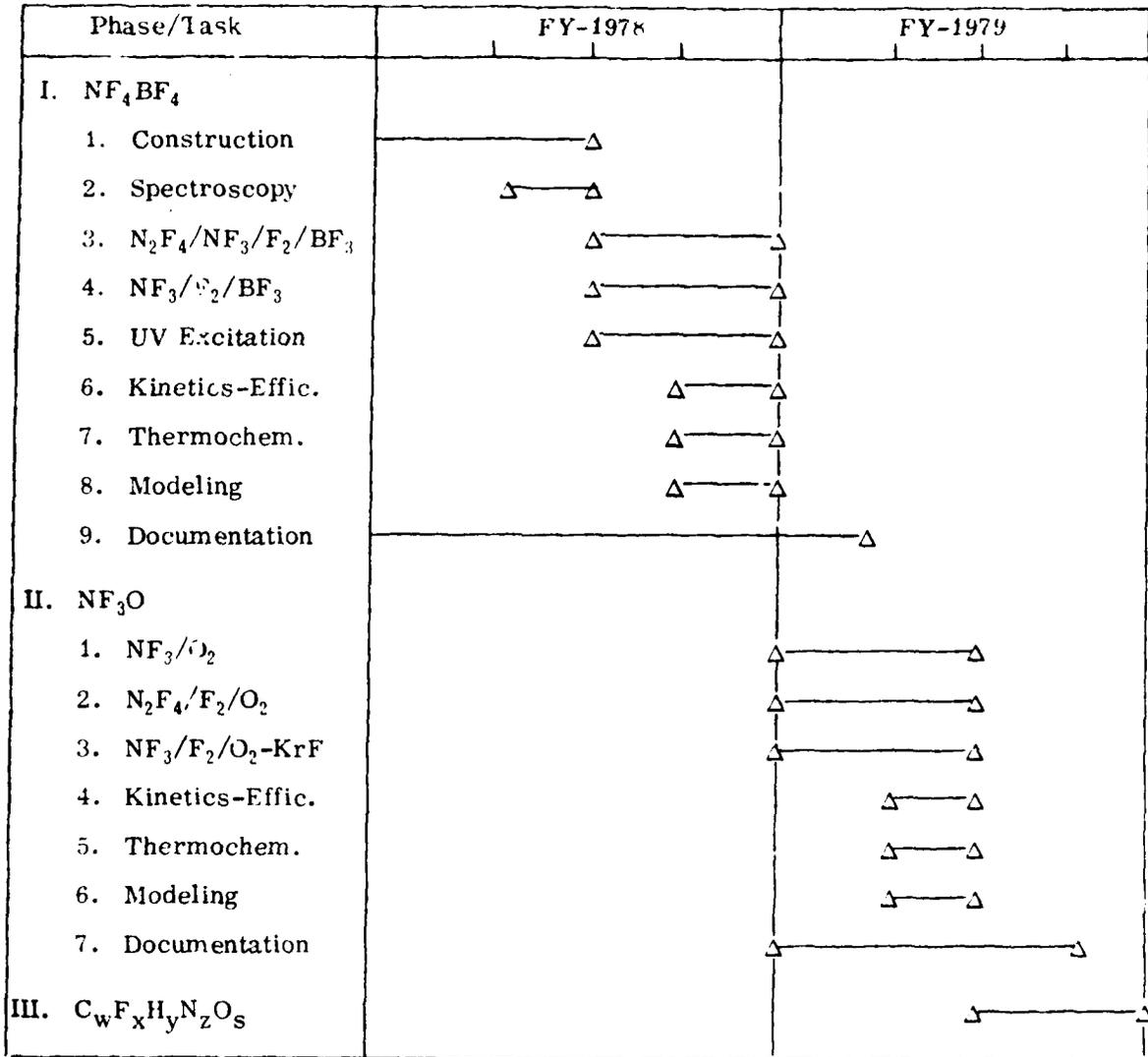


Figure 1 — Approximate time schedule.

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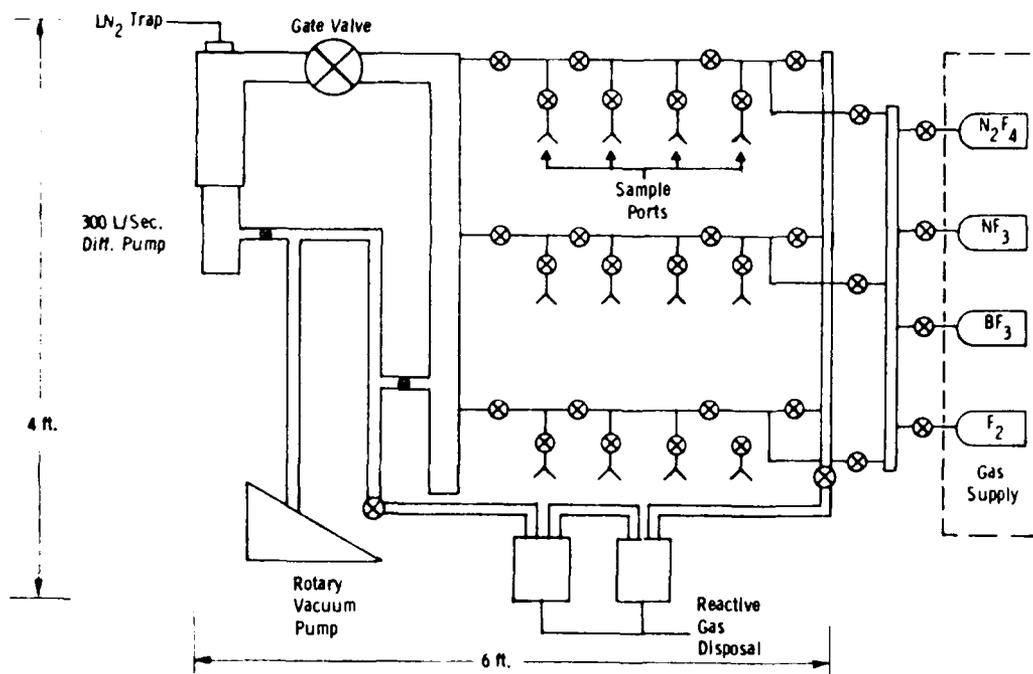
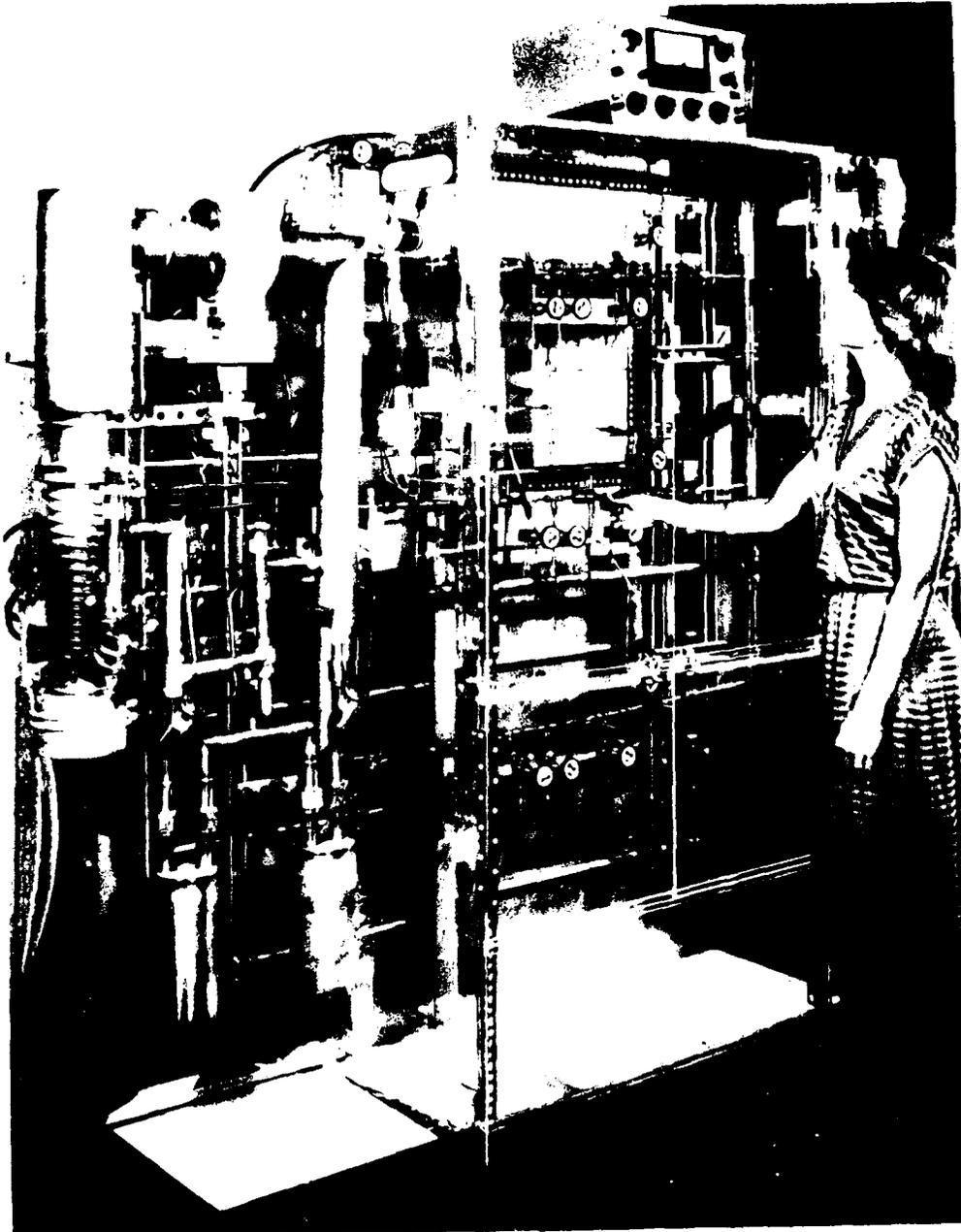


Fig. 2 - Schematic of the corrosive gas handling apparatus



1. A woman operating a textile mill machine.



FIG. 4. REAR VIEW OF THE PORTABLE CORROSIVE GAS HANDLING FACILITY

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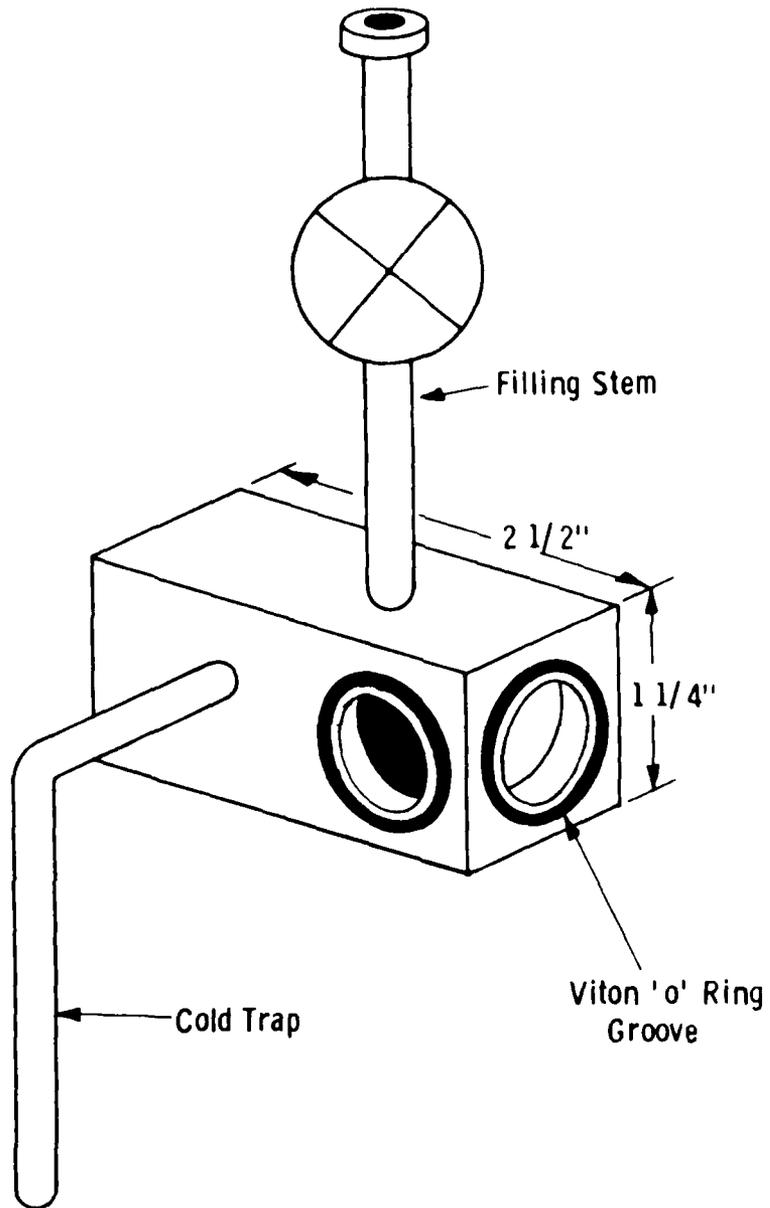


Fig. 5 - 4-window stainless steel, spectroscopy and irradiation cell

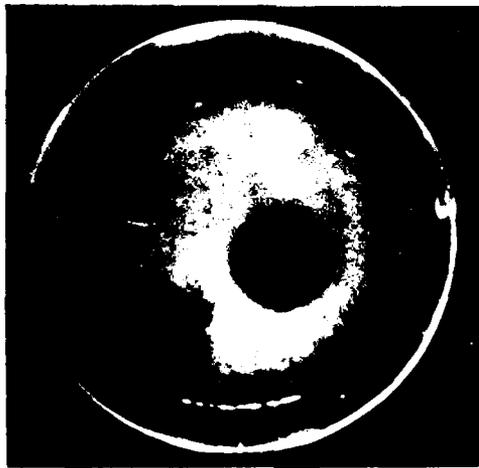
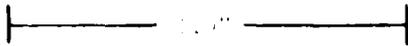
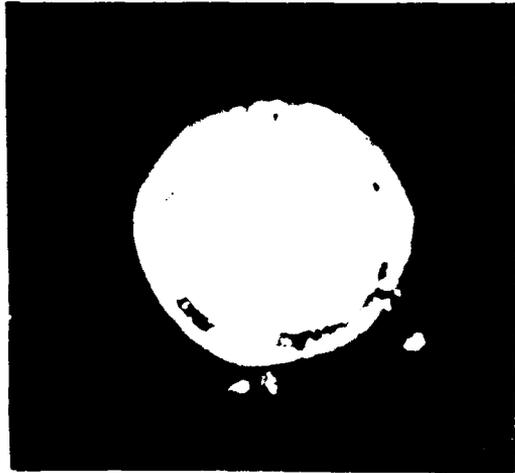
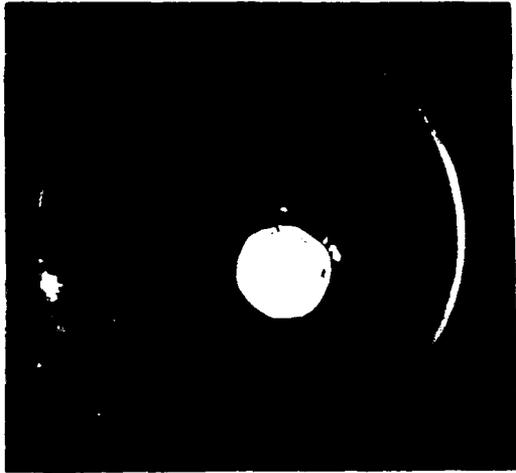


Figure 1. (a) Micrograph of a small circular object with a curved line. (b) Micrograph of a large bright circular object. (c) Micrograph of a circular object with a central dark spot.

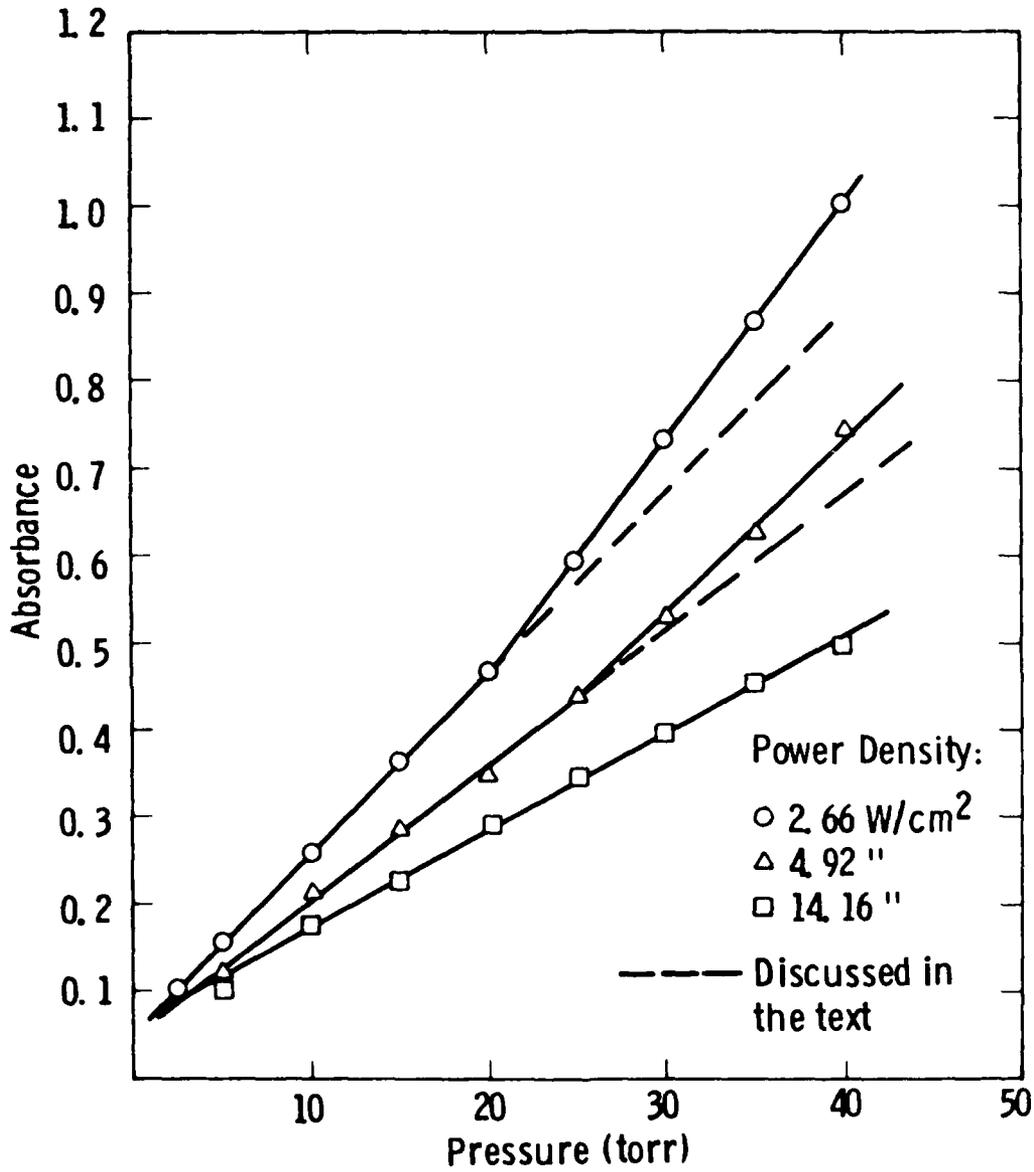


Fig. 7 - Absorbance as a function of cell pressure for several laser powers

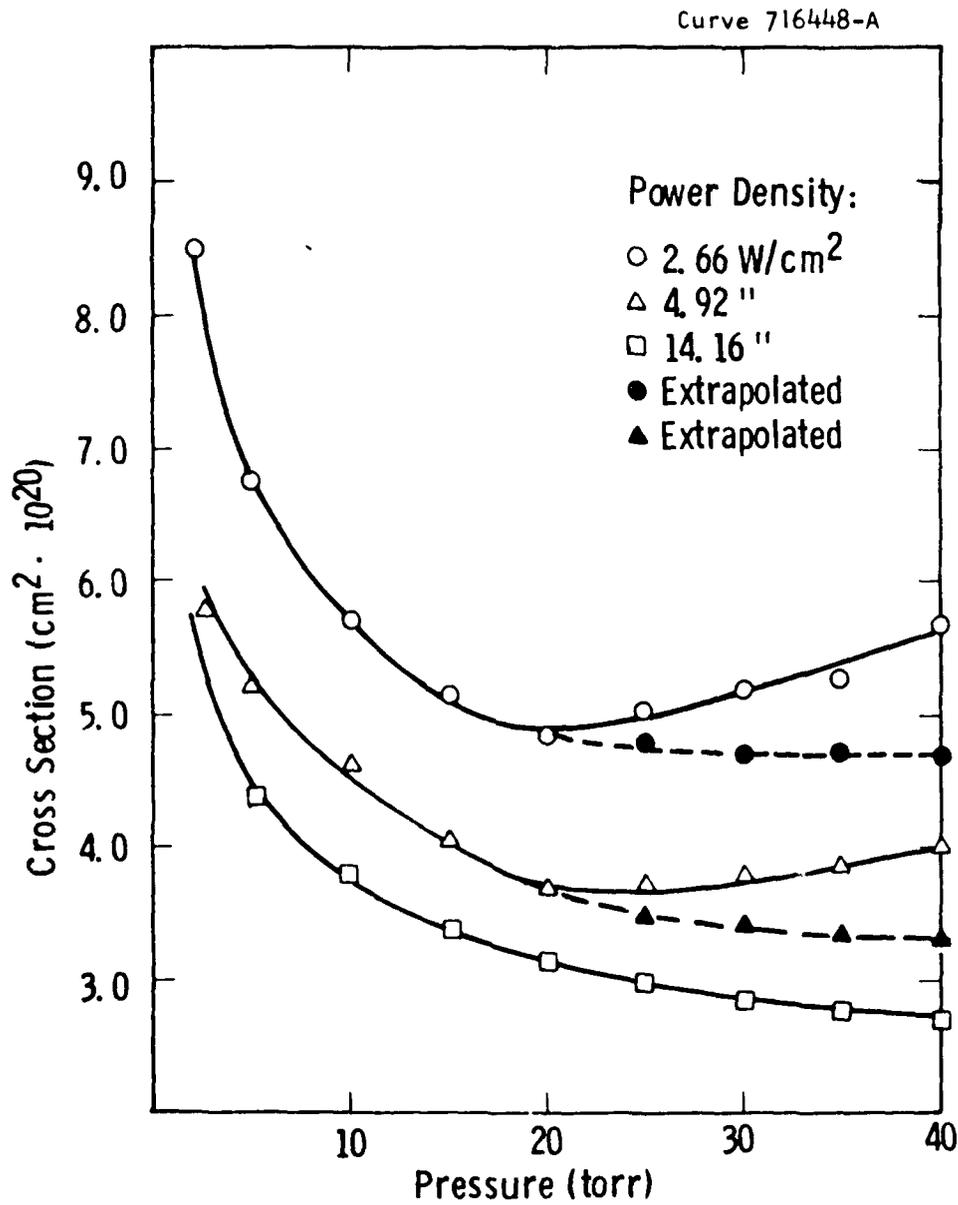


Fig. 8 - Absorption cross section as a function of laser power density. (Dashed lines were computed from the extrapolated data in Fig. 3.)

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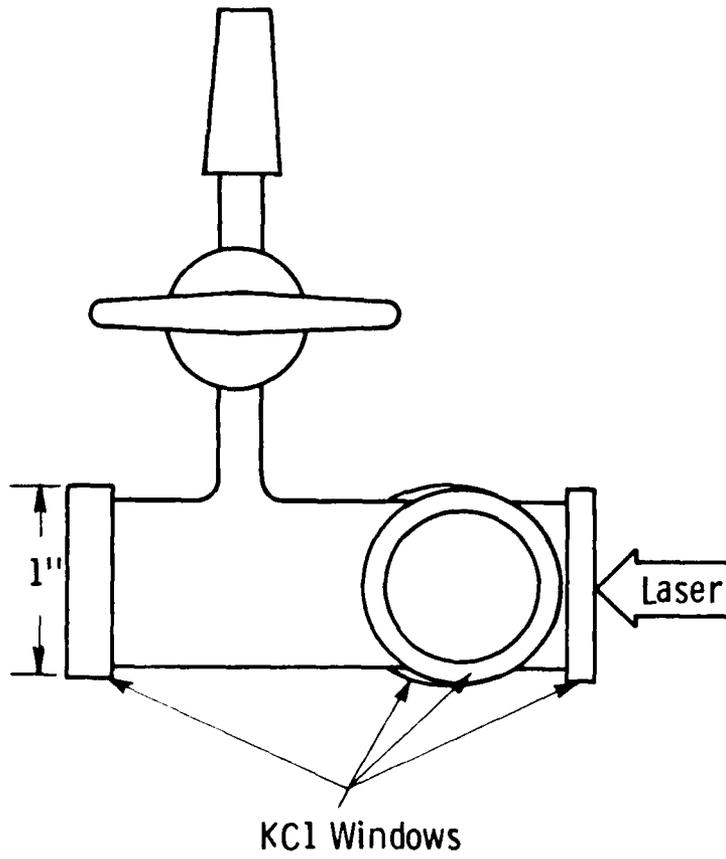


Fig. 9 - Sample cell

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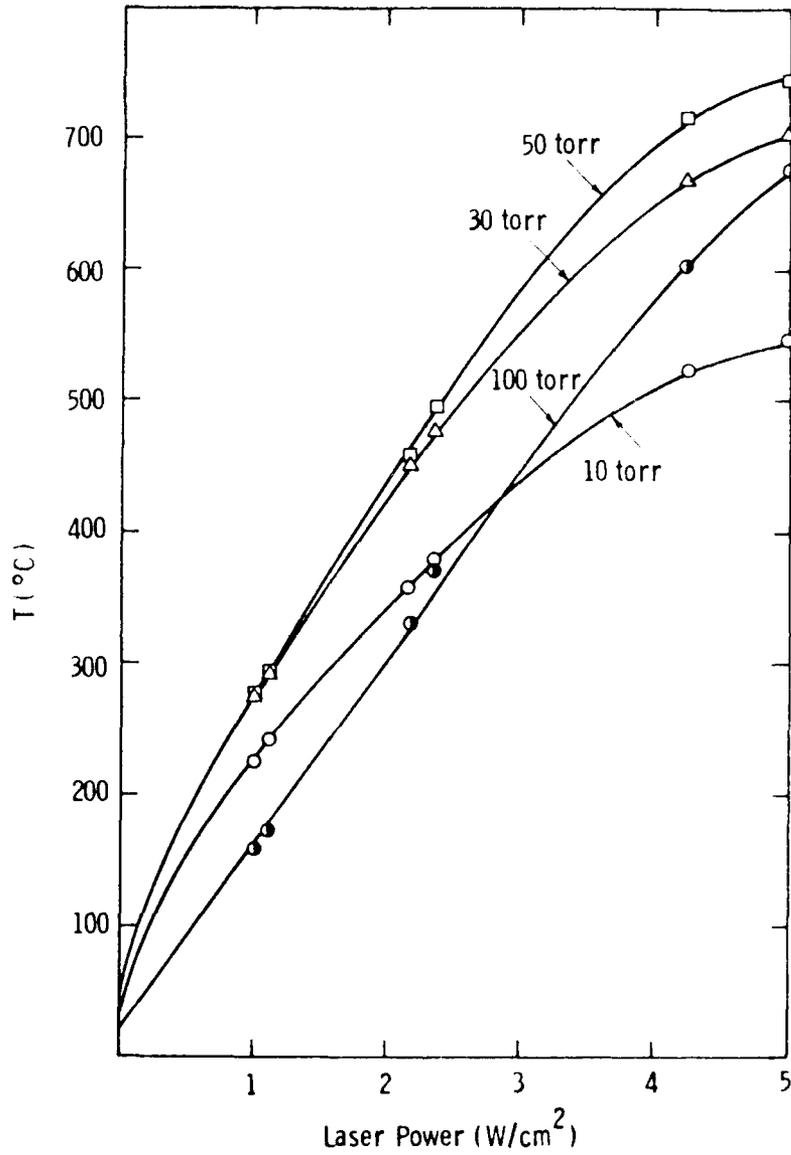


Fig. 10— Temperatures in CF_2Cl_2 on the beam axis with the cell in the horizontal position and the thermocouple 5mm from the beam entrance window

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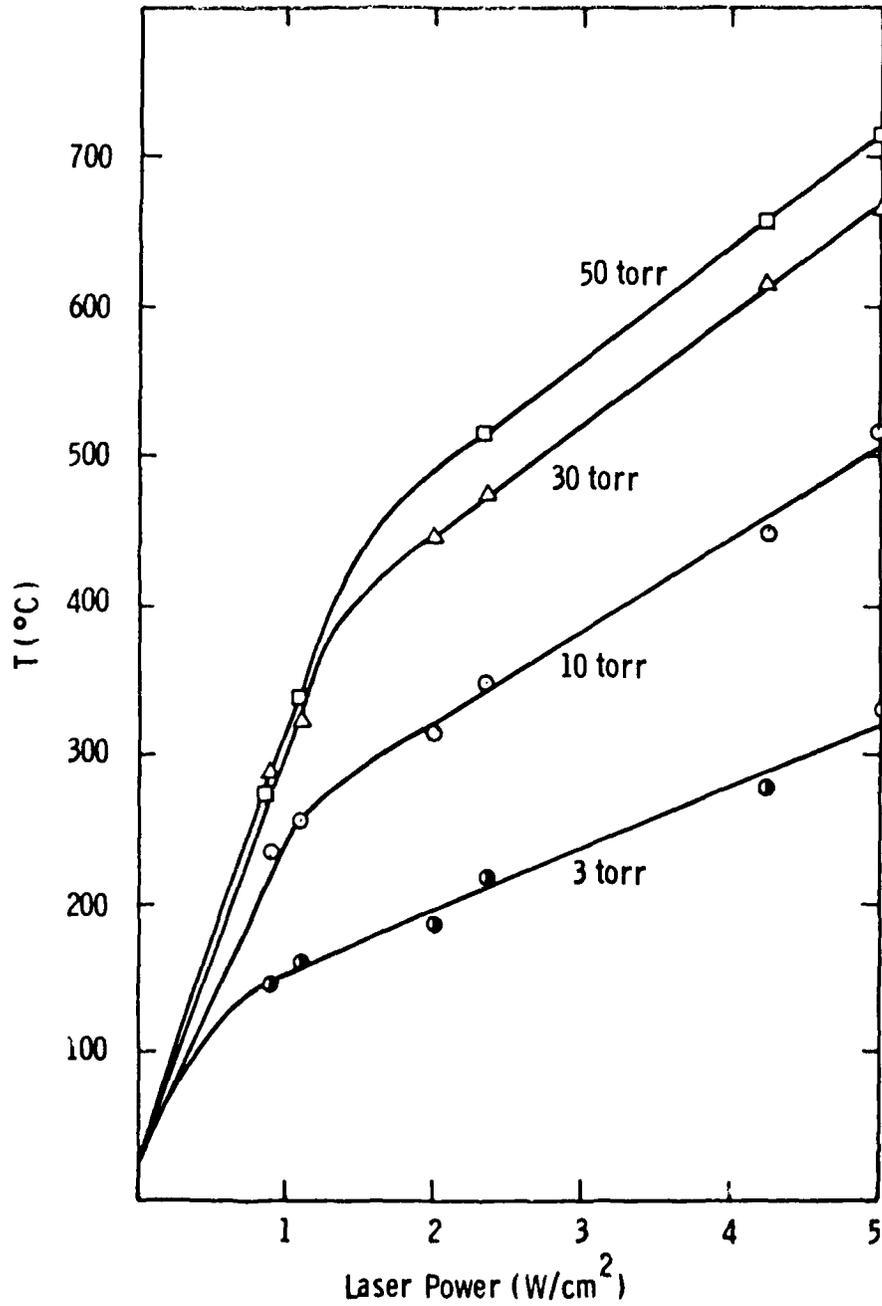


Fig. 11 - Temperatures in CF_2Cl_2 on the beam axis with the cell in the vertical position and the thermocouple 4 mm from the beam entrance window

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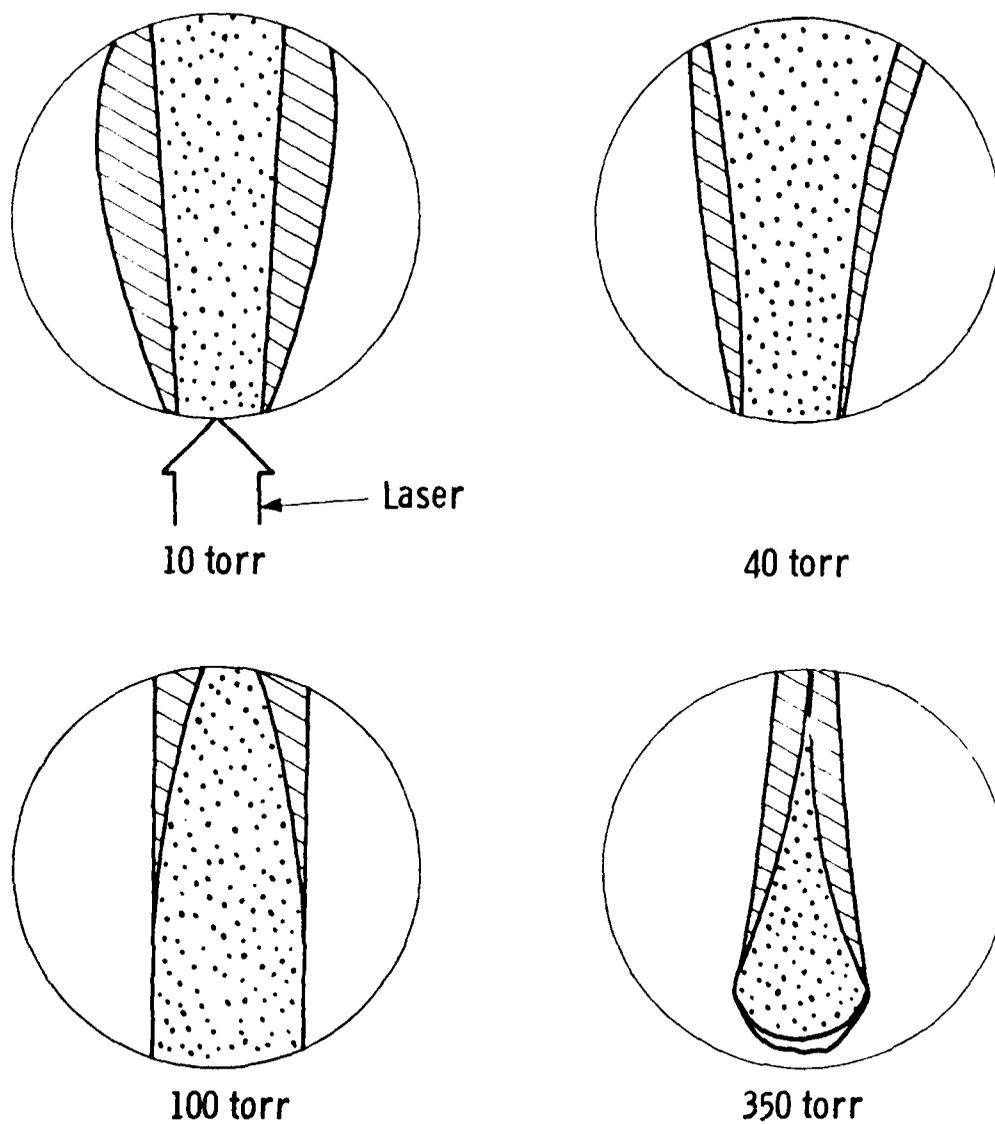


Fig. 12— Vertical irradiation of CF_2Cl_2 by a CO_2 laser R (18) .
9.4 μm band, 5W. The gas contained in the cross hatched
volume is at a temperature between that of the bulk gas and
the central portion of the laser heated volume

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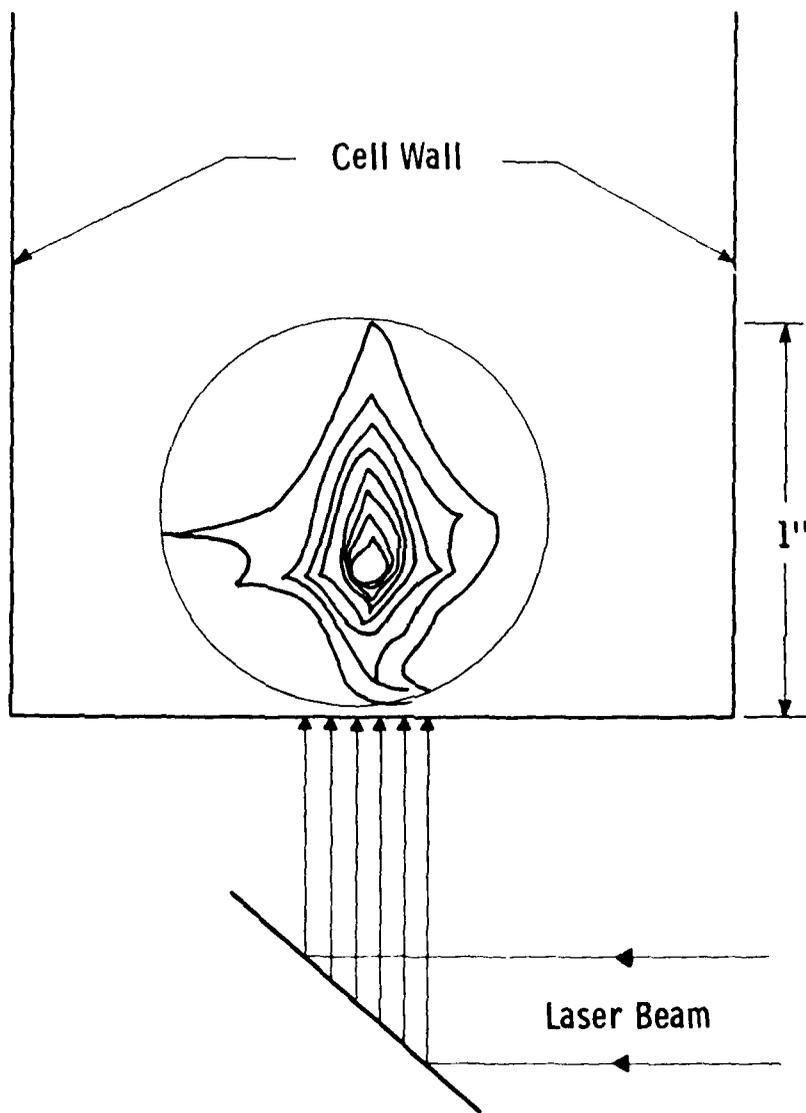


Fig. 13— Superimposed contours of isotherms as imaged using a Bofors Thermal Imaging Camera. 500 torr CF_2Cl_2 irradiated by 4 W R(24), $9.4 \mu\text{m}$ CO_2 laser line

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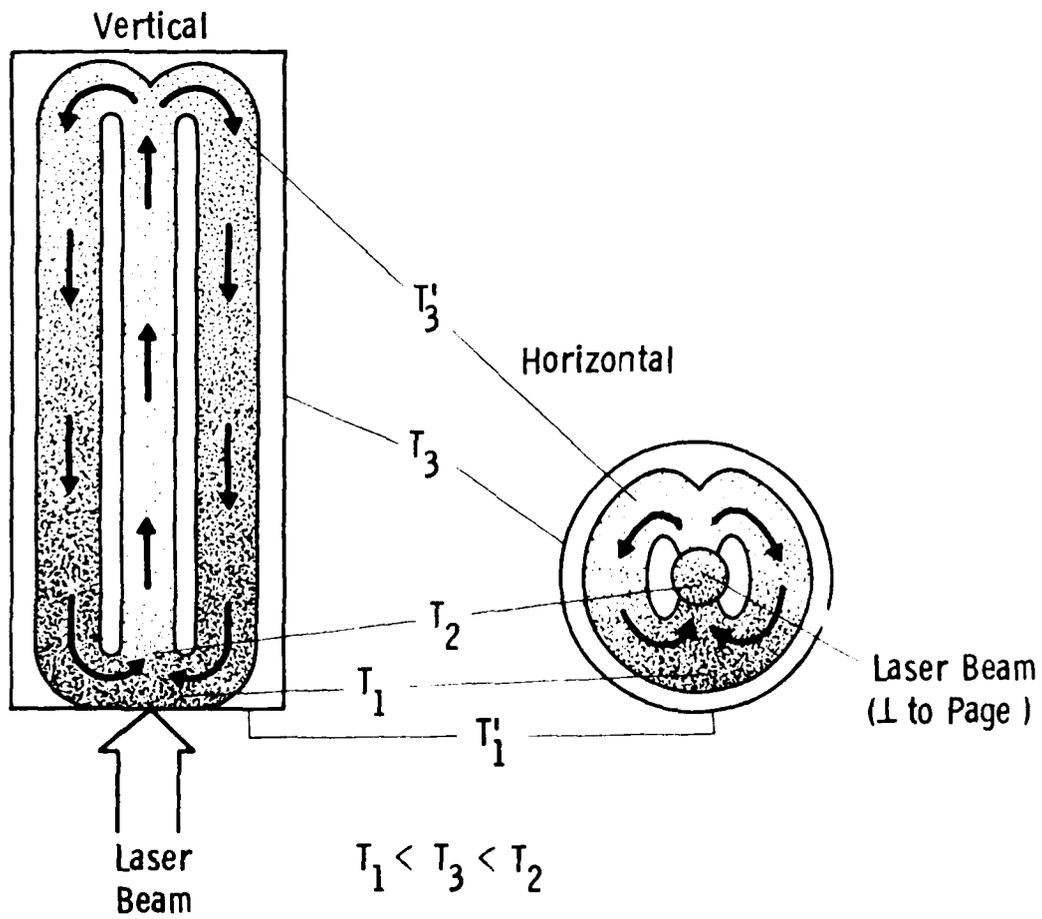


Fig. 14— Comparison of the convection paths, density, and temperature gradients for vertical and horizontal cylindrical laser irradiation experiments. (Dark areas indicate high density)

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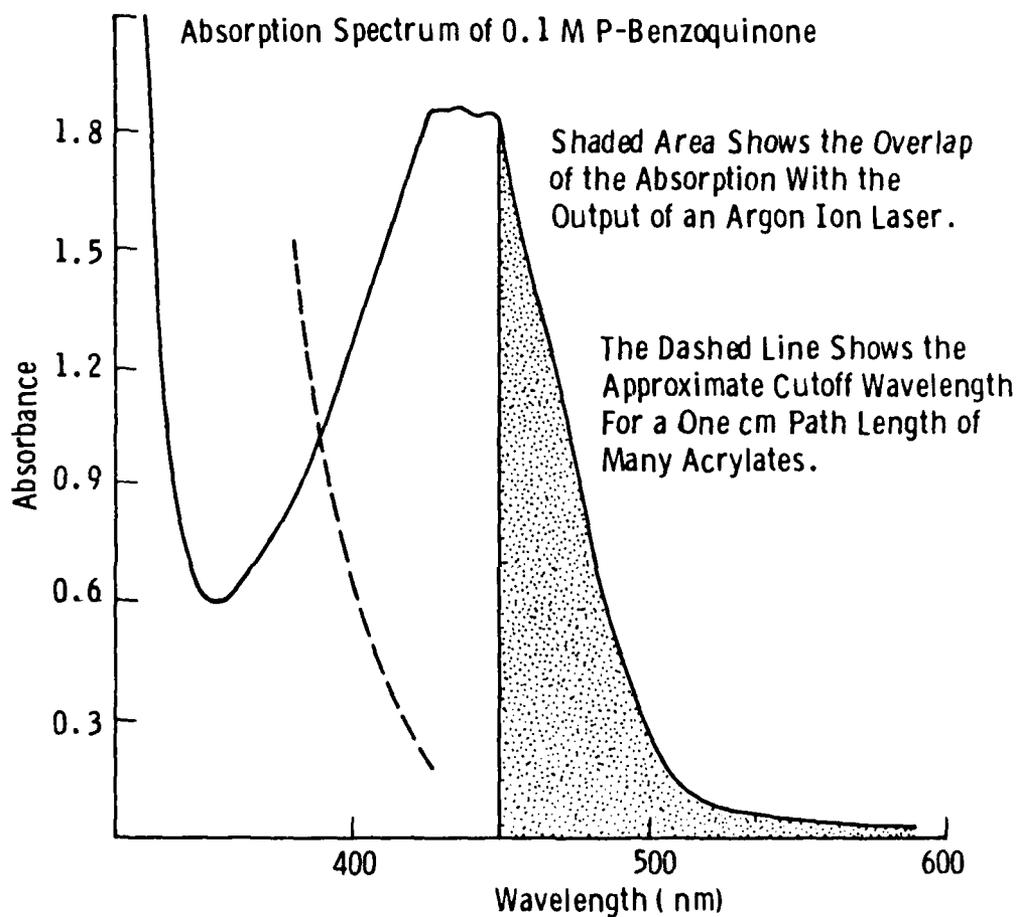
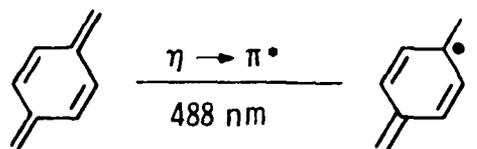
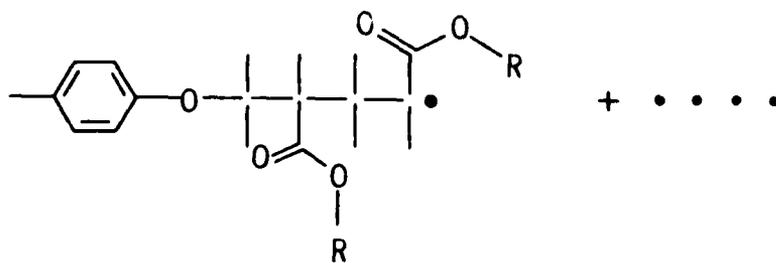
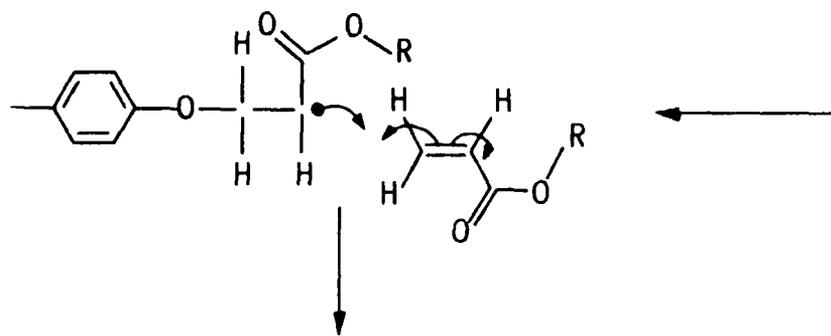
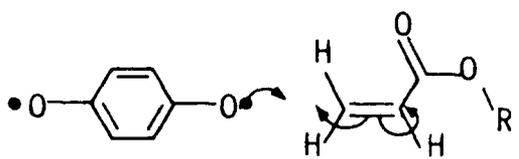


Fig. 15 - UV-visible spectrum of p-benzoquinone

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Absorption



Chain Extension

Fig. 16 - Polymerization mechanism

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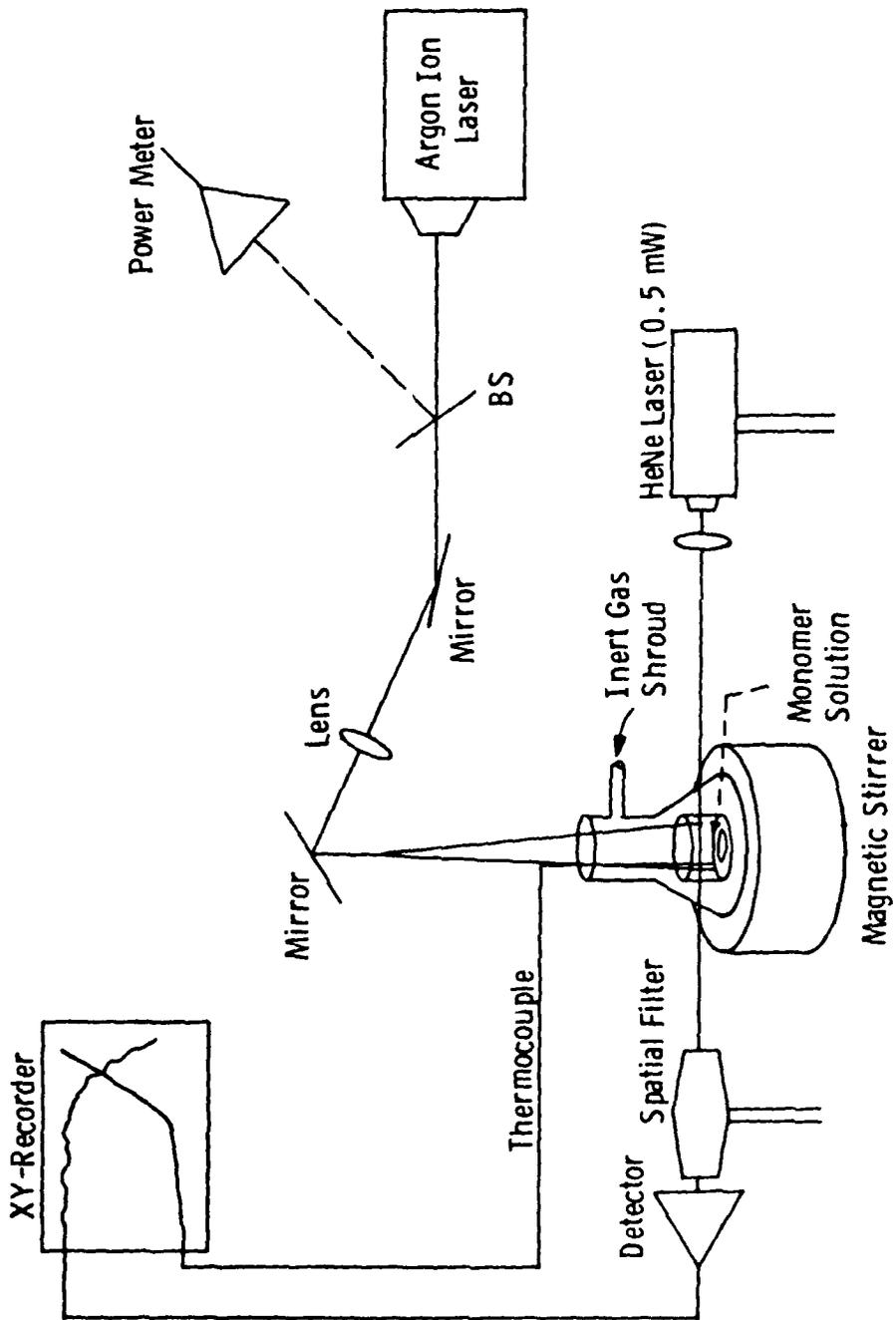


Fig. 17 — Laser induced polymerization set up

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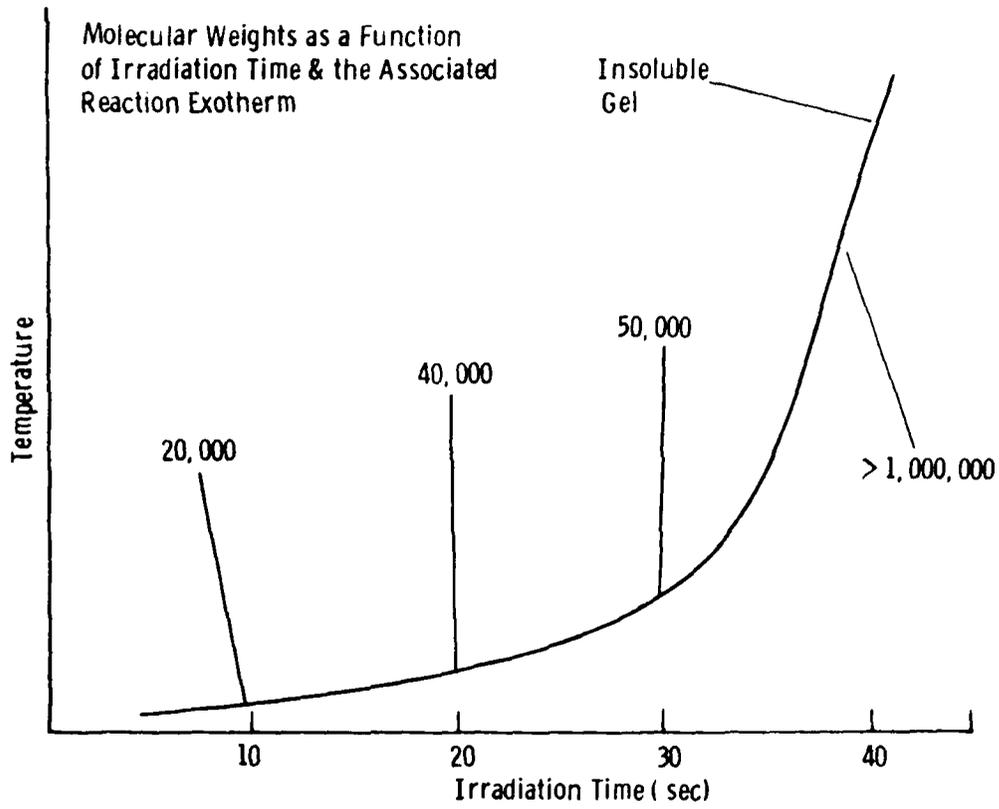


Fig. 18 - Reaction exotherm plot

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