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PHOTODISSOCIATION DYE LASER

Abraham Kasdan

Exxon Research and Engineering Company

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The photodissociation dye laser (PDL) program is an effort to develop a new class of tunable liquid lasers operating in the visible region of the spectrum. In the PDL scheme, laser action is expected to occur between an excited electronic state and the ground electronic state of radicals produced by the photodissociation of specific classes of molecules in solution. This scheme is expected to result in several significant advantages over conventional dye lasers.

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The PDL program is in its initial proof of principle phase. The main thrust of the effort to date has been directed towards obtaining data on those processes that are relevant to assessing the possibility of laser action in one of the selected materials--hexaphenylethane.

Fluorescence and absorption spectroscopy has been performed on this system. Radical fluorescence lifetimes have been measured and photodissociation into an electronically excited radical state has been demonstrated.

Potential values of optical gain have been calculated from fluorescence intensity measurements, and the effect of deleterious photochemical reactions has been studied.

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ABSTRACT

The photodissociation dye laser (PDL) program is an effort to develop a new class of tunable liquid lasers operating in the visible region of the spectrum. In the PDL scheme, laser action is expected to occur between an excited electronic state and the ground electronic state of radicals produced by the photodissociation of specific classes of molecules in solution. This scheme is expected to result in several significant advantages over conventional dye lasers.

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Fluorescence and absorption spectroscopy has been performed on this system. Radical fluorescence lifetimes have been measured and photodissociation into an electronically excited radical state has been demonstrated.

Potential values of optical gain have been calculated from fluorescence intensity measurements, and the effect of deleterious photochemical reactions has been studied.

1. INTRODUCTION AND SUMMARY

The photodissociation dye laser (PDL) program is an effort to develop a new class of tunable liquid lasers operating in the visible region of the spectrum. In the PDL scheme, laser action occurs between an excited electronic state and the ground electronic state of radicals produced by the photodissociation of specific classes of molecules in solution. In this study, a class of highly strained ethanes, the hexaarylethanes, is being investigated as potential laser media. Continuous wave operation of such lasers is expected based on the depletion of the radical ground state (the lower laser level) by recombination to the original parent ethane structure. As in conventional dye laser systems, wavelength tunability is assured because the numerous vibrational and rotational modes of the complex molecule result in a manifold of quasi-continuous vibronic energy levels associated with each electronic level.

The photodissociation dye laser is expected to exhibit several significant advantages over conventional dye lasers. The radical can be thought of, to a first approximation, as a one-electron system. As a result, the electronic structure of the radical consists of doublet levels rather than the singlet and triplet level structure characteristic of the paired electrons of conventional dye molecules. Consequently, problems associated with non-radiative intersystem-crossing transitions which result in deleterious absorption by the lowest triplet level at the laser wavelength in conventional dye molecules are eliminated.

The second advantage of the PDL scheme is related to the upper laser level lifetime. In conventional laser dyes, the spontaneous radiative lifetime of the first excited singlet level is typically on the order of a few nanoseconds. In radical systems, however, there is evidence, both theoretical and experimental, that the first doublet-doublet electronic transitions are in some cases, partially forbidden. From the point of view of the PDL scheme, this means that the radiative lifetime of the upper laser levels is one to two orders of magnitude longer than that exhibited by the upper laser levels of conventional organic dyes. Consequently, a larger population density in the upper level may be obtained, thereby allowing the possibility of generating higher laser output power levels than can be presently attained with conventional dyes. This assumes that strong absorption from the upper level at the laser wavelength does not occur. In addition, the longer radiative lifetime favors the recombination of the radical ground state to the parent dimer at a sufficiently fast rate to permit a continuous population inversion and hence, cw laser action.

The PDL program is now in its initial proof of principle phase. A number of promising chemical candidates for the active medium have been identified. The main thrust of the effort reported herein has been directed towards obtaining data on those processes that are relevant to assessing the possibility of laser action in one of these candidates--hexaphenylethane.

Detailed fluorescence and absorption spectroscopy has been performed on the hexaphenylethane-triphenylmethyl radical system during the present reporting period. In particular:

1. Fluorescence lifetimes as a function of temperature have been measured in order to evaluate the effect of competing non-radiative rates on the upper state radical lifetime. The fluorescence lifetime of the upper laser level is 190 nsec at dry ice temperature (-80°C).

2. Radical fluorescence intensities produced by pumping the dimer absorption band have been measured as a function of temperature. Dimer photodissociation into an excited radical state has been demonstrated.

3. Absolute intensity measurements have been made which yield an upper bound value for the attainable gain from the hexaphenylethane-triphenylmethyl radical system, assuming no population in the lower laser level. Pumping by 200 kw at 3371 Å resulted in a calculated maximum possible gain of 0.02 cm^{-1} at the peak of the radical fluorescence at 5200 Å.

II. THE PHOTODISSOCIATION DYE LASER CONCEPT

In its most general form, the photodissociation dye laser may be understood as follows: A stable molecule, AB, in solution is optically pumped to its first excited singlet state. The absorbed pump energy exceeds the molecule's dissociation energy and two radicals are formed upon dissociation. The excess energy is partitioned as electronic and vibrational excitation in one or both of the radicals $A\cdot$ and $B\cdot$. In particular, we consider radical $A\cdot$ to be electronically excited. A partial population inversion is produced between the first excited and the ground state of the radical. Laser action occurs in $A\cdot$ and the resulting $A\cdot$ and $B\cdot$ ground state molecules are unstable against recombination. The processes may be written as:

$$AB + h\nu_{pump} \longrightarrow (AB)^*$$

$$(AB)^* \longrightarrow A\cdot^* + B\cdot$$

$$A\cdot^* \longrightarrow A\cdot + h\nu_{laser}$$

$$A\cdot + B\cdot \longrightarrow A_2 + B_2 + AB$$

In the final recombination step, not all of the radicals form the original molecule AB, but the dimeric forms A_2 and B_2 are also produced. Continuous laser action would require replenishment of the starting material, AB. Let us consider in more detail the special case where $B \equiv A$ so that the starting molecule is dimeric.

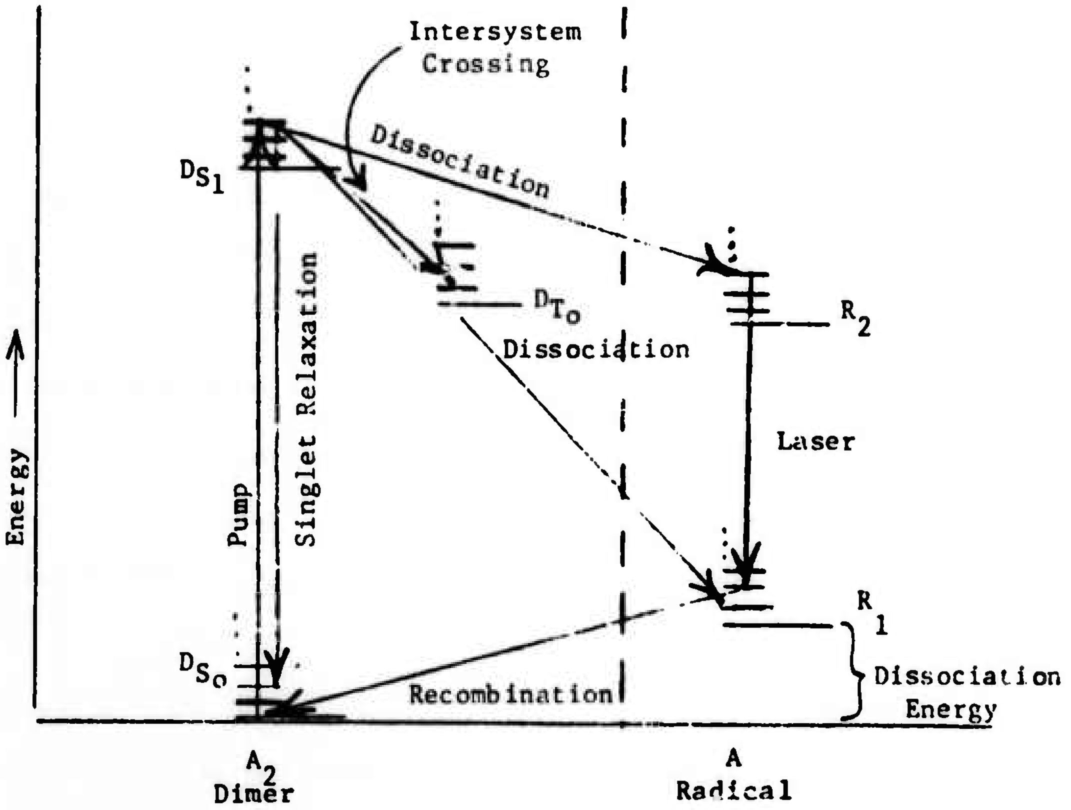
The general energy level scheme for such a photodissociation dye laser molecule is shown schematically in Figure 1. The stable parent dimer, having no unpaired electrons, exhibits the usual singlet and triplet level structure. The ground and excited electronic singlet levels are denoted by D_{S_0}, D_{S_1}, . . . and the triplet levels are denoted by D_{T_0}, D_{T_1}, . . .

The lowest electronic levels of the radicals, obtained from the symmetric photodissociation of the dimer, are shown adjacent to the dimer structure. The radical, having a single unpaired electron, exhibits a doublet structure. In the figure the radical ground state is shown displaced upward in energy from the dimer ground state by an amount equal to the dimer dissociation energy.

The vibrational level spacing in both the dimer and radical ranges between 150-1500 cm^{-1} while the rotational spacing ranges between 15-150 cm^{-1}. Therefore, as in conventional dye lasers, a quasicontinuum exists for each electronic level comprised of the thermally broadened rotational and vibrational levels.

A characteristic of the photodissociation dye laser molecule is that the D_{S_1} and D_{T_0} levels in the dimer lie above the dimer dissociation energy. Consequently, upon optically pumping the dimer to D_{S_1} the molecule will undergo dissociation into two radicals. Dissociation may occur via two possible paths. The first is directly from the optically pumped D_{S_1} level. However, the D_{S_1} level may, in principle, undergo a rapid intersystem crossing to the D_{T_0} level. Dissociation of the dimer may occur from this level.

Upon dissociation, the excitation energy is partitioned between a manifold of levels in the quasi-continuum of both the excited and ground state of the radical. The radical ground state initially has a negligible population; consequently, a partial inversion in the radical can be produced. The stimulated emission is tunable as in conventional dye lasers because of the quasi-continuous distribution of the upper and ground levels. An interesting point is that for radicals considered suitable for the photodissociation dye



$A_2(D_{S_o}) + h\nu_{pump} \longrightarrow A_2(D_{S_1}, \nu'')$: excitation of dimer

$A_2(D_{S_1}, \nu'') \longrightarrow A_2(D_{S_o}, \nu')$: singlet relaxation

$A_2(D_{S_1}, \nu'') \longrightarrow A_2(D_{T_o}, \nu')$: intersystem crossing

$A_2(D_{S_1}, \nu'') \longrightarrow A(R_2, \nu''') + A(R_1, \nu')$: dissociation

$A(R_2, \nu''') \longrightarrow A(R_1, \nu'') + h\nu_{laser}$: laser action

$A(R_1) + A(R_1) \longrightarrow A_2(D_{S_o})$: recombination

Figure 1. Photodissociation Dye Laser Molecule Structure and Kinetics

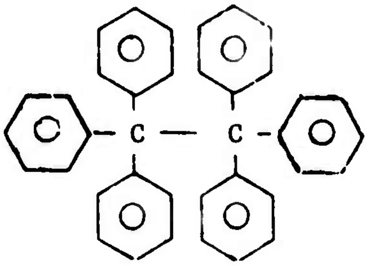
laser both the calculated and measured oscillator strengths for the first doublet-doublet electronic transition are always small. Thus, even though these transitions are allowed by the selection rules, they exhibit a partial "forbiddenness". Consequently, the radiative lifetime of the laser transitions can be expected to typically be a factor of a hundred times longer than in conventional dye lasers. This has been experimentally verified in some cases as will be discussed later. The longer lived upper laser level can permit a larger population density to be obtained and thereby allows the possibility of high power output.

The ability of the photodissociation dye laser to operate on a cw basis requires, as usual, that the depletion rate of the lower laser level exceed the radiative transition rate from the upper to the lower laser level. The lower laser level is the radical ground state which is unstable to recombination back to the original parent dimer. Thus for a steady-state population inversion to be maintained, the radical recombination rate must be greater than the laser transition radiative rate.

III. PROPERTIES OF THE SELECTED PDL MOLECULES

A class of organic molecules known as the hexaarylethanes exhibit many of the prerequisites necessary for a PDL active media. During the first six months of the program five compounds from this class were selected and synthesized for further study. Details on the synthesis technique and established properties of these materials were given in the last semiannual report (1). On the basis of the available data and preliminary observations, one of these materials - hexaphenylethane was chosen as the most promising candidate for an initial study. The experimental effort during the period covered by this report involved measurements on the hexaphenylethane system. What follows is an overview of the relevant properties of hexaphenylethane known prior to our experimental effort.

The hexaphenylethane molecule can be represented schematically as:

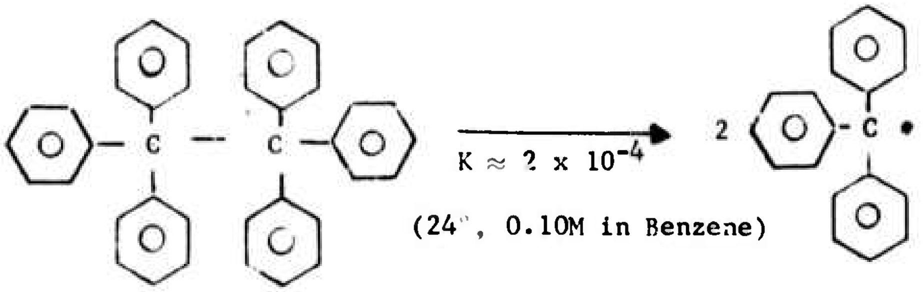


Although the accepted structure is actually non-planar, with a quiroid-type atomic arrangement, the above representative is adequate for the purposes of this discussion.

A. Chemical Properties

1. Dissociation into Free Radicals

It has been clearly established for some time that hexaphenylethane thermally dissociates in non-reactive solvents to produce the intensely colored triphenylmethyl radical (2):



Hexaphenylethane
(Colorless Solid)

Triphenylmethyl Radical
(Yellow in Solution)

The existence of the radical has been proven by a multiplicity of analytical techniques. For example, cryoscopic molecular weight determinations of such compounds in solution have shown that the apparent molecular weights were well below that of the dimer. In addition, spectrophotometric measurements have established that solutions of the dimer do not obey Beer's law; the intensity of absorption increases with dilution as would be predicted for the dissociation of a colorless compound into a colored radical. Finally, absolute methods of radical detection - magnetic susceptibility and electron spin resonance spectroscopy - have shown beyond doubt the thermal dissociation of hexaphenylethane into ground state triphenylmethyl radicals.

Two factors determine the position of the hexaphenylethane-triphenylmethyl equilibrium: (a) Steric effects and (b) Radical stability.

(a) Steric Effects - This factor favors the formation of radicals in two ways. First, there is a relief upon dissociation of the steric interactions in the ethane. In essence, the central carbon-carbon bond in the hexaphenylethane is weakened by the steric repulsion of the aromatic rings produced by interactions between the ortho-substituents. The bond weakening can be experimentally verified by comparison of the bond-length and strength of the central carbon-carbon bond in hexaphenylethane and the nonsterically-hindered ethane:

	Hexaphenylethane	Ethane
Bond Length	1.58 Å	1.54 Å
Bond Strength	11.5 kcal/mole	85 kcal/mole

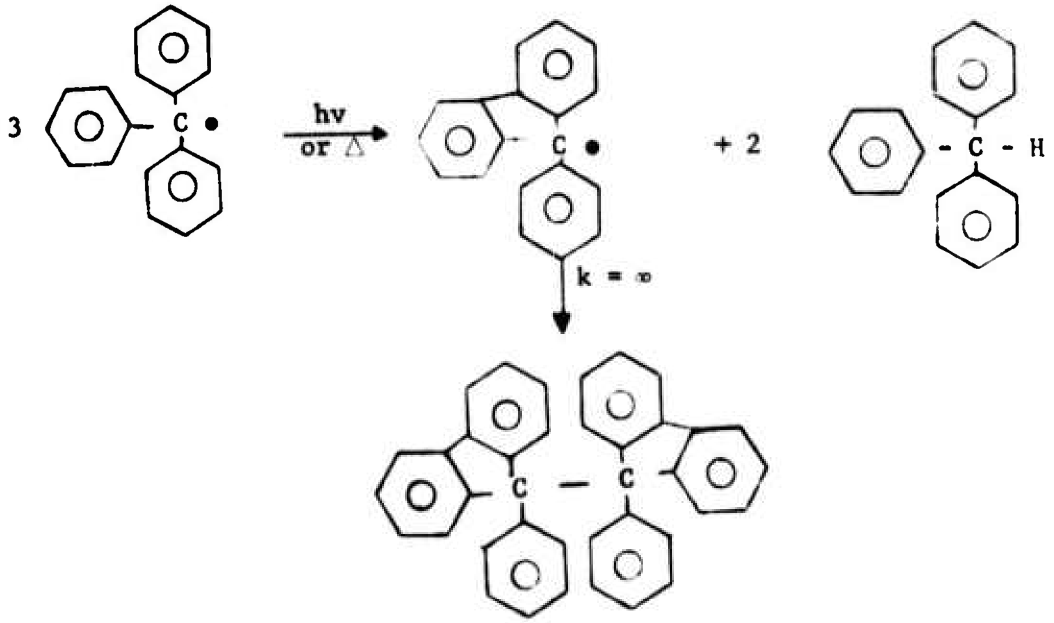
The second steric effect is typified by a steric hindrance to recombination once a radical is formed.

(b) Radical Stability - The stability of the triphenylmethyl radical is provided by a resonance stabilization effect resulting from the delocalization of the free electron throughout the three aromatic rings of the structure.

2. Deleterious Reactions

(a) Disproportionation

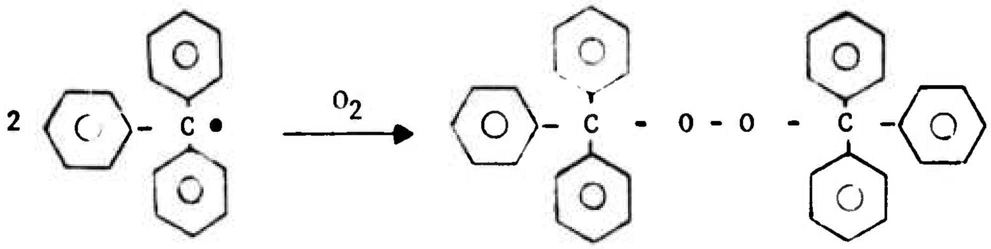
A number of chemical properties act to complicate the use of hexaphenylethane as a PDL active media candidate. These properties arise from the reactivity of the produced radicals. The first of these is their propensity towards disproportionation. This transformation is promoted by heat or light and is illustrated below:



In essence, two molecules of the radical become reduced at the expense of a third radical which is oxidized. For the triphenylmethyl radical, the products are triphenylmethane and the dehydro-dimer of 9-phenylfluorene. Measurements of the effect of this photochemical or thermal degradation on the use of hexaphenylethane as a laser media will be present later in this report (See Section IV.D).

(b) Addition Reactions

The second deleterious reaction path which occurs when radicals are produced is the addition reaction. This involves the rapid absorption of atmospheric oxygen to form colorless triphenylmethyl peroxides:



As the radicals react, more dissociation must occur in order to maintain the dimer-radical equilibrium constant. In this way, a continuous depletion of both the radical and dimer concentration occurs until all the hexaphenylethane in solution has reacted to form the peroxide precipitate. As pointed out in the first semiannual report (1), careful preparation under vacuum conditions and subsequent storage and handling under a nitrogen atmosphere yield solutions that are quite stable with respect to such reactions. Spectrophotometric measurements of the radical concentration over a period of time in solutions we have prepared indicate a decrease of only several percent per week; and this decrease is probably due primarily to thermal disproportionation.

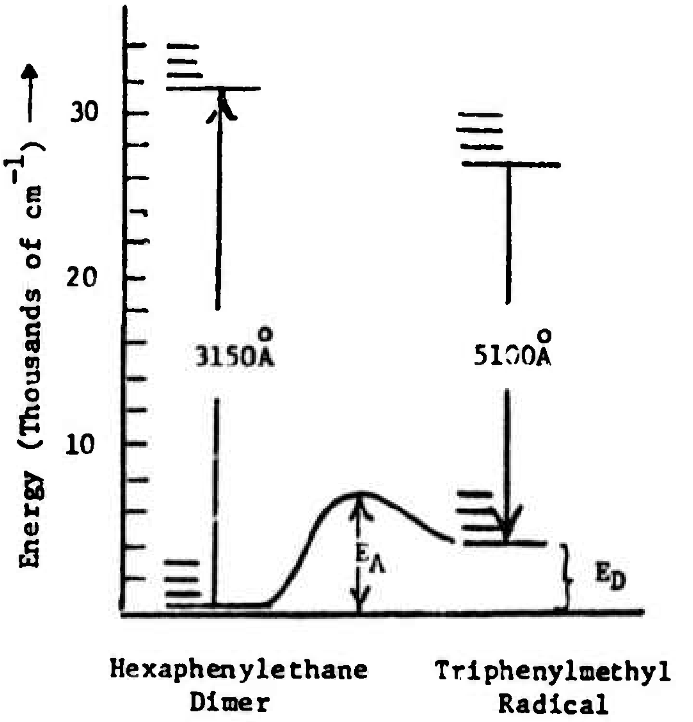
B. Spectroscopic Properties

The reported major bands in the electronic absorption spectra of hexaphenylethane and the triphenylmethyl radical are shown below along with the measured extinction coefficients (3):

Hexaphenylethane	Triphenylmethyl Radical
λ_{max} = 3150 Å (using KBr pellet technique)	λ_{max} = 3450 Å, ϵ = 11,000
λ_{max} = 3130 Å (dissolved in cyclohexane)	λ_{max} = 5100 Å, ϵ = 210
	(both in cyclohexane)

The major absorption bands can be associated with electronic transitions. The resulting dimer and radical energy level structure is shown in Figure 2. The first excited singlet level of the dimer, D_{S_1}, is ~ 31,750 cm^{-1} above the ground state. The activation energy for dissociation is ~ 7000 cm^{-1} (4) while the dissociation energy is ~ 4000 cm^{-1} (5). The ground vibrational level of the first excited electronic state in the triphenylmethyl radical lies at 19,410 cm^{-1} and the second excited electronic level is at ~ 29,000 cm^{-1} above the ground state.

The mirror image symmetry of the absorption and fluorescence bands are illustrated in Figure 3. The spectra were originally reported by Lewis et al. (6) and were measured by suddenly cooling a solution of hexaphenylethane in EPA (5 parts ether, 5 parts isopentane, and 2 parts ethanol by volume) to liquid N_2 temperature (-190°C). It was reported that rapid cooling preserved the highly colored radicals in the clear EPA glass, and that under these conditions, there was no evidence of disproportionation. Unfortunately, no details regarding the measurement techniques used in taking the fluorescence data were presented--nor was the excitation source or wavelength described.



E_A = Activation Energy = ~7000 cm^{-1}

E_D = Dissociation Energy = ~4000 cm^{-1}

Figure 2. Energy Level Structure of the Hexaphenylethane-Triphenylmethyl System.

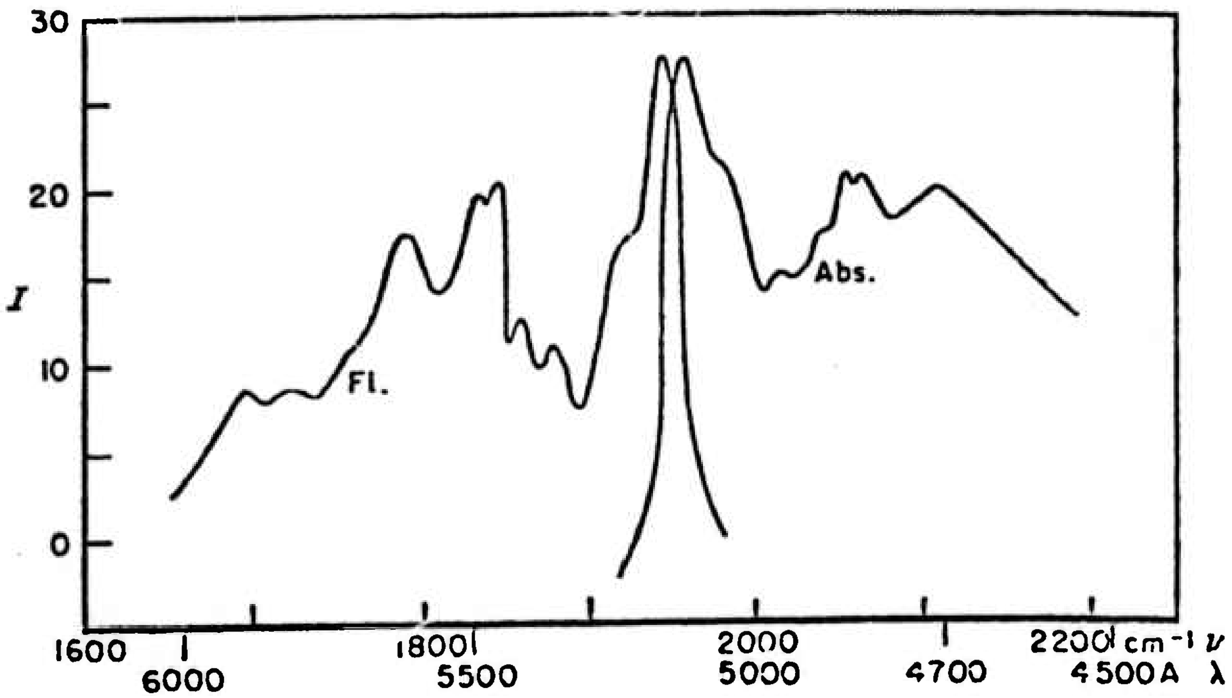


Figure 3. Mirror Symmetry of Absorption and Fluorescence Bands of the Triphenylmethyl Radical (in EPA mixed solvent at -190°C). Ref. (6).

More recently, Okamura et al. (7) performed time resolved fluorescence measurements on the triphenylmethyl and other methyl-substituted radicals which were trapped in rigid solvents at low temperature. The triphenylmethyl radical was prepared by the photolysis of triphenylmethane molecules at -190°C in a quartz cell using a low pressure mercury lamp. An N_2 laser emitting a 10 nsec, 40 kw peak power pulse at 3371 Å was used as the excitation source. The fluorescence decay consisted of a single exponential with the measured decay times being 280 nsec with ethyl alcohol as solvent, and 330 nsec using isopentane as the solvent. The very long fluorescence lifetimes were taken as evidence that the first doublet-doublet electronic transition in the radical has a forbidden character, although such transitions are allowed by the usual selection rule considerations. The possibility that the observed lifetimes were actually longer than the natural lifetimes because of complex formation of the excited state with the solvent, was ruled out by the fact that the difference of measured lifetimes in polar and nonpolar solvents was not appreciable.

IV. EXPERIMENT EFFORT AND RESULTS

In the present investigation, solutions of hexaphenylethane dissolved in iso-octane (a UV-transmitting solvent) have been studied. As already pointed out, hexaphenylethane in solution undergoes appreciable thermal decomposition at room temperature into triphenylmethyl radicals. For example, what would be a 10^{-3} M solution of hexaphenylethane in the absence of thermal decomposition actually results in ~ 25% dissociation at room temperature--yielding ~ 7.5×10^{-4} M hexaphenylethane and ~ 5×10^{-4} M triphenylmethyl radical.

Since the dissociation energy, H, is known (11.8 kcal/mole) the equilibrium constant K can be calculated as a function of temperature ($K = Ae^{-H/RT}$) if its value at one temperature is known. Since $K \equiv \frac{[R]^2}{[D]}$, where [R] and [D] are the radical and dimer concentrations respectively, the resulting concentrations can be calculated as a function of temperature for a given initial dimer concentration $[D_o]$. The results of such a calculation are shown in Figure 4. The measured value of $K = 4.1 \times 10^{-4}$ at 20°C was used (5). Although this value was obtained using benzene as solvent, it has been shown (5) that solvent variations do not change the value of the equilibrium constant significantly.

The solutions we have prepared, using the method outlined in the first semi-annual report (1), have resulted in ~ 2×10^{-3} M radical concentration at room temperature. This value is obtained from an absorbance measurement in the visible (see Figure 5), using the previously measured value of the extinction coefficient $\epsilon = 210\ \ell\text{-mole}^{-1}\text{-cm}^{-1}$ (3) for the peak of the visible triphenylmethyl absorption (~ 5150 Å). Note that except for the absence of much of the structure evident in the low temperature visible absorption data (Figure 3), the room temperature absorption data is otherwise identical.

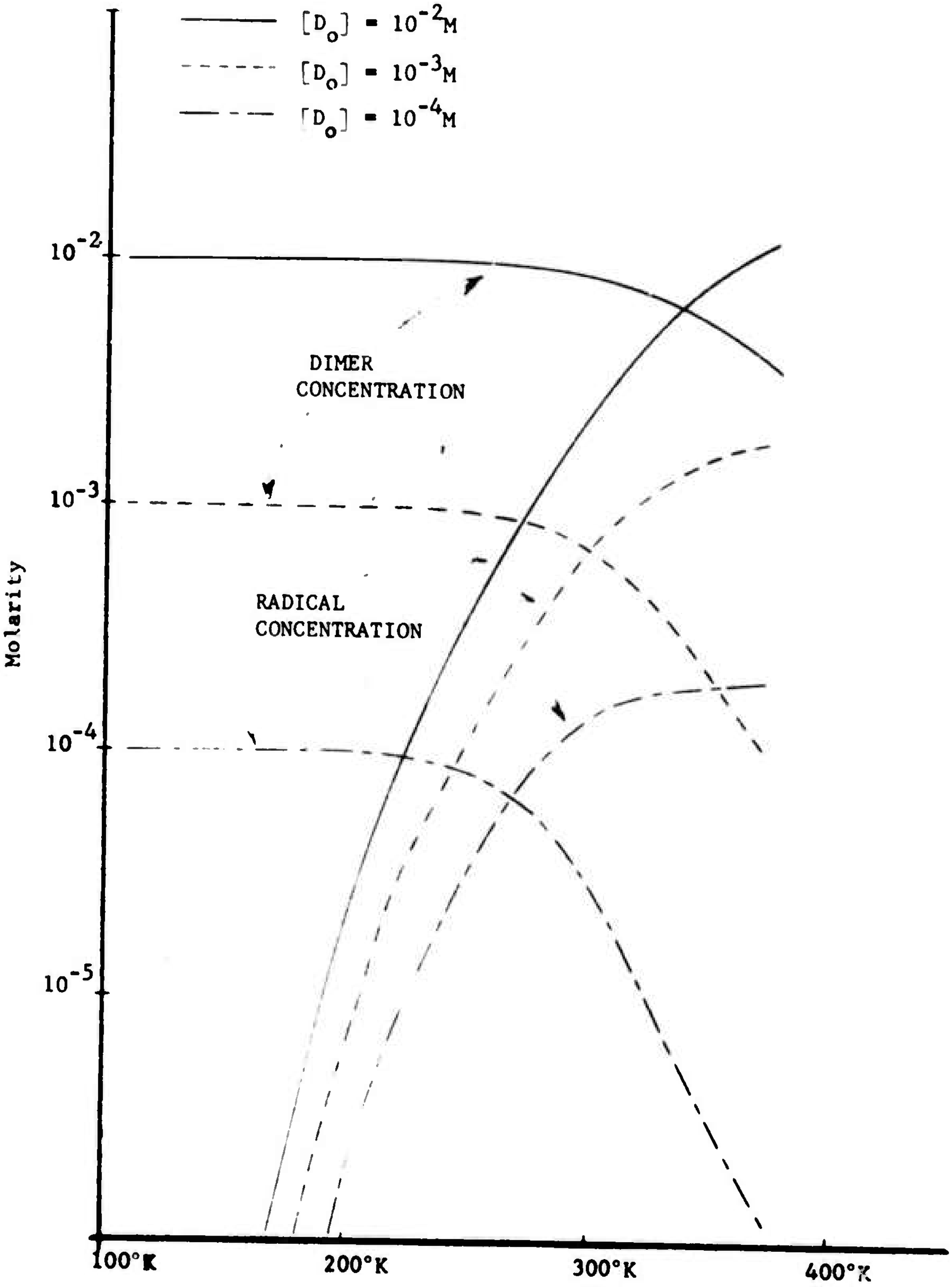


Figure 4: Triphenylmethyl Radical and Hexaphenylethane Dimer Concentrations in Solution as a Function of Temperature and Undissociated Dimer Concentration.

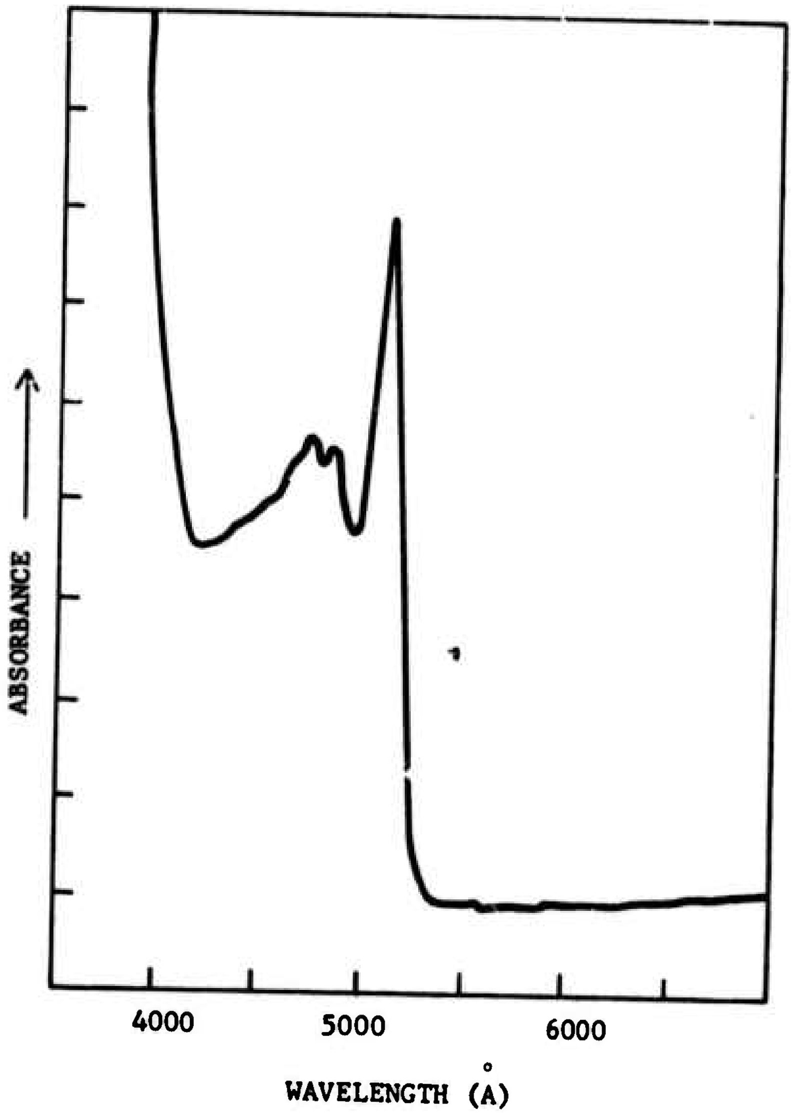


Figure 5. Visible Absorption Spectrum of the Triphenylmethyl Radical Taken at Room Temperature. (Hexaphenylethane in Iso-octane).

For wavelengths $<$ 3500 Å, the absorption of the hexaphenylethane solutions at the concentrations used in our experiment is $>$99%. If dilute solutions are prepared, the UV absorption curve shown in Figure 6 is obtained. The absorption is characterized by a broad feature with a peak at ~ 3350 Å. No structure is resolvable although a shoulder on the short wavelength side is evident. It is believed that this feature is due to the unresolved combination of dimer absorption (reported in the literature to peak at ~ 3150 Å) and radical absorption to a second excited state (reported to peak at ~ 3450 Å).

In order to study the fluorescence characteristics of the PDL molecules, a tunable UV laser source was assembled at the beginning of the program, the details of which have been presented in the first semiannual report (1). As part of this assembly we have constructed a 0.5 MW N_2 laser which has been used as a direct excitation source as well as a pump source for a Molectron DL 300 dye laser. Frequency doubling of the visible dye laser output results in a tunable probe in the 2600-3700 Å range.

It was initially observed by us, that when a room temperature solution of hexaphenylethane is irradiated with the N_2 laser directly (3371 Å), a bright greenish-yellow fluorescence results. The fluorescence spectrum was obtained with a Spex 1 meter spectrometer by signal averaging the photomultiplier pulses with a boxcar integrator, and is shown in Figure 7. The spectrum corresponds to the reported low temperature spectrum of the triphenylmethyl radical, although the multiple peaks exhibited in the low temperature spectrum are not evident. The broad feature at ~ 4000 Å is not due to either hexaphenylethane or the triphenylmethyl radical. Its significance will be discussed in Section IV.D. Note that the room temperature absorption and fluorescence spectra of the thermally generated triphenylmethyl radicals (Figures 5 and 7) exhibit the same mirror image symmetry reported in the low temperature measurements.

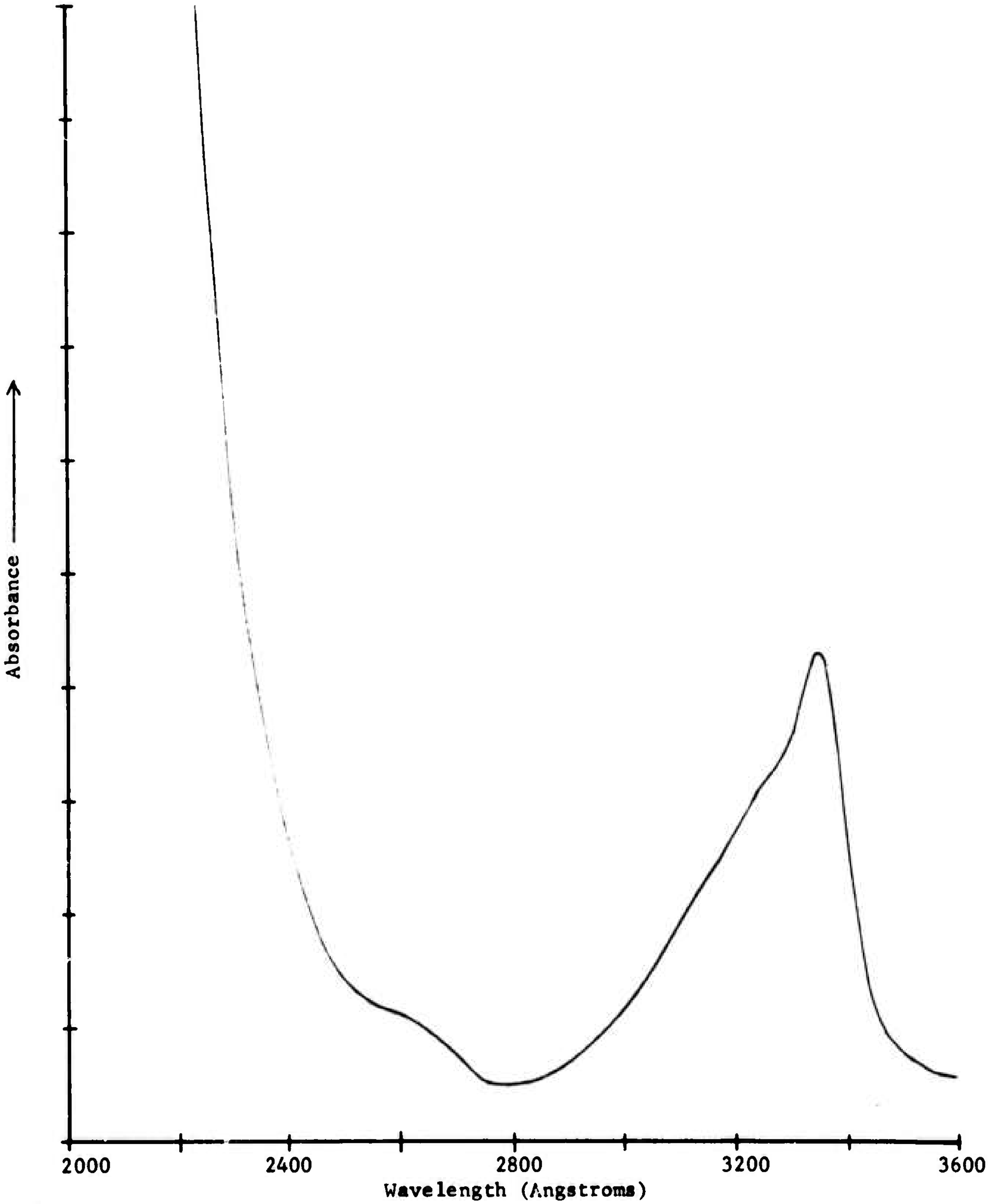


Figure 6. UV Absorption Spectrum of Hexaphenylethane Solution at Room Temperature (in iso-octane).

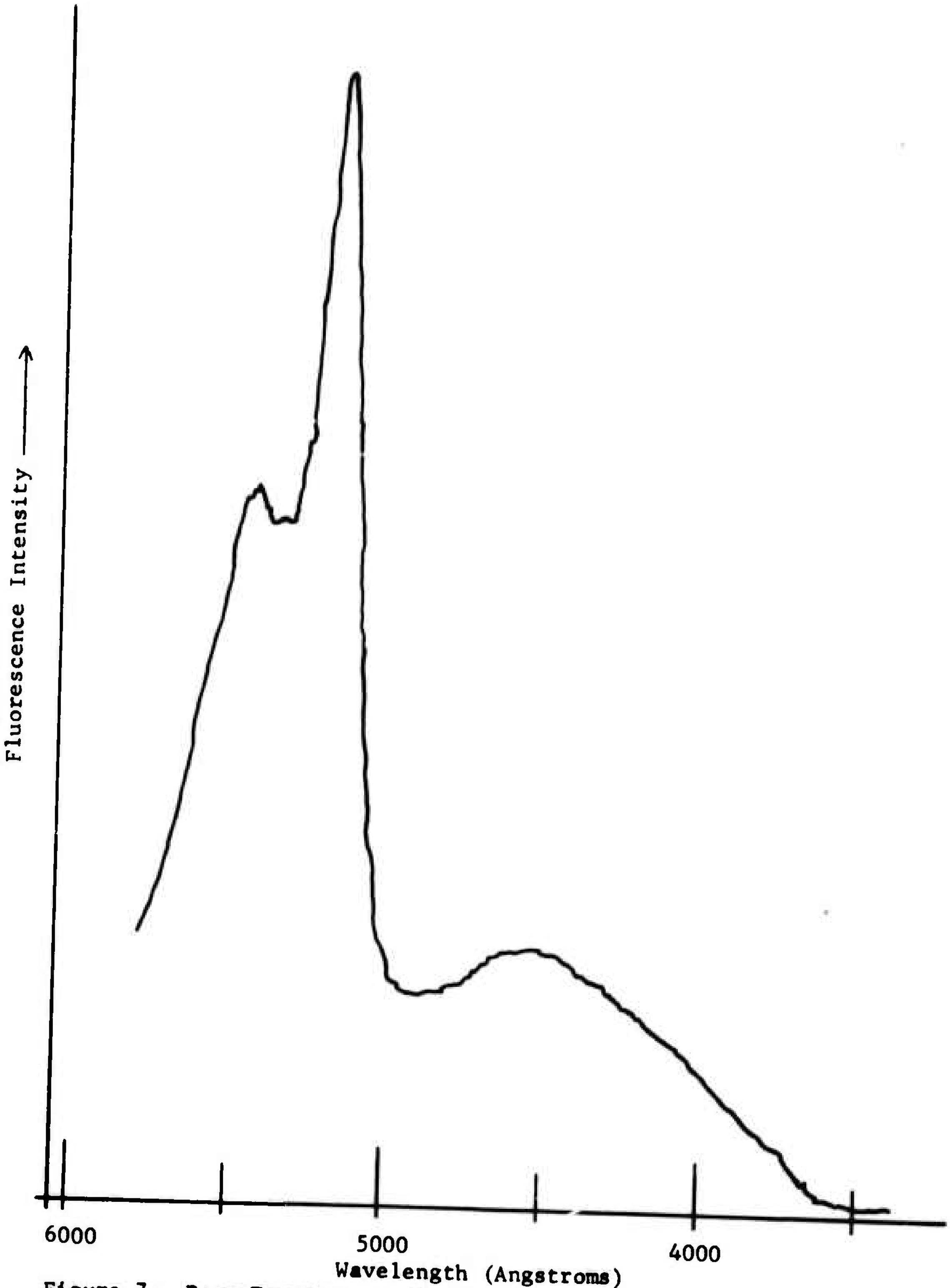


Figure 7. Room Temperature Fluorescence of a Hexaphenylethane Solution (in iso-octane). The Characteristic Triphenylmethyl Radical Fluorescence is seen as well as a Broad Feature in the Blue. Excitation is with an N_2 Laser (3371 Å).

A. Excitation of the Visible Absorption Band

(1) Temperature Dependence of the Fluorescence Lifetime

As previously mentioned, the reported fluorescence lifetime of the triphenylmethyl radical at 77°K is ~ 300 ns (7). However, the initial lifetime measurements we performed at room temperature yielded ~ 10 ns lifetimes at all points on the observed spectrum (5150 Å-6000 Å). These measurements were made by exciting the first absorption band of the thermally generated radicals directly by a 5 ns dye laser pulse at 5150 Å. Excitation at this wavelength, rather than in the UV, precludes any complicating effects arising from simultaneous dimer excitation since the visible absorption band is due exclusively to the presence of the triphenylmethyl radical.

The reason for the difference in the two lifetime measurements can be understood if a temperature dependent non-radiative decay rate,k_{nr},is added to the radiative rate,k_r. The observed lifetime is then equal to $1/(k_r + k_{nr})$. At low temperatures the non-radiative rate is reduced, thereby increasing the observed lifetime. In order to achieve maximum possible inversion as a laser media, a PDL system should operate in a temperature regime where the fluorescence lifetime is as long as possible. A temperature dependence study of the fluorescence lifetime was therefore undertaken.

In order to perform such measurements, a simple fluorescence cell capable of being cooled and operated at low temperature without moisture condensation problems on the windows was devised. A schematic diagram of the cell is shown in Figure 8. A conventional jacketed quartz spectrophotometer cell was set up so that cooled N_2 gas flowed through the jacket surrounding the hexaphenylethane. A thermocouple placed in the solution provided for temperature measurement. The cell was filled with the hexaphenylethane in a dry box under an N_2 atmosphere and subsequently

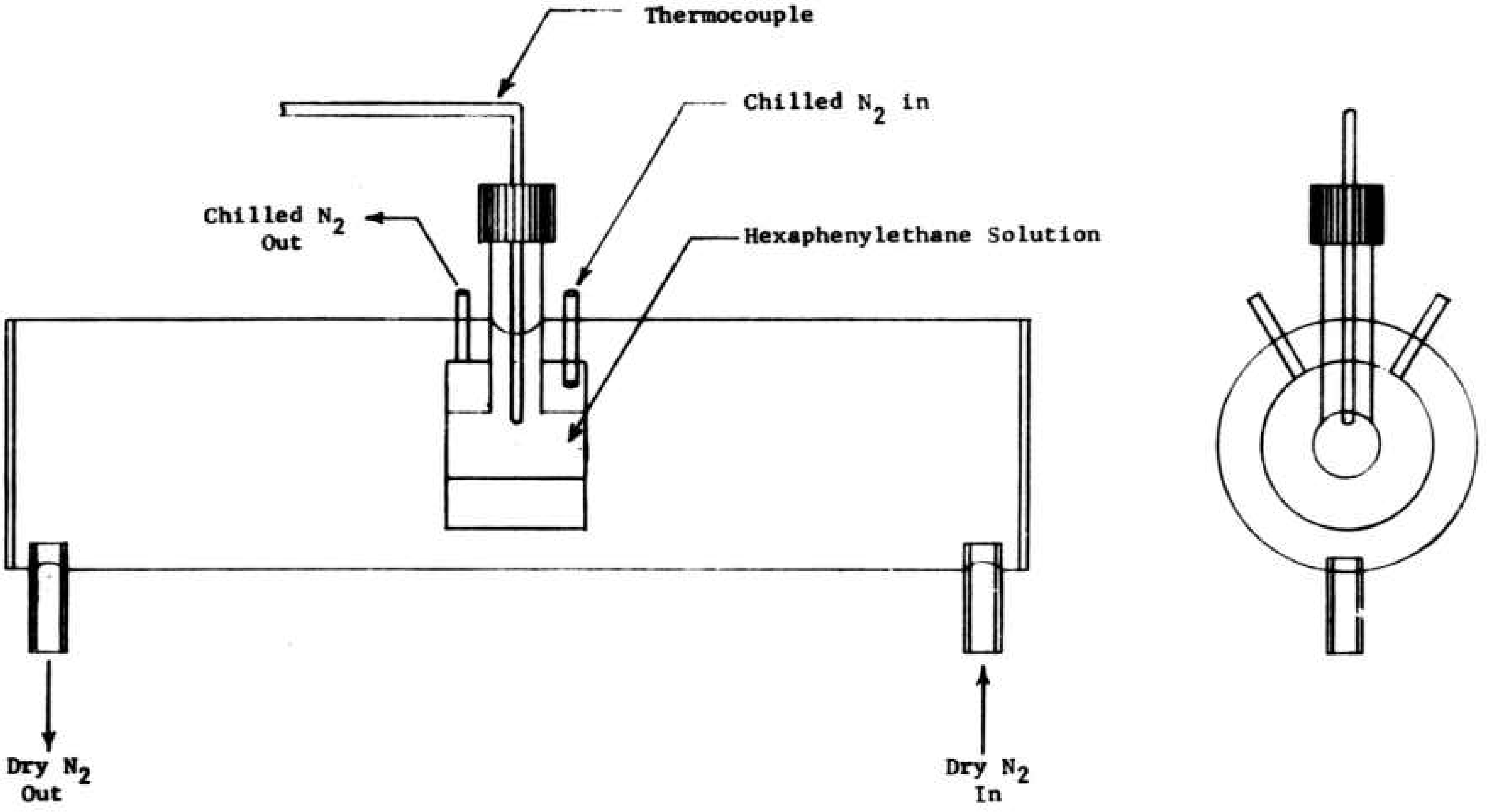


Figure 8. Schematic Diagram of Low Temperature Fluorescence Cell.

sealed to prevent oxygen from reacting with the radicals. The entire cell was surrounded by a plexiglass cylinder with appropriately positioned quartz windows so that the fluorescence could be viewed at right angles to the excitation light. Room temperature dry nitrogen gas was continuously flowed through this outer chamber so that water vapor which would otherwise condense on the cell windows was eliminated from the cell. By controlling the flow of the cold N_2 gas, temperature stability could easily be maintained to $\pm$ 1°C. Using this configuration fluorescence data from room temperature down to -90°C were obtained. The solution was excited at the peak of the radical absorption band in the visible (5150 Å) by a 5 ns dye laser pulse. The fluorescence was passed through a Perkin-Elmer monochromator and was monitored at right angles by an RCA C31025C photomultiplier tube and a 7904 Tektronix oscilloscope.

All the fluorescence decay curves were analyzed to be single exponentials, as expected. The fluorescence lifetime was seen to increase rapidly from the room temperature value of ~ 10 ns to greater than 200 ns at -90°C. A compilation of the data from a number of different runs is shown in Figure 9. This dramatic increase in the fluorescence lifetime results from a decrease in the non-radiative rate constant k_{nr}. This non-radiative rate is due to a combination of internal conversion processes and collisional deactivation of the excited level by solvent molecules, and it is reasonable to expect that both such effects exhibit a temperature dependence which acts to decrease the corresponding rate constants with decreasing temperature. Presumably if the temperature of the hexaphenylethane system is lowered even more, the fluorescence lifetime will approach the values reported by Okamura et al. (7) at -190°C. Since the solvent we used (iso-octane) turns into an opaque white solid upon freezing, we could not acquire data at any lower temperatures.

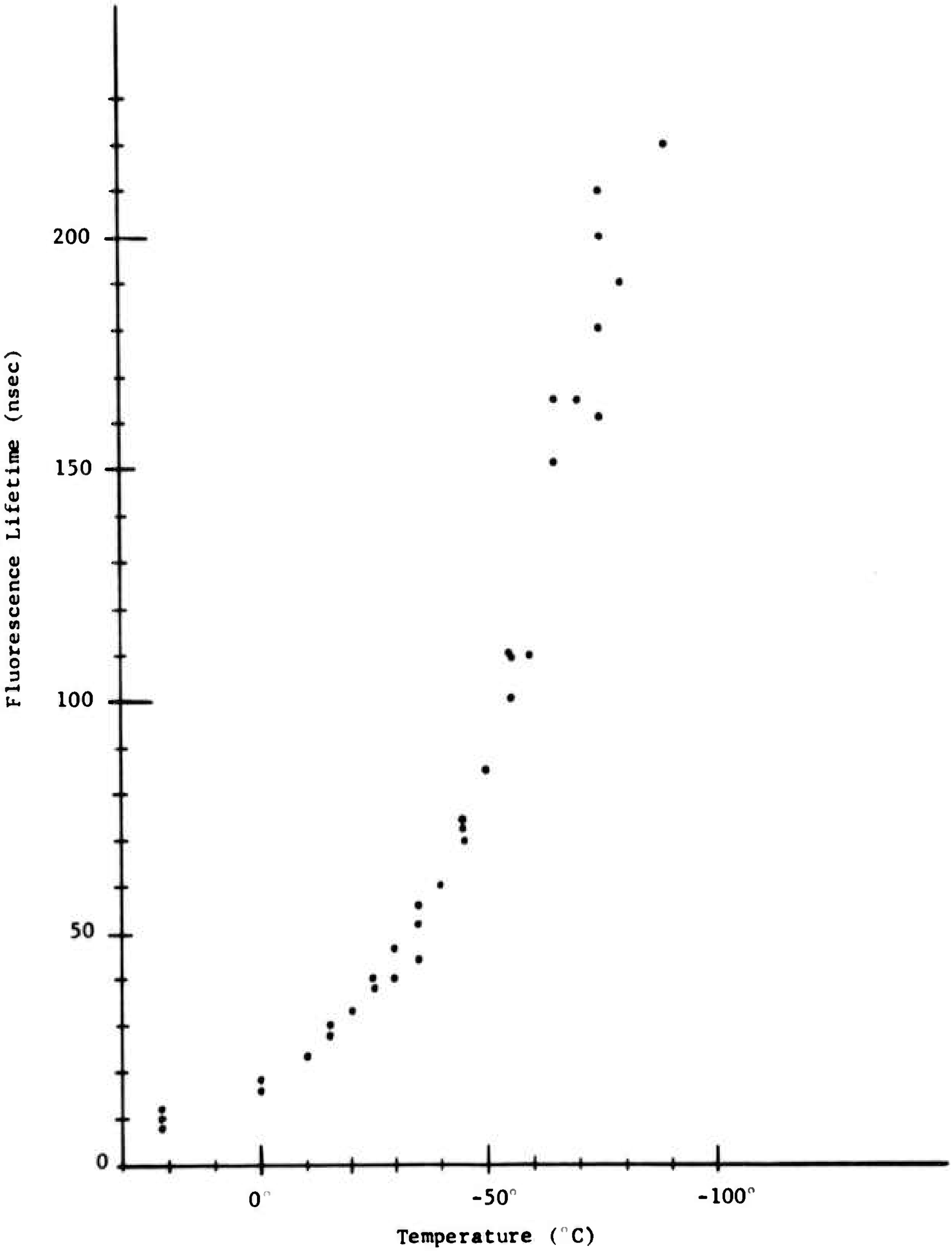


Figure 9. Temperature Dependence of the Triphenylmethyl Radical Lifetime. (Excitation Wavelength is at 5150 Å).

From the laser viewpoint, a longer fluorescence lifetime of the upper level would allow more energy storage in the medium. Better coupling of flashlamp sources would also be possible. In order to achieve this with hexaphenylethane as the active medium, the liquid would have to be cooled. The most convenient operating temperature for such a system would be at -78°C, achieved by a dry ice jacket around the active media. At this temperature, the fluorescence lifetime of the upper laser level would be ~ 190 ns.

(2) Temperature Dependence of the Fluorescence Intensity

Using the same experimental set-up described above, the fluorescence intensities were monitored as a function of cell temperature after irradiation with a 5150 Å dye laser pulse. At this wavelength only radical excitation is energetically possible. Typical results are shown in Figure 10. The radical fluorescence is observed to decrease by about a factor of three as the temperature is lowered to ~-30°C, but very little subsequent decrease is noted as the sample is slowly cooled to even lower temperatures.

If one treats the radical as a two state system, and assumes rate constants k_p and k_T, where k_p describes the excitation rate to the upper state and k_T the total decay rate back down to the ground state ($k_T = k_r + k_{nr}$), solution of the resulting rate equations gives the excited state population as a function of time. The peak of the fluorescence intensity (I) is then related to the rate constants and the initial ground state population density, $[R_o]$, by the expression

$$I \,\alpha\, \frac{k_r\, k_p}{k_p + k_T}\, [R_o]$$

If the equilibrium constants reported in the literature are correct, the population density $[R_o]$ should decrease by about two orders of magnitude in going from room temperature to -90°C. The total decay rate k_T changes from $\sim 10^8$ at +20°C to $\sim 5 \times 10^6$ at -90°C. The pump rate under the experimental

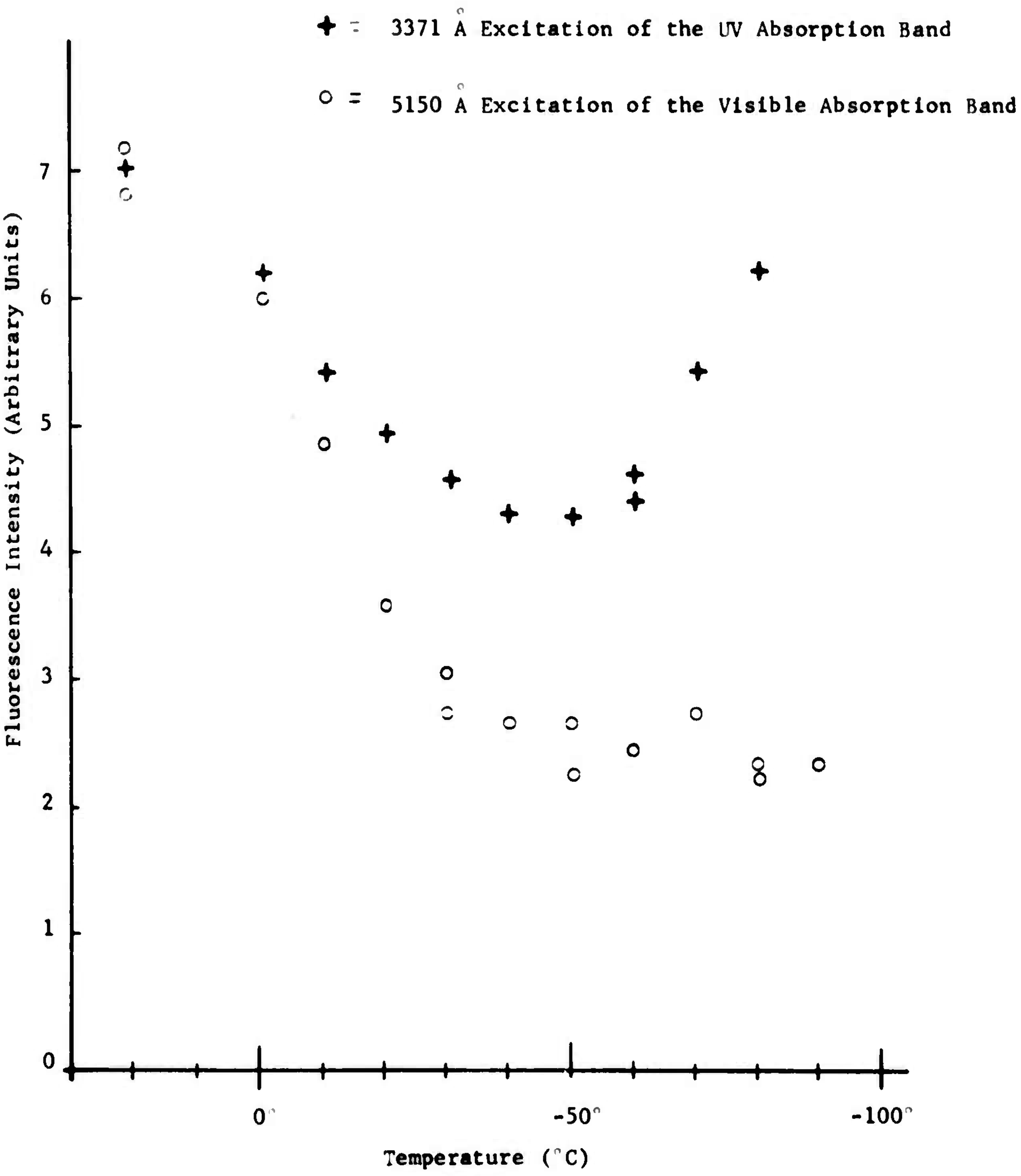


Figure 10. Temperature Dependence of the Triphenylmethyl Fluorescence Intensity Illustrating the Difference Between UV Excitation and Visible Excitation. The Fluorescence Intensities are Normalized to Each Other at Room Temperature.

conditions is calculated to be ~ 2 x 10^7. Using these values one can conclude that the fluorescence intensity should drop by a factor of twenty in going from room temperature to -90°C. Why a decrease of this magnitude is not observed experimentally is not clear. Perhaps the values cited in the literature for the equilibrium constants and/or the extinction coefficients are in error. Much of the experimental work to gather such data was performed more than 40 years ago, and significant experimental details are left out from many of the original references, making an evaluation of the accuracy of the data difficult.

B. Excitation of the UV Absorption Band

(1) Temperature Dependence of the Fluorescence Intensity

The hexaphenylethane-triphenylmethyl system is complicated by the fact that the dimer and radical exist at room temperature. As shown, the strong UV absorption of both the dimer and radical results in a broad absorption band which peaks at ~ 3350 Å. As a result, the fluorescence observed upon excitation with a nitrogen laser (3371 Å) may be produced via two possible channels. The thermally generated radicals could be pumped directly to their second excited state, whereupon rapid internal conversion to the first excited state would result, with subsequent fluorescence to the ground state. On the other hand, upon absorbing the UV photon, hexaphenylethane could undergo photodissociation-- producing excited state radicals which then fluoresce to the ground state. The PDL scheme relies on the latter channel as the production mechanism for the electronically excited radicals. In order to determine to what extent each of these channels contributes to the observed fluorescence, the temperature dependence of the fluorescence intensity was investigated. If the temperature could be lowered to the point where there is no appreciable thermal generation of triphenylmethyl radicals, any observed radical fluorescence would have to be due to dimers photodissociating into excited radical states. Unfortunately, the results of the last section indicate that even at the lowest experimental temperatures, fluorescence from thermally-generated radicals is still non-negligible.

Nevertheless, the presence of photodissociation-generated excited radical fluorescence can still be determined. If the observed fluorescence is due solely to the excitation of thermally generated radicals, then the choice of excitation wavelength should have no effect on the temperature dependence of the fluorescence intensity. Specifically, pumping the UV absorption band with the 3371 Å output of an N_2 laser should yield the same temperature dependence as seen when the visible absorption band of the radical is excited. However, if excitation in the UV causes, in addition to direct radical excitation, the photodissociation of hexaphenylethane dimers into excited state radicals, then the temperature dependence of the fluorescence intensity should be markedly different. This is because the dimer concentration increases with decreasing temperature (see Figure 4) and therefore the fluorescence intensity due to a photodissociation process is expected to increase as well. The concentration of thermally generated radicals decreases with decreasing temperature, and, as has already been shown, so does the fluorescence intensity associated with direct excitation of these radicals. The experimental data shown in Figure 10 does show a distinct difference in the observed temperature dependence measurements, depending on whether only the radical is excited (pumping with 5150 Å) or whether both radical and dimer (pumping at 3371 Å) are excited.

The temperature dependence of the UV data can be understood by assuming that both direct excitation and photodissociation are involved in the fluorescence process. Initially the decrease in thermally generated radical population is the dominant factor, but at lower temperatures the photodissociation process becomes evident by the rise in fluorescence intensity. Unfortunately, because the pumping geometries and excitation volume were different in the two experiments it was not possible to obtain a quantitative contribution from each process to the fluorescence intensity. However, the data qualitatively supports the idea that UV absorption by the dimer causes photodissociation into excited state radicals.

(2) Temporal Behavior of the Fluorescence

Several important conclusions regarding the temporal behavior of the fluorescence decay can be drawn from the rate equation analysis outlined in the first semiannual report (1). If only excitation of thermally generated radicals occurs, then the fluorescence should follow a single exponential decay: $I(t) = I_o e^{-k_T t}$ where $k_T = k_r + k_{nr}$. This fact has been observed experimentally. However, when excited state photodissociation occurs as well, the fluorescence decay should be described by the sum of two exponentials: $I(t) = Ae^{-k_T t} + Be^{-k_D t}$ where k_D describes the dissociation rate.

Analysis of the fluorescence decay curves produced by UV excitation, however, shows that the time dependence is still described by the single exponential decay $e^{-k_T t}$. For this to be consistent with the photodissociation concept, one must conclude that the k_D rate constant is very large. If

$k_D > 10^9$, then for times greater than ~ 1 ns, the decay will be dominated by the first term and the second exponential would not be observable under our experimental conditions because of the response times of the phototubes and instrumentation.

C. Absolute Fluorescence Intensity Measurements

An absolute measurement of the room temperature triphenylmethyl fluorescence intensity was made by calibrating the observed fluorescence signals against the light output from a standard lamp of known brightness. The experimental procedure was as follows:

A known length of the fluorescence cell was transversely excited by the 3371 Å output of the N_2 laser. The fluorescence was focused onto the entrance slits of a monochromator and detected by a photomultiplier tube and fast oscilloscope. The sample was then replaced by a calibrated standard lamp, and the mechanically chopped output was focused by the same lens geometry onto the monochromator. Considerable care was taken to ensure that the collection geometry and solid angle filling factors were kept the same for both the fluorescence cell and the standard lamp. The wavelength at which the calibration was performed was 5200 Å, which corresponds to the peak of the triphenylmethyl fluorescence. By taking into account the appropriate geometrical factors, a value for the excited state population density N, can be deduced from the measured intensities using the expression

$$N = \frac{4\pi \, \Delta\nu}{h\nu \, A\ell\delta\nu} \; \frac{B_s}{I_s} \; I_f$$

where $\Delta\nu$ = bandwidth of fluorescence (taken to be ~ 500 Å)

$\delta\nu$ = acceptance bandwidth of the monochromator

ℓ = excitation length (= 2 cm)

A = Einstein coefficient

B_s = known spectral lamp brightness in units of

$$\left(\frac{\text{power}}{\text{area-steradian-wavelength}}\right)$$

I_f, I_s = the resulting phototube current produced by the fluorescence and standard lamp, respectively.

The results of these measurements show that a 200 kW, 8ns N_2 laser pulse produces ~ 2×10^{15} radicals/cc in the electronically excited state. Since ~ 2×10^{17} photons/cc are absorbed during each pulse the quantum yield for production of excited state radicals is ~.01.

The fluorescence intensity was also observed to increase linearly with pump power, demonstrating that the excitation process is not multiphoton in character, and that possible absorption of the fluorescence by higher lying states is not significant.

If one assumes that the lower laser level is empty, then the excited state population density can be related to the maximum possible gain one can expect from this system. The gain coefficient $\alpha(\nu)$ can be written as

$$\text{The gain coefficient } \alpha(\nu) = \frac{c^2 AN}{8\pi \nu^2 \Delta\nu}$$

Using our calculated value for N, the above expression gives an upper bound value of .02 cm^{-1} for the gain coefficient at the peak of the triphenylmethyl fluorescence curve, under our experimental conditions.

D. Photochemical Stability

A serious problem in the use of hexaphenylethane as a laser medium is its photochemical stability. Figure 11 shows five successive measurements of fluorescence from a room temperature hexaphenylethane solution excited by a 200 kW N_2 laser pulse at a repetition rate of 3Hz. Initially, the fluorescence spectrum is dominated by the characteristic triphenylmethyl radical fluorescence. However, a broad peak centered at ~ 4200 Å is also seen. Each scan took about 10 minutes to complete. The curves are labelled with their respective starting times. As can be readily seen, successive UV excitation results in a decrease of the triphenylmethyl fluorescence intensity and a growth in the intensity of the broad peak. After about half an hour of continuous excitation (5400 pulses), the triphenylmethyl fluorescence intensity is reduced to half its value. In less than an hour (~ 10,000 pulses) the triphenylmethyl radical fluorescence has virtually disappeared and the fluorescence intensity is totally dominated by the peak in the blue spectral region.

This photochemical instability is the result of the irreversible disproportionation reaction discussed earlier (See Section III.A). The blue fluorescence is attributed to the formation of 9-phenylfluorene, a by-product of the reaction. This reaction proceeds at an even faster rate when the sample is exposed to ordinary sunlight. Indications exist, however, that the photochemical stability is enhanced if the solution is cooled below room temperature. In solid matrices, hexaphenylethane does not exhibit this photosensitivity at all (8). This is due to the bimolecular nature of the process.

Excitation Wavelength: 3371 Å
Excitation Power: 200 kw/pulse @ 3 Hz Repetition Rate

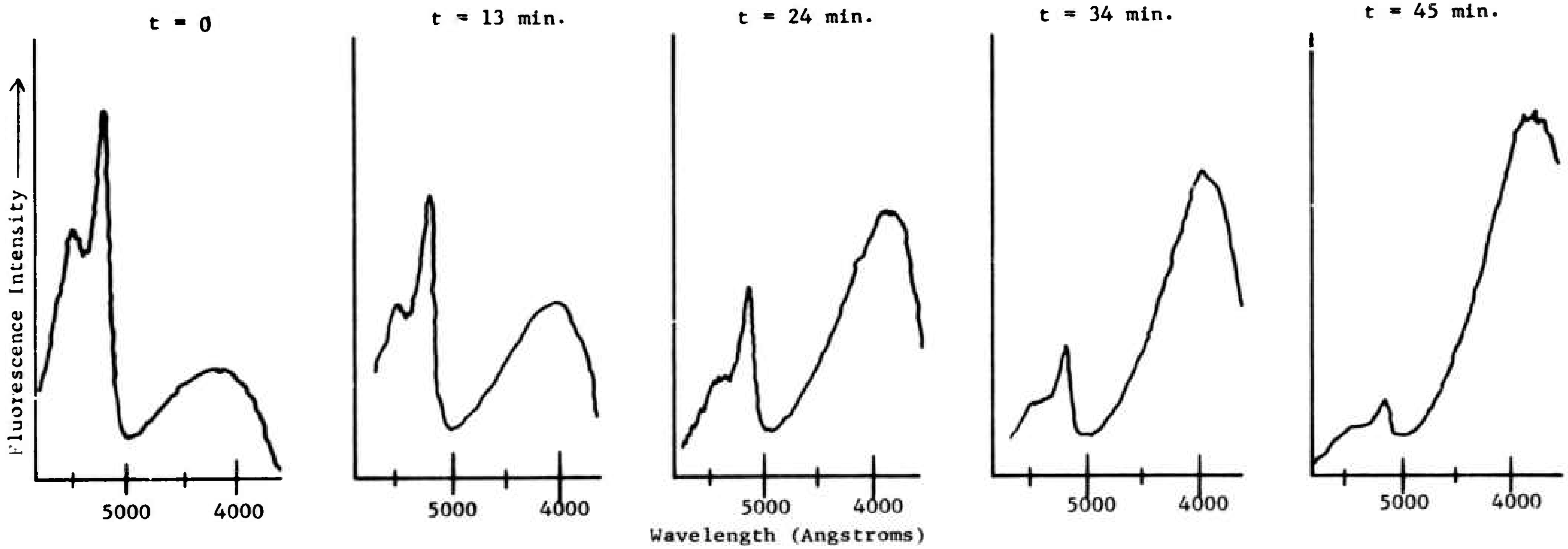


Figure 11. Successive Scans of the Hexaphenylethane Fluorescence Showing the Effect of the Disproportionation Reaction. The Triphenylmethyl Fluorescence Intensity Decreases With Time, and the Blue Fluorescence of one of the By-Products of the Reaction (9-phenylfluorene) is Seen to Increase.

V. CONCLUSIONS AND FUTURE WORK

Hexaphenylethane has been studied as a possible photodissociation dye laser medium. This system was chosen as a potential PDL candidate for the initial study in this "proof of principle" phase of the program because of its readily observable fluorescence and its historically well characterized properties.

On the positive side, photodissociation of the dimer into excited state radicals has been demonstrated, and long fluorescence lifetimes have been measured. Potential optical gains of $\sim .02\ \text{cm}^{-1}$ have been calculated from absolute fluorescence intensity measurements utilizing N_2 laser excitation.

On the negative side, in order to attain a 200 nsec fluorescence lifetime, the system must be operated at dry ice temperatures (-80°C), the material must be handled in an oxygen-free environment because of the extreme reactivity of the thermally-generated radicals, and photochemical stability is very poor.

One topic that warrants further consideration is the dependence of the fluorescence intensity on the excitation wavelength. Although the peak of the hexaphenylethane-triphenylmethyl UV absorption band lies very close to the 3371 Å nitrogen laser wavelength, the cross section for photodissociation into excited state radicals may peak at a different wavelength, and as a result, larger quantum yields of fluorescence may be realizable.

After such measurements, an evaluation of different possible pumping mechanisms (laser vs flash lamp) can be made and the feasibility of demonstrating laser action in the hexaphenylethane system assessed.

A more detailed study of the other PDL molecules synthesized at the start of this program will also be undertaken. The problems associated with radical reactivity will be substantially reduced in these systems, because the equilibrium constants for these molecules ensure total dimerization at room temperature.

VI. REFERENCES

1. A. Kasdan, "Photodissociation Dye Laser", Semiannual Technical Report, Contract No. N00014-73-C0048, April, 1975.

2. A summary of the background information, relevant literature, and pertinent lead references for hexaphenylethane are included in the following sources.

   a. A. R. Forrester, J. M. Hay and R. H. Thompson, "Organic Chemistry of Stable Free Radicals," Academic Press, Inc., New York (1968).

   b. C. J. M. Stirling, "Radicals in Organic Chemistry," Oldbourne Press, London (1965).

   c. Glenn H. Brown, Ed., "Photochromism," Techniques of Chemistry, Vol. III, Wiley-Interscience, New York (1971).

   d. Henry Gilman, Ed., "Organic Chemistry--An Advanced Treatise," Volume 1, 2nd Ed., John Wiley and Sons, Inc., New York, (1963), pp. 581-630.

3. Lankamp, Nauta, and MacLean, Tetra. Letts 2, 249 (1968).

4. Ziegler, Orth, and Weber, Ann. 504, 131 (1933).

5. Ziegler and Ewald, Ann. 473, 169 (1929).

6. G. N. Lewis, D. Lipkin, and T. T. Magel, T. Am. Chem. Soc. 66, 1579 (1944).

7. T. Okamura, K. Obi, and I. Tanaka, Chem. Phys. Letts. 20, 90 (1973).

8. G. N. Lewis and D. Lipkin, J. Am. Chem. Soc., 64, 2801 (1942).