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PHOTOPHYSICAL STUDIES OF SELECTED C_{84} ISOMERS, C_{80} SPECIES, AQUEOUS C_{60} COLLOID, AND A C_{60}-AMINO ACID DERIVATIVE

by

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

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ABSTRACT

Photophysical Studies of Selected C₈₄ Isomers, C₈₀ Species, Aqueous C₆₀ Colloid, and a C₆₀-Amino Acid Derivative

by

Eric C. Booth

Ground- and excited-state studies of ill-characterized fullerenes are presented. The first isomerically enriched study of C₈₄'s major isomers finds they differ significantly in T₁ energies. Their T₁ lifetimes span two orders of magnitude, from 643 µs for D₂(IV) to 5 µs for D₂₀(II). The minor isomer, C₄(a), has a 127 µs T₁ lifetime. Temperature-dependent decay kinetics and triplet-triplet spectra also show clear isomeric variations. These changes are remarkable, since they originate in subtle geometry differences.

The C₈₀{D₅d} isomer lacks appreciable transient absorption. Its slow quenching of ¹Δₘ O₂ emission indicates C₈₀{D₅d}’s T₁ state is within 1 kT (~ 300 cm⁻¹) of 7880 cm⁻¹. O₂-quenching experiments showed that Ho₃N@C₈₀{I₁₀}’s T₁ energy lies above 7880 cm⁻¹. This incaN quenches C₇₀ triplet states, and data suggest their T₁ energies are similar.

The ground-state optical behavior of n-C₆₀ (aq) is dominated by scattering effects. This colloid’s transient attenuation is primarily refractive. Redshifted ¹Δₘ O₂ emission from the colloid indicates the polarizable C₆₀ environment lowers electronic energy levels. The “bucky amino acid” (BAA) shows derivatization-blueshifted transient absorption. This derivative has a T₁ level substantially higher than 7880 cm⁻¹, and is only a modest quencher of singlet oxygen.
ACKNOWLEDGEMENTS

My work on this thesis project has been influenced in many ways, both great and small, by a wide range of students, professors, and research groups. This preliminary section is meant to acknowledge those whose lives and work have intersected my own. Let me apologize in advance if I have inadvertently excluded anyone.

Professor Bruce Weisman has been one of the primary influences on this paper. Without him, I would have had neither the experimental means to analyze the samples, nor the quantum-mechanical knowledge necessary to make sense of the results. His guidance over the past five years has been invaluable; he has provided me with the long-range perspective needed to keep the research project on track, and has shown me patience when my own supply ran thin. In addition, he has provided me with critically important help in preparing for my future outside Rice. For these things, and many others, I owe him my gratitude.

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Dr. Kevin Ausman of Rice University, for supplying us with n-C_{60} (aq) and helping to coordinate the activities of the many labs involved in research on this colloid:

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Also, I must thank my parents for the impetus they provided to get this work completed. It was very difficult for me to get this project started, as I honestly doubted the importance of anything I could say in such a paper. By spurring me to move on, my mother and father gave me the momentum I needed to get past my self-doubt, and convince myself—as well as others—that this research had genuine value.

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CHAPTER I. INTRODUCTION

1.1. Opening Comments

This thesis, by its nature, is an omnibus paper. It incorporates experimental analysis of many different samples, in a number of solvents and states, united under the aegis of fullerene photophysics. This, of course, necessitates an explanation of the author’s motives in studying these carbon allotropes and their interaction with light. Of course, before these aims can be understood, one must know exactly what these phenomena and molecules are.

1.2. Photophysical Phenomena

We are primarily interested in the energetic fate of light after it has been absorbed within a molecule. The standard means of depicting these processes is with a Jablonski diagram (Figure 1.1.) For molecules that have an \( S_0 \) ground state (and most of them do, with a few important exceptions), absorption of a photon will drive electrons from that state up through the manifold of singlet energies. Initially, most of this excess energy is sloughed off via radiationless, vibronic transitions (internal conversion). When these electrons reach the \( S_1 \) state, they may return to the ground state via additional internal conversion, or through emission of their excess energy as photons (fluorescence). Alternatively, the electrons can undergo a “spin-forbidden” transition, entering the manifold of triplet-state energies in a process called intersystem crossing. In this state, electrons can undergo absorptive transitions, just as they do in the singlet manifold.

Returning to the \( S_0 \) level from the lowest-lying triplet level (\( T_1 \)), however, is a spin-forbidden process. For excited molecules to do this in isolation, their triplet-state electrons must either undergo internal conversion, or emit photons (phosphorescence),
via spin-orbit coupling with the nuclei of nearby atoms. In molecules lacking heavy nuclei, this coupling is a relatively infrequent process. As a result of this phenomenon, molecules can sequester energy in their triplet state for appreciable spans of time (from a few microseconds, to tens of milliseconds) following excitation.\(^1\)

![Jablonski diagram](image)

**Figure 1.1. Jablonski diagram.**

The unfavorable nature of internal relaxation from \(T_1\) brings bimolecular phenomena into play. One of the most important of these processes is oxygen quenching. Since oxygen has a triplet ground-state, and a relatively low-lying (7880 cm\(^{-1}\)) singlet excited state, it must (by conservation of angular momentum) absorb energy from any higher-energy triplet-state molecule it encounters. At sufficiently high excited-state concentrations, triplets can also lose their energy via mutual annihilation or in collisions
with their ground-state counterparts (self-quenching). Finally, triplet-state molecules can transfer their energy to other, singlet-state compounds that have equivalent, or lower, $T_1$ energies. (Figure 1.2.)

Phosphorescence $T_1 \xrightarrow{k_{rad}} S_0$

Intersystem Crossing $T_1 \xrightarrow{k_1} S_0$

Oxygen Quenching $T_1 + O_2 \xrightarrow{3 \sum_u} S_0 + O_2 \xrightarrow{1\Delta_g} S_0 + O_2$

T-T Annihilation $T_1 + T_1 \xrightarrow{k_{TT}} S_0 + T_1$

Energy Transfer $T_1 + S'_0 \xrightarrow{k_{ET}} S_0 + T'_1$

Self Quenching $T_1 + S_0 \xrightarrow{k_{SQ}} 2S_0$

Figure 1.2. Fates of the triplet state.

1.3. Fullerenes and Related Compounds

Since their discovery in 1985, fullerenes have been the focus of much interest amongst scientists. Once bulk production of these species became possible, investigation of the allotropes’ physical and chemical properties began in earnest. Spectroscopists rapidly became interested in fullerene’s physical properties. Polyaromatic and $\pi$-conjugated organic systems have a range of triplet-state lifetimes and energies, accessible via pump-probe measurements. By analogy, it was thought—and, by experiment, quickly revealed—that fullerenes and their derivatives possessed similar properties. In particular, it was found that $C_{60}$ forms the triplet state with a quantum efficiency near 1, as does $C_{70}$. The fullerenes were also found to have protracted, and widely differing, triplet lifetimes with distinct absorption properties. This spurred investigators to determine whether other fullerenes would have similar characteristics. Therefore, the author’s
project, and the variety of different fullerene types investigated within it, constitutes an extension of this basic research.

1.3.1. Physical Forms

With the fruition of bulk fullerene production, analysis of these compounds went from the gas phase, to the solid and, finally, solvated liquid phases. The failure of initial attempts to dissolve $C_{60}$ in acetone led to the use of benzenoids, and other nonpolar organics, to create distributions of fullerenes in liquid media. In 1994, however, Scrivens et al. discovered that one could prepare colloidal dispersions of $C_{60}$ in water via an involved solvent-exchange procedure. Further research demonstrated that the fullerene colloid could be made with simpler techniques, making this material available to further physical and chemical investigation.

1.3.2. Derivatives

The field of fullerene chemistry is so immense and wide-ranging that it would be a hopeless task to even attempt a one-paragraph summary of its background. Suffice it to say, that, in the past couple of years, there has been great interest in using fullerene-based compounds as antioxidant agents in biological systems. One of these compounds, an amino-acid-adduct of $C_{60}$, was evaluated by the author in an attempt to determine its potential efficacy.

1.3.3. Endohedral Fullerenes

Shortly after the fullerenes were discovered, it was found that their carbon cages could entrap metal atoms. Discoveries of other such “endohedral” fullerenes, most notably those encapsulating noble-gas atoms, quickly followed. Spectroscopy on one of the latter species, $Kr@C_{60}$, showed an accelerated triplet-state decay, providing
clear evidence of an endohedral heavy-atom effect.\textsuperscript{13} Recently, it became feasible to encapsulate molecules within carbon cages.\textsuperscript{14} Studies of one such endohedral fullerene are described later in this thesis.

1.3.4. Higher Fullerenes

Once researchers began chromatographic separations of Huffman-Krätschmer fullerene-containing soot, it became apparent that there were many isolable forms of fullerenes heavier than \( C_{60} \) and \( C_{70} \).\textsuperscript{15} Mathematical analysis of these species soon revealed that these “higher fullerenes” generally have multiple isomers. Stable fullerenes must have cage arrangements that satisfy the isolated pentagon rule (IPR). While all fullerenes must have 12 pentagons by definition, no two pentagons may share a bond. This would induce severe strain in the carbon cage; thus joined pentagons typically not seen in isolable fullerenes. This mandates that each fullerene from \( C_{60} \) up through \( C_{76} \) may only have one stable-valence isomer. However, for any fullerene with 78 or more carbons, the cage can be arranged in multiple IPR-obeying ways. For example, \( C_{84} \) has 24 possible IPR isomers.\textsuperscript{16} In practice, however, not all of a higher fullerene’s isomers are observed; in the case of \( C_{84} \), only seven isomers have been isolated from Huffman-Krätschmer soot.

Other groups have conducted photophysical analyses of higher fullerenes, primarily \( C_{84} \).\textsuperscript{17,18} However, these analyses were always complicated by the fact that, until recently, higher fullerenes of a given mass could only be obtained as isomeric mixtures, even after substantial HPLC work.\textsuperscript{19} Although recent developments in chromatography have made it possible to obtain fractions highly enriched in individual
isomers, these still exhibit enough cross-contamination to make photophysical analysis challenging.

1.4. Motives for Study: Potential Applications

With some understanding of the photophysics of molecules, and a sense of why fullerenes are of interest in this regard, we may now consider how this confluence of physics and chemistry may be put to use. Some have employed these to model the internal workings of photosynthetic systems.\textsuperscript{20,21} Others have employed fullerenes as energy acceptors in molecular solar-cell designs.\textsuperscript{22,23} There is also interest in the potential of these compounds to act as saturable absorbers, for optical limiting, Q-switching of lasers, etc.

Biomedical applications form the most important background for much of this work. The ability of compounds to generate or quench singlet oxygen is of particular interest in this area. Molecules with relatively high triplet energies and long triplet-state lifetimes generate $^1\Delta_g$ O$_2$—an intensely reactive and toxic species—efficiently. This makes them useful as chemotherapeutic agents in the photodynamic treatment of cancer; since the singlet oxygen is only generated upon irradiation, the drug’s killing action can be confined to the tumor.\textsuperscript{24} Fullerenes have the aforementioned triplet-state properties, spurring a number of groups to pursue their use in PDT.\textsuperscript{25-27} By the same token, species with low-lying triplet states may “quench” $^1\Delta_g$ O$_2$ by sapping its energy in collisional reactions. Thus, medicines based on these low-energy compounds will suppress the destructive effects of singlet oxygen.
CHAPTER II. EXPERIMENTAL DETAILS

2.1. Samples

2.1.1. n-C$_{60}$ (aq)

Initially, it was thought that it was impossible to dissolve fullerenes in polar solvents. In 1994, however, it was reported that colloidal aqueous suspensions of C$_{60}$ can be formed. These sols, which are thought to be comprised of particles 80 to 100 nm in diameter, can be made in two ways:

a) by making a combination of water and organic C$_{60}$ solution, then letting the nonpolar solvent evaporate;$^{8,28}$ or

b) by long-term, mechanical stirring of C$_{60}$ into water.$^{29}$

Since these colloids are of obvious environmental and toxicological significance, it is important to establish their physical and chemical properties.

2.1.2. “Bucky amino acid”

Recently, there has been much interest in making fullerene derivatives with antioxidant properties. To this end, Barron and Yang have created a synthetic method to produce a water-soluble, biocompatible C$_{60}$ mono-adduct. First, the parent fullerene is made to react with 2-butanal across a (6,6) bond, giving what is called a “bucky ketone.” This starting material is further derivatized, to replace the carbonyl oxygen with an ammonium linkage to the side chain of phenylalanine. This creates a “bucky amino acid,” or BAA. (Figure 2.1.)
2.1.3. \( C_{80} \) isomers

2.1.3.1. \( C_{80} \{D_{5d}\} \)

\( C_{80} \) has been termed one of the three "missing fullerenes," due to its extremely low abundance in Huffman-Krätschmer soot. Recently, however, two \( C_{80} \) isomers were
synthesized by Dennis and Shinohara, as a byproduct of the latter’s work in generating endohedral metallofullerenes. One of these was first noted as a very-late-eluting fraction in HPLC separations using Buckyprep columns\textsuperscript{30}; analysis with \textsuperscript{13}C NMR established its D\textsubscript{5d} symmetry.\textsuperscript{31} (Figure 2.2.)

It was felt that this species would be an ideal subject for photophysical analysis. Its strong retention on HPLC columns helps to keep it free from contamination by fullerenes of different mass, and by isomers of different structure. Moreover, its structure is directly related to C\textsubscript{60} and C\textsubscript{70}, via an extension of the famous ten-carbon-addition sequence: C\textsubscript{60} \{I\textsubscript{h}\} \rightarrow C\textsubscript{70} \{D\textsubscript{5d}\} \rightarrow C\textsubscript{80} \{D\textsubscript{5d}\}. Since the two lower species have high $\Phi_{\text{ISC}}$ values, strong transient absorptivities, and long triplet lifetimes, it was thought that C\textsubscript{80} \{D\textsubscript{5d}\} might display analogous properties.

2.1.3.2. Ho\textsubscript{3}N@C\textsubscript{80} \{I\textsubscript{h}\}

This particular endohedral compound is a product of a new, selective synthesis technique pioneered in the laboratories of Dunsch and Dorn. (Figure 2.3.)

![Figure 2.3. Ho\textsubscript{3}N@C\textsubscript{80} \{I\textsubscript{h}\}.](image-url)
In standard incar formation schemes, the metallic element one desires to encapsulate is added to the graphite rods of the arc reactor used for Huffman-Krätschmer fullerene synthesis. Modifying this process, by introducing a reactive gas such as ammonia into the reaction chamber, results in the quantitative formation—i.e. -98% of total extractable product—of a specific higher fullerene isomer enclosing a particular metal nitride molecule. (However, the total yield is greatly reduced.) It is believed that the unique specificity of this process is due to mutual stabilization of the carbon shell and the nitride. In the case of Sc₃N@C₈₀ {Iₖ}, DFT results indicate that the transfer of six electrons from the scandium nitride to the carbon shell allows both to reach energy minima during their formation.³² It is possible that a similar process may occur for the holmium nitride incar. Unfortunately, the holmium atoms preclude computational analysis of this hypothesis, as the lanthanides are not defined in the basis sets of commercially available quantum chemistry programs.

2.1.4. C₈₄ major isomers

The isomeric nature of C₈₄, and the analysis of its isomers, was the subject of the author’s Master’s thesis. Substantial progress was made toward characterizing the properties of these species in the prior round of research. However, technical difficulties (that shall be discussed imminently) prevented the appreciable separation—and, thus, assignment of the properties —of the two most abundant isomers, D₂(IV) and D₂d(II). To address this problem, purified D₂(IV) and D₂d(II) samples were obtained from Dennis’s group in London. Dissolved in toluene, these isomers have appreciably different colors; D₂(IV) appears brownish-green, whereas D₂d(II) has a grass-green hue. (Figure 2.4.)
2.1.4.1. \( \text{C}_{84} \{ \text{D}_2(\text{IV}) \} \)

This species (called ‘\( \text{D}_2(\text{IV}) \)’ for short) is the 22\(^\text{nd} \) of 24 possible, IPR-obeying isomers generated by the Manolopoulos-Fowler algorithm, and is the last of four possible \( \text{D}_2 \)-symmetric \( \text{C}_{84} \) cages. It is the most abundant \( \text{C}_{84} \) species, and constitutes about 50\% of the total \( \text{C}_{84} \) content of Huffman-Krätschmer soot. (Figure 2.5.)

2.1.4.2. \( \text{C}_{84} \{ \text{D}_{2d}(\text{II}) \} \)

This isomer (called ‘\( \text{D}_{2d}(\text{II}) \)’ for short) is the 23\(^\text{rd} \) of 24 possible, IPR-obeying isomers generated by the Manolopoulos-Fowler algorithm., and is the second of two possible \( \text{D}_{2d} \)-symmetric \( \text{C}_{84} \) cages. It is the second-most abundant \( \text{C}_{84} \) species, and constitutes about 25\% of the total \( \text{C}_{84} \) content of Huffman-Krätschmer soot. (Figure 2.5.)
2.1.5. \( C_{84} \) minor isomer: \( C_{84} \{C_s(a)\} \)

As this isomer (called \( C_s(a) \) for short) is the first of two \( C_s \)-symmetric species in order of elution from the PYE column, it is dubbed \( a \). If the assignment of Azamar-Barrios et al. is correct, this isomer is the 14\textsuperscript{th} of 24 possible, IPR-obeying isomers generated by the Manolopoulos-Fowler algorithm, and is the third of five possible \( C_s \)-symmetric \( C_{84} \) cages.\textsuperscript{33} It is approximately the fifth-most abundant \( C_{84} \) species, and constitutes about 5\% of the total \( C_{84} \) content of Huffman-Krätschmer soot. (Figure 2.5.)

![Orthogonal views of \( C_{84} \) isomers](image)

**Figure 2.5.** Orthogonal views of three \( C_{84} \) isomers investigated, along with abundances. (Adapted from Manolopoulos and Fowler, "Molecular Graphs, Point Groups and Fullerenes," J. Chem. Phys, 15 May 1992, v. 96, no. 10, p.7610.)
2.2. Methods

2.2.1. Separation: Comments Regarding Higher Fullerene

Chromatography and its Limitations

Since the bases of the following procedures have been discussed extensively in the literature, they will not be reiterated here. Instead, the following section will discuss practical considerations in their implementation, and present the results of their use. See the author’s “Photophysical Properties of Selected [84] Fullerene Isomers” for details.

2.2.1.1. rHPLC

While the rHPLC technique is indispensable for higher fullerene work, technical factors have made its continuation impractical within our laboratory. The central issue here is the partitioning process itself. By reducing solvent strength (and thus increasing retention of the analyte on the stationary phase), both peak separation and peak broadening will increase. To get the optimum resolution, then, one must alter the solvating power of the mobile phase to get the highest ratio of separation to broadening. In ordinary HPLC, this is not a major problem; one simply adjusts the solvent composition as needed. With rHPLC, however, only isocratic elution is feasible, as solvent mixtures would separate during the recycling process, giving unpredictable results. While stronger mobile phases can be used if less partitioning to the stationary phase is needed, this is not necessarily feasible. Solvents more powerful than toluene:

1) are too viscous for liquid chromatography (e.g. decalin);
2) pose severe safety risks (e.g. CS₂); and/or
3) have damaging effects on health and the environment (e.g. ortho-dichlorobenzene).
After comparing the author’s results with those of Dennis and Shinohara, it became evident that the performance shortcomings experienced here were primarily a function of solvent choice, rather than damper optimization. Firstly, close investigation of the Dennis group’s chromatograms revealed the same “floor” that had been observed in the author’s rHPLC work.34 (Figure 2.6.)

![Absorbance vs. Retention Time](image)

**Figure 2.6.** rHPLC chromatogram of incar/fullerene separation in Dennis’s group. Note rising baseline, indicative of diffusion/mixing from pulse damper. (Illustration from Porfyraakis et al, “Endohedral Fullerene Dimers as Potential Building Blocks for a Quantum Computer,” Proceedings of the International Symposium on Fullerenes, Nanotubes, and Carbon Nanoclusters, vol. 13, p. 531.)

This is significant, since it reveals that the construction of the two groups’ instruments was fundamentally identical. The floor is an unavoidable byproduct of solute diffusion and eluent/solvent mixing created by the pulse damper’s activity. While it can be minimized, it can never be totally eliminated, as Dennis and Shinohara’s chromatogram
shows. Secondly, the Nagoya group did its rHPLC separations with CS₂ rather than toluene, as indicated:

1) indirectly by the 400 nm cutoff of their UV-vis spectra; and

2) directly by Shinohara's shipping of C₈₀ {D₅₄} in CS₂.

However, since the author's lab lacks the equipment for safely handling multi-liter quantities of CS₂, this rHPLC refinement could not be implemented. Column heating, another option for reduced retention, was not attempted.

On the basis of these and other factors, we chose to discontinue our rHPLC work here, and begin a collaboration with Dennis on the major isomers of C₈₄. Unfortunately, these samples had problems with incomplete purification, as will be discussed later. While it has been suggested that the cross-contamination of these fractions may have been due to operator error, the incident suggests that even this technique may be fundamentally limited in its ability to separate higher fullerene isomers. The mixing effects of the pulse damper and the pump's dead volume are apparently a major cause of the incomplete resolution.

2.2.1.2. SMB

These difficulties with rHPLC impelled us to consider alternative separation techniques. One possibility is the simulated moving bed (SMB) process, which implements multi-pass chromatography without rHPLC's technical problems. As a means toward this end, two Cosmosil semi-prep 5-PYE columns were connected in series through a Rheodyne 7000 6-port switching valve, as per the procedure described in the author's previous thesis. After immersing these columns in an ice bath (the author's misguided attempt to increase the solute's partition to the stationary phase), 0.5 mL of a
ternary mixture of C₈₄ isomers \{D₂(IV), D₂d(II), C₅(a)\} were injected. This was eluted with isocratic toluene at 1.75 mL/min; four column switchings were performed, giving a total running time of about 6 hours.

Under these conditions, the two major isomers were not separated. However, analysis of the spectral traces showed that a 620 nm feature became progressively more prominent as the final peak eluted. (Figure 2.7.)

![Chromatogram](image)

**Figure 2.7. Chromatogram from SMB run, showing spectral change over course of final elution, with isomeric features indicated.**

This peak is present in the observed ground-state absorption profile of D₂d(II); therefore, its growth with time indicates that the two major C₈₄ isomers were disproportionated within the main peak.

Due to the inordinately long time required for this separation attempt, no further SMB work was attempted. However, as indicated above, the conditions used in this run
were far from ideal. This experiment's failure to separate D$_2$(IV) from D$_{2d}$(II), then, does not suggest any fundamental shortcomings in the SMB method. Indeed, it is remarkable that these isomers were partially resolved, given the small number of cycles and excessive stationary phase retention. By using room-temperature CS$_2$, with its lower viscosity and higher solvent strength, one could get shorter runs, use more cycles, and obtain higher resolution. This option is particularly infeasible in the author's lab, since it would involve the handling of even greater quantities of hazardous solvent than would conventional isocratic HPLC (due to the constant flow of solvent through the system over multiple passes).

2.2.1.3. WSKC

Another possibility is the use of a chemical separation method. By derivatizing C$_{84}$ with a compound that binds preferentially at sites of a given curvature, one could theoretically exaggerate the isomers' differences in $\pi$-$\pi$ interactions with the stationary phase, thus increasing resolution. Alternatively, if a compound reacts preferentially with one isomer, chromatography will yield an underivatized fraction that is enriched in the other isomer(s). Following the procedure described by Wang, Saunders, Khong and Cross,$^{36}$ (ergo, the name 'WSKC') we sought to form Diels-Alder adducts of 9,10-dimethylanthracene (9,10-DMA), a polyaromatic hydrocarbon, with C$_{84}$ isomers. An earlier failure to form adducts was initially attributed to photo-oxidation of the PAH. However, inspection of the ground-state spectra of a 9,10-DMA (tol) solution showed no noticeable difference before and after one year of shelf life. This information, along with consideration of the equilibrium constant of the reaction, led us to conclude that the lack of product was actually due to insufficient concentrations of the reactant species.
To remedy this problem, a stronger solvent was needed. After some consultation, we found that the major isomers and 9,10-DMA had to be dissolved in 1-methylnaphthalene. After the compounds were transferred into this solvent and left to react, an initial attempt to separate the product from this mixture was made. When the solution was injected onto an ice-chilled PYE column (to prevent dissociation), nothing eluted after the underivatized C_{84} peak. With the column temperature raised to 25\degree C, a “mesa” of product emerged, then gradually leached out over the course of nearly 3 hours (Figure 2.8.).

![Chromatogram of “mesa” at 404 nm.](image)

**Figure 2.8. Chromatogram of “mesa” at 404 nm.**

This indicates that the concentration of the sample was too high; since the column separated the methylnaphthalene from the adducts, the latter species precipitated in the weaker solvent of the mobile phase.

A second round of attempts to resolve the adducts was made. This involved a factor-of-35 dilution in toluene immediately prior to the first injection onto chilled PYE,
Figure 2.9. Chromatograms of WSKC mixtures a) immediately following and b) 90 minutes after dilution. Note disappearance of adducts due to back-reaction.

as a means of preventing precipitation. The resulting chromatogram showed an underivatized C₈₄ peak, followed by two later-eluting, tailing peaks. A second run was made immediately after the first, using the same material that had been diluted some 90 minutes earlier. In this separation, the tailing peaks had disappeared, indicating that they corresponded to the mono- and bis- adducts. (Figure 2.9.)
Once again, raising the column temperature resulted in ejection of retained material; apparently, the pre-dilution was not sufficient to prevent the crystallization of adduct. While no spectral change across the adduct peaks was noted, a computer crash immediately after the elution of the "mesa" destroyed all data from the runs, precluding a formal assessment of this issue.

To assess the possibility that the 9,10-DMA selectively formed adducts with one of the isomers, the underivatized fraction from the initial second-round separation was evaporated down and had its ground-state spectrum taken. This was compared with the UV-vis absorption features of the starting material. Differences between the two spectra were noted, especially blue of 400 nm (Figure 2.10.). The disappearance of the 570 nm maximum in the underivatized fraction suggested de-enrichment of the D_{2}(IV) isomer, as did the broadening of the 400 nm maximum. However, the very low optical density of the underivatized C_{84} fraction made it difficult to determine the real nature of these differences. Faced with this set of unpromising results, we opted to discontinue WSKC work at this point.

Why did these attempts at chemical separation fail? A persuasive explanation has been offered by Hirsch. As indicated above, the reaction of 9,10-DMA with fullerenes is a dynamic balance between the reactants and products. When adducts are injected onto a column, the back-reaction will continue. However, during the chromatographic separation, the forward reaction will no longer be favored, as the PAH will be promptly swept away by the mobile phase. Therefore, even if there are chemical differences between the adducts formed by the various isomers, these subtle variations will be erased.
Figure 2.10. Ground-state spectra of major isomer mixture before and after separation of WSKC reaction mixture.
This argument can be extended to the case of preferential reactivity. Even if it does occur, it will be a moot point; the variations between isomers will be relatively small, and obscured by the dissociation of the C$_{84}$-DMA species.$^{38}$

One more question about the WSKC process remains to be answered. The Yale group reacted the PAH with $^3$He@C$_{84}$. Subsequent column separation, de-derivatization and cleanup gave fractions with the same set of $^3$He NMR chemical shift environments, but differing peak intensities within the set. The multiple frequency shifts were attributed to the individual isomers, and their varying relative magnitudes were attributed to disproportionation of C$_{84}$ isomers amongst the fractions.$^{36}$ How, in the face of these data, can one reasonably claim that chromatography of the Diels-Alder adducts cannot yield isomeric separation? The answer involves two points:

1) $^3$He NMR is a necessarily indirect probe of isomeric identity. Wang et al. did not provide UV-vis spectra of the separated fractions; nor were reference $^3$He spectra made for $^3$He@C$_{84}$ isomers resolved via the rHPLC method. In the absence of such data, one cannot definitively conclude that the differences between the Yale group's fractions were due to differences in isomer concentrations.

2) The preceding issue, while relevant, begs the question—if the species giving different $^3$He shifts were not the isomers, what were they? The author hypothesizes that the variety of peaks Wang et al. observed in these NMR experiments was actually indicative of C$_{84}$O contamination. It has been well-established that C$_{60}$ and C$_{70}$ spontaneously form oxides.$^{39,40}$ This presumably occurs when they react with ozone in ambient air, to give a variety of epoxides and annulenes.$^{41}$ Moreover, it has been qualitatively observed that C$_{84}$ samples, when exposed to oxygen over time, will oxidize
to form insoluble material. On the basis of these observations, it seems reasonable to believe that a series of $C_{84}O$ epoxides and annulenes could have been partially resolved by the Yale group's separation protocol.
2.2.2. Analysis: instrumentation

2.2.2.1. Transient absorption spectroscopy with notch filter

![Diagram of transient absorbance spectrometer, modified to incorporate holographic filter for subtraction of scattered laser light.](image)

The instrumentation and procedures used for the observation of metastable states in the compounds studied were discussed in the author's previous thesis, and will not be elaborated upon here. While the apparatus used for this purpose was effective, it did have a fundamental limitation that had to be addressed. The dielectric filters used to redirect
the 532 nm laser light into the sample, and exclude that light from the detector stage, have very broad cutoff peaks. As a result, much of the wavelength range available for probing and detection was obscured, and thus unusable. Changing to another excitation wavelength is not necessarily a reasonable solution, either. The alternate harmonics of the Nd-YAG laser are not so useful. Few fullerenes have absorptions at the first harmonic (1064 nm), and those that do have very small epsilons. On the other hand, when this laser’s emission is when converted to the third harmonic (355 nm), the beam power generated is inadequate for exciting samples in this application.

In order to address this problem, a holographic notch filter (HNF) was obtained. This optical element, which has widespread use in Raman spectroscopy, efficiently rejects laser light with a very narrow band (∼3 nm) while leaving closely adjacent wavelengths nearly unattenuated. Since the performance of an HNF is very sensitive to its angular orientation, incident light must be collimated for maximum filtration effectiveness.43

The filter’s installation was not a totally straightforward task. Since the dielectric reflectors had to be completely removed for the HNF to be effective, the excitation pathway also had to be reworked. The new orientation of the pump beam (or “pump”) had to satisfy two requirements:

1) It had to have the maximum possible overlap with the sample volume illuminated by the probe beam (or “probe”); and

2) It had to miss the probe lamp’s bulb, in order to avoid the creation of spurious transients from laser heating of the tungsten filament.
Initially, it was proposed that collinear, copropagating excitation be used. This would have involved folding the pump into the probe with an uncoated optical flat, and placing the HNF (and its associated lenses) ahead of the monochromator's entrance slit. The manufacturer's literature indicated that the filter could have tolerated the incident power levels such an orientation would have created. However, fears of damaging the expensive HNF mandated a post-monochromator geometry. To make this possible without sending laser light directly into the monochromator (a recipe for grating damage), a prism was used to fold the pump away from the entrance slit at an angle nearly collinear with the probe. Properly oriented, the laser beam would then strike the frame of the shutter, and not go into the probe optics. (Figure 2.11.) Finally, to improve the overlap of the beams, and to ensure that the probe beam would more closely match the f-number of the input optics, the probe optics were moved back, and the lens at the entrance slit was changed. However, this new geometry had to be rescinded, as it impeded transient emission experiments. The instrument's "input cone" had been deliberately left underfilled during its initial configuration, in order to facilitate the instrument's use for both absorption and fluorescence experiments.

2.2.2.2. Cryostat: cryogenic glasses

The cryostat's use for variable-temperature kinetics was also discussed in the previous thesis; the reader is referred to that document for more information. In addition to kinetics work, our Optistat$^{DN}$ was used for experiments with cryogenic glasses. This was done to address some of the limitations of PMMA films. While the polymer is very useful for suppressing bimolecular processes, it is impossible to recover a sample from the film once it has been cast. Moreover, the chemical environment of a PMMA matrix
tends to perturb electronic transitions of solutes within it. These problems can be circumvented by dissolving the sample in a hydrocarbon mixture. If this solution has the right constituents in the right proportions, it will not crystallize upon rapid cooling to liquid nitrogen temperature. Instead, it will form an amorphous, optically clear material which can then be used for absorption measurements. The low temperature sharpens the absorption peaks of the solute; the hydrocarbon solvent’s minimal interaction with π-conjugated electron systems also serves to sharpen the transitions.\textsuperscript{44} The temperature-sharpening effect results from the unvarying nature of the integral joining the initial and final states through the dipole moment operator.\textsuperscript{45} This enables its electronic transitions to be catalogued in greater detail, and with more accuracy, than would otherwise be possible.

One limitation of this technique is that large molecules, such as higher fullerenes, have poor solubility in most aliphatic solvents. Since the vast majority of cryogenic glasses must be made with mixtures of such hydrocarbons, C\textsubscript{84} isomers (and other, similar species) cannot be analyzed with these glasses. Therefore, it was necessary to find a combination of glass-forming solvents that would: 1) Have the ability to dissolve appreciable quantities of higher fullerenes; and/or 2) Not be aromatic themselves. To test these mixtures, a variety of solvent combinations were prepared in test tubes, and dunked in nitrogen. A five-component toluene-containing glass, which yielded the best results in these experiments, was then tested in the cryostat with dissolved C\textsubscript{60}. In this experiment, as with all the other glass experiments in the cryostat, the sample chamber was purged of air and moisture by three cycles of rapid pumping down to ~150 Torr, immediately followed by backfilling with ultra-high-purity nitrogen gas, and a 20 s equilibration
period. By avoiding very low pressures in the sample chamber, this approach prevented problems with differential vaporization of the solvents in the glass mixture. Additionally, the nitrogen gas also serves as a heat exchange medium, transferring thermal energy from the sample to the cryostat's heat exchanger.

While the toluene glass had adequate dissolving power, it excessively perturbed the ground-state spectrum of the fullerene. For example, the A$_1$ transition, ordinarily intense and sharp at 77 K, was quite weak in the toluene glass; the A$_0$ transition, also known to be strong in cryogenic experiments, did not appear at all in the toluene-containing mix.

After consulting the literature and conducting more tests with combinations of pure solvents, another mixture was selected. This second glass-forming solvent combination consisted of equal volumes of methylcyclohexane and decahydronaphthalene (a.k.a. decalin),$^{46}$ the latter component was selected because it is a strong solvent for fullerenes. When C$_{60}$ was dissolved in this mixture, the resulting glass gave sharp absorption features in both the A and γ transition regions. These features were comparable to those seen in the standard, 1:1 methylcyclohexane:isopentane glass.$^{13}$ (Figures 2.12, 2.13.)
Figure 2.12. Ground-state absorption spectra, from 370-426 nm (A transition region), of C$_{60}$ in 77 K glasses: a) 1:1 methylcyclohexane:decahydronaphthalene; b) 1:1 methylcyclohexane:isopentane. Note similarity of spectral profiles. [Image b) adapted from Yamamoto et al, “Isolation and Spectral Properties of Kr@C$_{60}$, a Stable van der Waals Molecule,” J. Am. Chem. Soc, v. 121, #7, p. 1594, 1999.]
Figure 2.13. Ground-state absorption spectra, from 580-640 nm (γ transition region), of C_{60} in 77 K glasses: a) 1:1 methylcyclohexane:decahydronaphthalene; b) 1:1 methylcyclohexane:isopentane. Note similarity of spectral profiles. [Image b) adapted from Yamamoto et al, “Isolation and Spectral Properties of Kr@C_{60}, a Stable van der Waals Molecule,” J. Am. Chem. Soc, v. 121, #7, p. 1594, 1999.]
Following this, attempts were made to prepare a \( \text{C}_8 \{ \text{C}_5(a) \} \)-containing glass. For reasons to be discussed later, fully deuterated versions of the methylcyclohexane and decahydronaphthalene had to be used. The author, in collaboration with C. Dicus, also conducted experiments with a third variant of the glass. This mixture was a 1:1:1 combination of ethyl iodide:methylcyclohexane:decahydronaphthalene. The ethyl iodide was added to trigger spin-forbidden intersystem crossings in analyte molecules, via heavy-atom induced spin-orbit coupling.

Unfortunately, the vast majority of the cryogenic glass experiments were unsuccessful; two failure modes were observed. The solvents would either crystallize massively before reaching 77 K (forming a white, opaque solid unsuitable for transmission measurements), or shatter upon reaching liquid nitrogen temperature (with similar optical consequences). While a number of measures were taken to address these problems, none of these procedures seemed to ameliorate the difficulties encountered:

-- Some runs were made using partial cooling, i.e. the sample temperature was lowered to 100 or 120 K, rather than being brought all the way down to liquid nitrogen temperature. Since a hydrocarbon glass is effectively a supercooled liquid, this procedure was thought to increase the mechanical robustness of any given mixture by keeping it closer to its freezing point (making it less thermodynamically unstable).\(^{47}\) This was not entirely effective, and introduced an additional element of irreproducibility. Some glasses would remain clear to lower temperatures than would others, preventing direct comparisons between different samples and experiments.
-- In order to address the possibility that the crystallization resulted from insufficiently rapid cooling in the cryostat, a “precooling” procedure was tested. In this series of steps, the sample probe was first removed from the cryostat. After using a blank plate to seal the Optistat’s sample chamber, it was then pumped down, backfilled with nitrogen gas, and cooled to 77K. On reaching liquid nitrogen temperature, additional gas was added until the sample chamber’s internal pressure rose back to 760 Torr. After loading the glass solution into the cuvet, and inserting the cuvet into the sample holder, the solution was then immersed in liquid nitrogen. Once the boiling halted, the sample holder was removed from the bath as the sample chamber was unsealed; the holder would then be quickly inserted into the cryostat and sealed in place. The chamber would then be re-degassed, following the aforementioned purging/backfilling procedure. Regrettably, this procedure generally caused shattering of either the hydrocarbon glass, the cuvet, or both. Indeed, the severe thermal stress involved in this “dunking” process would invariably destroy even heavily fused silica cuvets after a few cycles.

-- It is possible that the accumulation of stress in these vessels was accompanied by formation of micro-fissures in their inner walls. These cracks, of course, would then serve as nucleation sites that would disrupt the supercooled liquid state. However, use of new cuvets did not help matters.

-- It was hypothesized that the crystallization might be triggered by residual moisture in the components of the glass mixture, introduced before or during the cooling step. To ensure this contamination would not originate from the stock
hydrocarbons themselves, the author used solvents packaged under dry nitrogen in septum-sealed bottles. When this measure proved unhelpful, it was surmised that H₂O could become entrained in the mixture during the mixing of solvents, or during the dissolution of analyte. In response to this hypothesis, the hydrocarbons were mixed over molecular sieves, then transferred into the cuvet through an HPLC syringe filter (to remove the dust introduced by the sieves). Again, these steps proved futile.

Another hypothesis held that crystallization was induced by contaminant particles on the inner walls of the cuvet. However, cleaning of the cuvets with concentrated chromic acid had no beneficial effect on the outcomes of the glass experiments.

Yet another possible agent of glass failure is the volume of sample involved. If the amount of material is excessively large, heat transfer will occur unevenly throughout its bulk, leading to accumulation of stress. To reduce the volume of glass solution, and increase the surface area/volume ratio of the sample, thinner-than-usual cryogenic cuvets were tested. Unfortunately, these did not improve results.

Furthermore, additional experiments cast the “recoverability” advantage into doubt. As we shall see later, spectroscopic analyses of higher fullerenes can be skewed by such minor amounts of contamination that even HPLC separation will not necessarily help matters (due to leaching of adsorbed lower fullerenes). Consequently, sending glass solutions of such samples back through a column is not recommended. After considering all these difficulties, the author chose to discontinue the cryogenic glass work.
One factor that may have played a role in the repeated crystallization/shattering of the hydrocarbon glasses is their "eutecticity," or lack thereof. A eutectic mixture is one that solidifies at a single temperature, without prior crystallization of its individual components.\textsuperscript{48} This is significant, because systems that readily form an amorphous phase share the property of being near, or at, eutectic stoichiometry. This is a general property of all glass-forming mixtures, organic ones included.\textsuperscript{49} However, in the case of cryogenic glasses for optical spectroscopy, there has apparently been no systematic effort made to determine the closeness of the mixtures to their eutectic ratios. This analysis could be done by putting various hydrocarbon mixtures into the cryostat, and monitoring their temperatures as they are cooled at a controlled rate. With decreasing chamber temperature, individual components of the mixture will solidify until the liquid reaches the eutectic composition; the sample temperature will then level off (the "eutectic halt") until complete solidification is attained. The longer the eutectic halt, the closer the sample is to the eutectic composition. Since it was not apparent how the sample probe could be rewired to accept a thermocouple lead, and since such an experiment would have consumed time that would be better spent on photophysical measurements, these eutecticity experiments were not attempted.

Another possible solution to the cryogenic glass problems that was not pursued was a means of cooling the hydrocarbon mixtures more rapidly than was possible with immersion in liquid nitrogen. It is known that the formation of amorphous solids is dependent on very fast cooling.\textsuperscript{49} However, when a sample is immersed in N\textsubscript{2} (l), the liquid immediately surrounding the mixture flashes into vapor, forming an insulating layer (via the renowned Leidenfrost effect) that impedes prompt temperature change in
the glass solution.\textsuperscript{50} To address these limitations of nitrogen cooling, groups doing cryo-TEM research on Langmuir-Blodgett films routinely immerse their samples in baths of liquid ethane at 90 K. Vapor bubbles form much less readily in this liquid, resulting in drastically accelerated cooling rates.\textsuperscript{51} However, the severe flammability of liquid ethane dissuaded us from testing this procedure.
CHAPTER III. RESULTS AND ANALYSIS

3.1. n-C_{60} (aq)

3.1.1. Ground-State Attenuation

One complication in the optical study of any colloidal solution is its inherent admixture of scattering and absorption features in ground-state UV-vis spectroscopy. (NB: This is why the term “attenuation,” rather than “absorption,” will be used when referring to the colloid’s spectral properties; the former word more adequately covers the dual nature of n-C_{60}’s response to light.) This fact was borne out in the current study of n-C_{60} (aq). Rayleigh scattering appears to dominate the colloid spectrum to the red of 775 nm; a $1/\lambda^4$ fit to the data gave very good results. (Figure 3.1.)

![Graph showing Rayleigh scattering region of n-C_{60} (aq).](image)

Figure 3.1. Rayleigh scattering region of n-C_{60} (aq).
Figure 3.2. Ground-state spectrum of n-C$_{60}$ (aq) at 298 K.

However, there are questions as to the applicability of this scattering model. Deviation from the Rayleigh fit occurs well to the red of C$_{60}$'s singlet onset (ca. 650 nm). Moreover, the colloid's dimensionless size constant $\alpha$, over the wavelength range from 775 to 1200 nm (the point at which H$_2$O absorptions become significant), lies between 0.31 and 0.49. If we assume that the refractive index of C$_{60}$ is equivalent to the 1.96 of carbon black (and ignore the complex component of the index that arises from absorption), the product of the index and $\alpha$ ranges between 0.62 and 0.95. While all these numbers are below one (the borderline considered to separate Mie and Rayleigh scattering), they are not so far below that value as to definitively support the Rayleigh model. Confirmation of the scattering mechanism would require solving Lambert's Law of extinction for the particle size, and comparing the result to the known TEM data. This, in turn, would require knowledge of the number density of the sol particles, and
gravimetry to estimate that density. In the absence of such gravimetric data, the author cannot proceed further along these lines.

The electronic transition region of the n-C$_{60}$ (aq) spectrum showed maxima at 344, 268 and 220 nm. (Figure 3.2.) This is quite interesting, since these peaks are appreciably red-shifted from what is observed for C$_{60}$ in other media. For example, in n-hexane solution, C$_{60}$ displays maxima at 328, 256 and 211 nm.$^{15}$ The chief maximum in toluene is centered at 336 nm; in solid films, the absorption peaks are seen at 339, 264 and 216 nm.$^{3}$ This seems to suggest that the real absorption (as opposed to turbidity-induced) features of the spectrum are created mostly by the C$_{60}$ molecules trapped within the inner regions of the sol particles. It has been generally observed that increasing the polarizability of a solvent (which is equivalent to increasing its dielectric constant) lowers a solute's electronic excitation energies.$^{52}$ One could thus argue that, this case, the fullerenes within the colloid particles are dissolved in a matrix of other C$_{60}$ molecules, and respond with less-energetic electronic transitions. With its extended, π-conjugated electron system C$_{60}$ would be an extremely polarizable “solvent.”
Figure 3.3. Beer’s law deviations observed in a serial dilution of n-C$_{60}$ (aq).

Inspection of the light-attenuation properties of various dilutions of n-C$_{60}$ (aq) revealed that the colloid consistently failed to obey Beer’s law; linear scaling of the spectrum was not observed as the concentration changed. (Figure 3.3.) This spectral distortion is generally observed in colloidal solutions, and is attributed to multiple scattering of photons within the bulk of the sample.$^{53}$ To confirm that this was the case, the Rayleigh scattering regions of two dilutions were inspected. Nonlinear scaling of the intensity of this scattering was observed with changing concentration; this is known to be indicative of a multiply-scattering colloid.$^{54}$ Attempts to circumvent this problem through narrow-path-length cells and aggressive dilution were inconclusive, as instrumental artifacts tended to overwhelm the n-C$_{60}$ (aq) spectrum at low concentrations.
Figure 3.4. Normalized fluorescence spectra of n-C$_{60}$ (aq) and C$_{60}$ (tol). Note former’s $^1\Delta_g$ O$_2$ luminescence.

3.1.2. Luminescence

The fluorescence spectrum of n-C$_{60}$ (aq) is very broad, peaking around 810 nm. Its maximum is located well to the red of the observed peak for C$_{60}$ (tol). (Figure 3.4.) The emitting species certainly displays the same spectral trends as the absorbing species; they must, therefore, be the same. However, it is unclear whether this result confirms either of the preceding arguments about the location of the absorber/emitter in the colloid.

A sharp emission peak from the n-C$_{60}$ (aq) was observed at about 1283 nm. With this sample in a degassing cell, the pressure of atmospheric gas over the colloid was decreased and increased repeatedly over the course of a few minutes. The strength of the 1283 nm emission was assessed following each degassing and ingassing event. Since the
Figure 3.5. $^1\Delta_g$ O$_2$ emission from n-C$_{60}$ (aq) as a function of O$_2$ concentration. The intensity of this emission was directly proportional to the oxygen concentration in the sample, the 1283 nm peak was attributed to singlet oxygen luminescence. (Figure 3.5.) These changes in intensity were also immediate and reversible. From these data, some clear inferences can be drawn:

1) Triplet states are being induced in (at least some of) the constituent molecules of the colloid particles. Without these, singlet oxygen luminescence could not occur.

2) These molecules must be at the periphery of the colloid particles. If the oxygen molecules had to diffuse into or become trapped within the particle bulk to give the luminescence, the prompt intensity changes with changing oxygen levels would not have been seen.
3) The $^1Δ_g$ O$_2$ in n-C$_{60}$ (aq), while not deep within the colloid particles (for the aforementioned reason), must be within the particles themselves. The 1283 nm emission is very strongly red-shifted in comparison to what is seen in other environments. For example, $^1Δ_g$ oxygen luminescence in CS$_2$ peaks at 1280 nm, as opposed to the 1277 nm observed in toluene. Moreover, since singlet oxygen in water emits at 1270 nm, this luminescence cannot originate from hydrated-state O$_2$ molecules. This, in turn, implies that the interior of the colloid particle is largely water-free—a sensible result, given the hydrophobicity of C$_{60}$. Such a result suggests, as before, that the singlet oxygen is held within a highly polarizable fullerene matrix.

4) The molecules entering the triplet state must also be in the same location as the ones responsible for the redshifted absorption and emission features. After all, non-sensitized molecules cannot enter the triplet state without first absorbing light. Consequently, the absorption and emission seen above probably originate from this “superficial” region of the particles. This also makes intuitive sense, as the light density within a uniformly irradiated, absorbing particle should be “inversely apodized.” At shallow depths, the number of absorbers per unit area will be small. Near the center of the particle, there will also be few light-absorption events, because most of the incident radiation will have been absorbed at higher layers.

5) Saturation of the energy-exchanging species is not occurring; that is, the number of molecules that actually sensitize singlet oxygen is less than the total number of excited molecules. Had saturation happened, the dependence of luminescence intensity on the oxygen concentration would have been strongly nonlinear.
Further comparison of the singlet oxygen luminescence in n-C_{60} (aq) with that from C_{60} (tol) indicates that the effective $\Phi_{1\Delta g}$ for the colloid is in the range of 3.5%, which lends credence to the previous assertion.

These singlet oxygen results have a significance that extends beyond photophysics. It has been reported that n-C_{60} (aq) exhibits toxicity in microorganisms, earthworms and fish.\textsuperscript{56} Therefore, it is important to establish the mechanism by which the colloid creates damaging effects in biological systems. It is well-known that $1\Delta g$ O$_2$ is very destructive to biomolecules.\textsuperscript{57} Since n-C$_{60}$ (aq) generates this species when exposed to light, it is reasonable to suspect that the colloid’s poisonous effects stem, at least in part, from its sensitization of singlet oxygen.

3.1.3. Transient Light Attenuation

Transient light attenuation was exhibited by the n-C$_{60}$ (aq) sample. The kinetics of this colloid’s change in optical density following pulsed excitation showed an initial sharp rise, followed by a slow decay component and a long pedestal lasting for a number of milliseconds. (Figure 3.6.)
Figure 3.6. Transient absorbance of n-C$_{60}$(aq), showing persistent kinetics.

None of the standard kinetic models corresponded particularly well to the data. Attempt to model the decay accurately with first-order, second-order, mixed first- and second-order, double-exponential, and stretched-exponential fits all failed, sometimes quite dramatically.

To address the question of what the origin of such strange transient behavior could be, we must consider three possible mechanisms;

a) Triplet absorption;

b) Formation of a charge-transfer complex; and

c) Thermal processes, i.e. refractive index changes produced by localized heating of the solvent.
Figure 3.7. n-C$_{60}$ (aq) kinetics, before and after oxygen addition. Note similarity of traces.

The kinetics of the n-C$_{60}$ (aq) transient attenuation were not appreciably altered by the removal of oxygen. (Figure 3.7.) This immediately indicates that triplet-state molecules do not play a predominant role in the colloid’s kinetics. Certainly, $^3$C$_{60}$ must be present in the immediate aftermath of the laser pulse (as the luminescence studies indicate); however, the attenuation decay would have been accelerated by singlet oxygen quenching, had the triplet state been the primary source of n-C$_{60}$’s transient kinetics. Moreover, the very persistent kinetics observed also indicate that triplets are not involved. One would definitely not expect the T$_1$ excited state of C$_{60}$ to last for many milliseconds, given its ca. 143 $\mu$s lifetime in toluene,$^{58}$ and the likelihood of rapid bimolecular deactivation from adjoining fullerenes in the sol particles.
Figure 3.8. NIR transient absorption spectra of n-C$_{60}$ (tol).

To sort out the remaining two possibilities for the attenuation mechanism, a transient spectrum of the sample was taken from 950-1350 nm. Charge-transfer processes involving C$_{60}$ normally generate C$_{60}$ anion, which displays a clear transient absorption maximum around 1070 nm. Inspection of the colloid transient spectrum did not show any such feature rising above the noise background; indeed, the spectrum was generally featureless in this region. (Figure 3.8.) From the absence of an unambiguous anion peak, we must conclude that the transient kinetics observed for n-C$_{60}$ are mainly due to refractive effects. These could be due to thermal lensing. Since a liquid's refractive index changes with temperature (due to its thermal expansion),$^{59}$ it follows that transient local heating would change the path, and observed intensity, of a probe beam. Optically-induced changes in scattering could also be responsible. This conclusion is qualitatively
supported by the short, negative-going kinetics seen when the colloid is transferred into a viscous PVP/PVA solution. (Figure 3.9.)

![Graph](image_url)

**Figure 3.9. Transient kinetics of n-C\textsubscript{60} in PVP/PVA (aq) at 740 nm and 298 K.**

Charge-transfer-state lifetimes would be increased, not decreased, by such treatment. The sign of a charged species's ΔA would not be affected by higher viscosity, either, as the properties governing this change (singlet and triplet epsilons, ground-state concentration, and Φ\textsubscript{f}) are internal to the molecule itself. Therefore, the changed kinetics of the n-C\textsubscript{60} must result from PVP/PVA solution's different heat capacity or refractive index.

### 3.1.4. n-C\textsubscript{60} (DMF)

Before leaving the subject of C\textsubscript{60} colloids, it is worthwhile to add some remarks concerning a serendipitous finding of the author. In an attempt to find a potential energy-
exchange species that could be used with BAA (the compound discussed in the next section), a few mg of C$_{60}$ were added to about 5 mL of DMF, then sonicated with stirring. Most of the fullerene appeared to remain on the bottom of the vial. However, during this process, a yellowish-brown color formed in the supernatant; this shade was comparable to that of the n-C$_{60}$ (aq), and very distinct from the magenta hue of solvated C$_{60}$. This was taken as a sign that some of the fullerene entered into the DMF as a colloidal suspension. After being poured off, the supernatant retained its color over several weeks without apparent change. While residual water contamination of this sample could have occurred, the use of fresh DMF, and C$_{60}$ stored under dry nitrogen, for its preparation makes this unlikely.

Such a system would be an interesting target for analysis. As a colloid in organic solvent, the properties of n-C$_{60}$ (DMF) could be compared to—and contrasted with—those of the aqueous colloid, to establish how the sol particles and their constituent molecules interact with their environment. In particular, this would help elucidate the chemical nature of the colloids. It has been hypothesized (but not yet observed) that there is an outer periphery of hydroxylated C$_{60}$ molecules on the aqueous colloid particles, due to their interaction with H$_2$O.$^{60}$ It thus stands to reason that the particles of the n-C$_{60}$ (DMF) sol should lack such a coating. Therefore, differences between the behavior of the two colloids would help shed light on these proposed structures and their influences.
3.2. C$_{60}$ derivatives: BAA

3.2.1. Ground-State Attenuation

The ground-state spectrum of BAA was first successfully acquired by Yang, in aqueous solution. The main parent feature retained in the derivative is the maximum around 261 nm; the adjacent "primary" peaks are only resolved as shoulders. {Jianzhong Yang, personal communication.} (Figure 3.10.)

![Graph showing UV-Vis absorption spectrum of BAA in H$_2$O.](image)

Figure 3.10. UV-Vis ground-state absorption spectrum of BAA in H$_2$O.

Further investigation of the DMF solution of BAA showed loss of the fine structure in the 440-700 nm region, although a tiny peak around 433 nm was noted.

BAA displays a pronounced tendency to aggregate. This was manifested by the fact that many samples of the compound gave strong Tyndall scattering after short
storage times; one instance is discussed below. There are two competing hypotheses to explain why this aggregation occurred. One holds that BAA acts as a radical scavenger, and that its molecules clump together as a function of the BAA’s reaction with unpaired-electron species. The second hypothesis asserts that BAA acts like a surfactant. That is, since it has a nonpolar fullerene “head” and a polar amino-acid “tail,” the BAA molecules may spontaneously group together in micellar structures. Attempts to reverse aggregation by addition of γ-cyclodextrin (to mask the nonpolarity of the BAA’s fullerene end)\textsuperscript{61} were unsuccessful; however, adding the cyclodextrin to the material in the penultimate synthesis step did seem to prevent aggregation over long storage times.

Figure 3.11. Singlet oxygen emission from aerated BAA in DMF at 298 K.
3.2.2. Steady-State Luminescence

To assess the antioxidant properties of BAA, the emission spectrum of the first (aggregated, DMF-solvated) sample was inspected in the singlet oxygen region. While a peak was observed in this region, it was extremely small, and could only be detected with extensive averaging. (Figure 3.11.)

There are two possible explanations for this observation: either

1) The BAA is not a sensitizer of singlet oxygen, and all the 1277 nm luminescence observed was from a contaminant; or

2) The BAA is a sensitizer of $^1\Delta_g$ O$_2$, but it gives a tiny quantum yield.

Initially, the first explanation was favored. Since stronger emission would have been expected if the predominant species in the sample were involved, this seemed to suggest that the BAA was not the source of the $^1\Delta_g$ luminescence observed. If one accepted this interpretation, one implication might be that BAA has a $T_1$ level lower than 7880 cm$^{-1}$, and thus possesses the desired anti-oxidant properties. However, this viewpoint fails to address the nature of the energy transfer processes generating the singlet oxygen, or the possibility that BAA has a negligible triplet quantum yield. These, as we shall see, are significant issues.
Figure 3.12. Degassed & ingassed BAA kinetics: a) 50 and b) 20,000 μs timebases.
3.2.3. Transient Attenuation

The second DMF-solvated sample initially showed no visible particulates or colloidal light scattering. However, after ca. 2 weeks on the shelf, a brown precipitate had formed at the bottom of the cuvet it was stored in; scattering from light beams passed through this sample was also clearly visible. These spontaneous changes indicated that the BAA had aggregated. Subsequent analysis of this aged sample in Broadband showed a curious set of properties. After degassing, the second BAA sample displayed two kinetic components—a short exponential decay with a lifetime of about 20 µs, and a long pedestal with a lifetime of about 2.5 ms. This long-duration term seems consistent with the presence of aggregates; similar persistent kinetics were seen in the C\textsubscript{60} colloid. Once atmospheric gas was reintroduced to the sample, however, the short component was instrument-function limited, which indicates efficient quenching by oxygen. The long component, while still present, was greatly reduced in intensity. (Figure 3.12.)

In light of the first proposed origin of the observed steady-state luminescence, the short-lifetime term's behavior is strange. If BAA is not a sensitizer of singlet oxygen, its triplet energy would be comparable to, or lower than, 7880 cm\textsuperscript{-1}. In this case, one would not expect the transient absorption of BAA to be curtailed so strongly by oxygen addition. The fact that the absorption is strongly quenched establishes the second explanation—that is, BAA's triplet energy must lie above the energy of singlet oxygen. However, such a result also begs the question of why, in this case, one does not observe higher-intensity \(^1\text{A}\textsubscript{s}\) emission from the sample. In an attempt to resolve this conundrum, a three-step process was hypothesized:
1) Singlet oxygen is generated by individual BAA molecules in the mixture;

2) The $^1\Delta_g$ O$_2$ then transfers its energy to BAA aggregates; and

3) Fast vibronic conversion within the aggregates transforms the electronic energy into local heating of the solution.

The compound’s transient absorption spectrum showed the parent fullerene’s characteristic T$_n$←T$_1$ profile, with the main peak blueshifted to 680 nm. (Figure 3.13.)

![Figure 3.13. Transient absorption spectrum of BAA in degassed DMF at 298 K.](image)

This type of shift has been observed before in other C$_{60}$ derivatives; for example, the global maximum of the triplet absorption spectrum of C$_{60}$O is seen at 710 nm. The larger magnitude of the shift in the BAA sample suggests that some of the species in the mix may be bis-adducts.
3.2.4. Transient Luminescence

To investigate the second element of the hypothesis, attempts were made to measure the 1277 nm luminescence of the aerated BAA solution in the immediate aftermath of a laser pulse. These data showed a decay trace with two components; one was instrument-function-limited, the other was a low-intensity tail. (Figure 3.14.a)) The first element of the kinetics also appeared in observations at 1200 nm. Both wavelengths are well to the red of where one would expect lower fullerenes (or their derivatives) to fluoresce. Consequently, it was deduced that this sharp rise was an instrumental artifact, indicative of refractive effects related to the colloidal species in the sample. The second kinetic component, which did not appear at 1200 nm, thus had to be due to singlet oxygen emission. Due to the very poor S/N ratio, high-power excitation had to be combined with 16,000 shots/wavelength to get usable data. Two baseline-corrected data sets were assembled from these experiments, then fitted to double-exponential kinetic models. One set was comprised of the 1277 nm data. Another data set was made by normalizing the 1277 and 1200 nm data sets, then subtracting the latter from the former. The fit to the first data set gave a $^1\Delta_g$ O$_2$ lifetime of 26 ($\pm$ 5) $\mu$s, with a $R^2$ of about 0.92; the fit to the second data set gave a lifetime of 11 ($\pm$1) $\mu$s with a $R^2$ around 0.74. (Figure 3.14.)

In the absence of a quencher, the literature indicates that $^1\Delta_g$ O$_2$ should have a characteristic lifetime of 14.0 ($\pm$ 0.6) $\mu$s in DMF solution. However, the mediocre-to-poor $R^2$ values obtained for these models, a result of the very noisy data, preclude definitive assignment of the singlet-oxygen decay kinetics in the
Figure 3.14. Kinetic fits to baseline-corrected, BAA transient luminescence data: a) 1277 nm and b) difference between normalized 1277 and 1200 nm traces.
BAA sample. In order to better establish the kinetics of $^1\Delta_g \text{O}_2$ in the presence of this fullerene derivative, another round of experiments was conducted, using Zn-TPP as a singlet oxygen sensitizer. A 1/2-dilution of a stock solution of the metallloporphyrin in DMF yielded a much higher concentration of $^1\Delta_g \text{O}_2$, that decayed with a characteristic lifetime of 17.7 ($\pm$ 0.8) $\mu$s. When a 1:1 combination of the Zn-TPP stock and the BAA sample was analyzed, it exhibited a singlet oxygen decay time of 16.1 ($\pm$ 0.2) $\mu$s. (Figure 3.15.)

![Graph showing fluorescence decay over delay time](image)

**Figure 3.15.** Decay of Zn-TPP-sensitized singlet oxygen in presence of BAA (DMF) at 298 K.

If the derivative is assumed to have a 15% lower ground-state extinction than its parent fullerene, it follows that the upper limit of BAA’s $^1\Delta_g \text{O}_2$ quenching constant is 3.8 ($10^8$) M$^{-1}$ s$^{-1}$. After adjusting the diffusion limit for the increased viscosity of DMF relative to toluene, we find that the maximum singlet-oxygen quenching rate of BAA is about 6.1%
of the diffusion limit. While this is not a remarkably low number, it does support the idea that energy transfer from $^1\Delta_g$ O$_2$ to BAA is an uphill, thermally-driven process. Indeed, the fact that this quenching rate is below $10^9$ M$^{-1}$ s$^{-1}$ indicates that the transfer of energy from singlet oxygen to the derivative is activation-controlled.$^{64}$

Since the observed decay of $^1\Delta_g$ O$_2$ was not accelerated significantly by the presence of BAA or its aggregates, we may provisionally posit that singlet oxygen is not appreciably quenched by the derivative. Consequently, the second and third elements of the aforementioned hypothesis should be shelved. This brings us back once again to the (still unresolved) issue of the $^1\Delta_g$ O$_2$ emission's low intensity. Since the preceding experiments demonstrated that BAA's T$_1$ energy is substantially greater than 7880 cm$^{-1}$, and since the $\Phi_{1\Delta_g}$ rate for such compounds is generally 1, we must assume that the low emission at 1277 nm is due to a low $\Phi_T$ value for this fullerene derivative.

Taken together, these considerations imply that the "bucky amino acid" may not be useful for biomedical applications. Since BAA is neither an efficient generator of singlet oxygen, nor an effective quencher of it, it appears that it would not be useful as either a PDT agent or an antioxidant. However, the latter conclusion hinges on the assumption that the behavior of $^1\Delta_g$ O$_2$ is a good model for the fates of other reactive oxygen species (ROS) in a biochemical environment. Given the wide-ranging chemical natures of ROS other than singlet oxygen—which can be radicals, anions, and/or peroxides$^{57}$—this is a questionable approach. The role of the superoxide anion (O$_2^-$) is particularly germane in this context. For example, one group has suggested that superoxide anion is the primary agent of induced oxidative damage in photodynamic
therapy involving fullerenes. A second group has proposed that singlet oxygen is formed from superoxide. Thirdly, S. Wilson's group, in working with a carboxylic-acid C$_{60}$ derivative, "C$_3$", has observed anti-oxidant activity from this compound, and attributed that action to C$_3$'s reaction with superoxide anions. It is possible that BAA's charged moiety would suppress superoxide through an ionic interaction; however, investigation of this process is beyond the scope of this thesis.

3.3. C$_{80}$ isomers

3.3.1. C$_{80}$ {D$_{5d}$}

3.3.1.1. Ground-State Absorption

The UV-vis absorption spectrum of C$_{80}$ {D$_{5d}$} in toluene shows two pronounced maxima. One sharp peak appears at 380 nm; the second, bluff-nosed peak is centered around 590 nm. These two features display molar absorptivities around 40,000 and 30,000 M$^{-1}$ cm$^{-1}$, respectively. (Figure 3.16.) The longer-wavelength peak is quite unusual amongst the fullerenes, which rarely show such pronounced electronic transitions in that spectral region.
3.3.1.2. Transient Properties

Contrary to expectations, no triplet-state absorptions were detectable from this sample. Initial signs of transient kinetics were seen in the C\textsubscript{80} that had been transferred into toluene. However, spectral analysis showed that these stemmed from C\textsubscript{60} contamination. This analysis was confirmed by chromatographic separation on PYE, which showed a clear C\textsubscript{60} peak. Unfortunately, the transient spectrum of the separated C\textsubscript{80} \{D\textsubscript{5d}\} material was still dominated by C\textsubscript{60} features. Further investigation showed that this interfering material was apparently leaching out from the HPLC itself. Blank eluent, after being collected and evaporated down, gave faint, but discernable, UV-vis absorption. This showed that even marginal residual contamination would be enough to prevent transient investigation of the C\textsubscript{80} isomer.
Upon returning to the original, clean, CS$_2$-solvated C$_{80}$ \{D$_{5d}$\} sample, the C$_{60}$ features disappeared. However, the remaining transient kinetic features turned out to be micro-boiling of the solvent induced by the laser pulses. With nitrogen backfilling, these features disappeared. To rule out bimolecular processes, part of the C$_{80}$ \{D$_{5d}$\} was cast into a film. This sample still showed no transient absorption whatsoever, even at 77K.

Other portions of the C$_{80}$ \{D$_{5d}$\} were mixed with C$_{70}$ in CS$_2$; varying concentrations were prepared. In these solutions, the transient absorbance kinetics were analyzed at a variety of wavelengths. The results from the first solution had to be thrown out because its C$_{70}$ concentration was so high as to create nonlinear absorbance effects in the bulk of the solution. At lower concentrations, there was clear quenching of the $^3$C$_{70}$. For example, at 980 nm, sequential decay kinetics were observed. (Figure 3.17.)

![Graph showing transient absorbance kinetics](image)

**Figure 3.17.** Transient absorbance kinetics of mixed C$_{70}$ & C$_{80}$ \{D$_{5d}$\} sample, along with sequential decay model.
The C\textsubscript{70} triplet decayed within about 6 \(\mu\)s, while the C\textsubscript{80} was estimated to persist for about 40 \(\mu\)s. Also, the pre-exponential term of the C\textsubscript{80} \{D\textsubscript{5d}\} is 0.028 that of C\textsubscript{70}. This result suggests one reason why it was so difficult to observe any transient absorption from the pure C\textsubscript{80} sample. An effort was made to correct for estimated ground-state concentrations; this required the use of toluene epsilon values (since extinction values for C\textsubscript{70} and C\textsubscript{80} in CS\textsubscript{2} were not available). If we take these epsilon values to be a reasonable approximation, the kinetics indicate C\textsubscript{80} \{D\textsubscript{5d}\} has an \(\varepsilon^\text{TT}_{980}\) of about 430 M\textsuperscript{-1} cm\textsuperscript{-1}, i.e. 11.2 times less than the C\textsubscript{70} triplet epsilon. Similar calculations for 740 nm data suggest C\textsubscript{80} \{D\textsubscript{5d}\}'s \(\varepsilon^\text{TT}_{740}\) is around 150 M\textsuperscript{-1} cm\textsuperscript{-1}, or 7.4 times less than the C\textsubscript{70} triplet extinction at that wavelength.

### 3.3.1.3. Luminescence Properties

In the mixed C\textsubscript{70}-C\textsubscript{80} solutions, quenched singlet oxygen luminescence was observed. Since C\textsubscript{70} is known to generate \(^1\Delta_g\) O\textsubscript{2}, it follows that the C\textsubscript{80} \{D\textsubscript{5d}\} is the quenching agent in these solutions. To take advantage of this, the four lowest-concentration samples were analyzed, and the rates of the C\textsubscript{80}’s oxygen quenching determined. These rates were then plotted as a function of the fullerene concentration. Since the rate at which \(^1\Delta_g\) O\textsubscript{2} disappears is proportional to the concentration of quencher present, the slope of the resulting data trace yields the effective singlet oxygen quenching constant of the solute. Here, it was found that C\textsubscript{80} \{D\textsubscript{5d}\} has an intrinsic \(^1\Delta_g\) O\textsubscript{2} quenching rate of about 3.4 \((10^9)\) M\textsuperscript{-1} s\textsuperscript{-1}. (Figure 3.18.) Since the diffusion limit in CS\textsubscript{2} at 298 K is estimated, from viscosity data\textsuperscript{68} and the Stokes-Einstein hydrodynamic relations,\textsuperscript{64} to be 1.8 \((10^{10})\) M\textsuperscript{-1} s\textsuperscript{-1}, it follows that the quenching of singlet oxygen by C\textsubscript{80} occurs at about
19% of this limit. Such a rate indicates that the triplet state of C$_{80}$ \{D$_{5d}$\} is not markedly lower-lying than 7880 cm$^{-1}$. However, it is not clear that this oxygen process is limited by activation energy, either; in that case, one would expect the oxygen-quenching rate to be even lower. In this netherworld between diffusion and activation limits, one can only conclude that C$_{80}$'s T$_1$ level lies within about 1 kT (~300 cm$^{-1}$) of the $^1\Delta_g$ O$_2$ energy.

3.3.2. Ho$_3$N@C$_{80}$ \{I$_h$\}

3.3.2.1. Ground State Absorption

In toluene, the UV-vis absorption spectrum of the Ho$_3$N@C$_{80}$ \{I$_h$\} has no sharp electronic transitions, though a small maximum is noted around 666 nm. Its absorption onset occurs ca. 730 nm, suggesting it has an S$_1$ - S$_0$ energy around 13,700 cm$^{-1}$. Pd-OEP
quenching was used to obtain the epsilon-calibrated spectrum of the holmium nitride \textit{incar}; its extinction coefficient is about 46,000 M$^{-1}$cm$^{-1}$ at 400 nm. (Figure 3.19.)

![Figure 3.19. Epsilon-scaled ground-state UV-vis absorption spectrum of Ho$_3$N@C$_{80}$\{I$_8$\} (tol).](image)

3.3.2.2. Transient Spectroscopy

Initial transient measurements on the Ho$_3$N@C$_{80}$ \{I$_8$\} sample showed bleaching around 470 nm; a positive transient was noted around 980 nm. Since these features, taken together, were suspiciously reminiscent of C$_{70}$, a transient spectral scan was performed. The resulting spectrum for the holmium nitride \textit{incar} was—aside from a bleaching inversion in the 500-560 nm region—nearly identical to the transient spectrum of C$_{70}$. This indicated that the predominant transient absorption features of the sample were due to contamination from this lower fullerene. (Figure 3.20.) Further investigation with LDI-TOF-MS confirmed that the Ho$_3$N@C$_{80}$ \{I$_8$\} solution did contain C$_{70}$; the latter’s
Figure 3.20. Transient spectra of: a) Ho₃N@C₈₀[I₁₁] (tol); and b) C₇₀ (PMMA).
concentration was estimated to be about 30 nM. It can be inferred that the product of the triplet quantum yield and the triplet absorptivity of the holmium nitride incar is qualitatively much lower than that for C\textsubscript{70}. In spite of the latter's much lower concentration, C\textsubscript{70}'s features dominate the transient spectrum.

Since the glassware used had been cleaned with chromic acid (a mixture that is very destructive toward any organic compound), it was concluded that the lower-fullerene contamination probably occurred during the original creation/preparation of the endohedrals. It may well have been a side product of the synthesis. Further consultations indicated that it would be infeasible to produce a second Ho\textsubscript{3}N@C\textsubscript{80} \{I\textsubscript{b}\} sample of substantially higher purity, given the very low levels of contaminant involved.\textsuperscript{69} At this point, further efforts to acquire the transient spectrum of the endohedral were halted.

3.3.2.3. Energy Transfer

After Pd-OEP was added to an aliquot of the holmium nitride incar for ground-state epsilon determination, oxygen was reintroduced into the sample and the resulting \textsuperscript{1}Δ\textsubscript{g} O\textsubscript{2} luminescence was measured. The characteristic decay lifetime of the 1277 nm emission observed under these circumstances was found to be 31 \textmu s. (Figure 3.21.) Significantly, this lifetime is what one would expect for toluene-solvated singlet oxygen in the absence of a quencher. From this, we may immediately conclude that Ho\textsubscript{3}N@C\textsubscript{80} \{I\textsubscript{b}\} has a triplet energy level that lies appreciably higher than 7880 cm\textsuperscript{-1}.

A second round of energy transfer measurements was conducted, using additional C\textsubscript{70} with the holmium nitride incar. After degassing, the transient absorption at 980 nm
Figure 3.21. Unquenched $^{1}\Delta_g O_2$ luminescence with Ho$_3$N@C$_{80}$ (tol) at 298 K.

Figure 3.22. Transient kinetics of C$_{70}$ & Ho$_3$N@C$_{80}$ ($I_h$) (tol) at 980 nm & 298 K.
subsided with a characteristic lifetime of 15 µs—far faster than the 23 ms intrinsic decay time one would ordinarily expect for C_{70}. (Figure 3.22.) This rapid quenching has two possible origins. One is that Ho_{3}N@C_{80} \{I_{h}\} extinguishes the C_{70} triplet state, because the former has a T_{1} energy substantially below 12,600 cm\(^{-1}\). The other possibility is that spin-orbit coupling between the incar’s holmium atoms and the electrons in C_{70}’s π-system causes fast intersystem crossing back to S_{0} through an external heavy-atom effect. While a 0.997 R\(^{2}\) value is attained with a single-exponential model, we cannot conclude from this whether one or the other of these two mechanisms must dominate; both of these processes have identical kinetic forms.

At this point, the author investigated the transient spectrum of this mixture, in the region where a sign difference between the incar and the C_{70} appears. At 542.5 nm, unusual biphasic kinetics were observed; an initial sharp, positive rise was rapidly followed by a longer-lived, bleaching feature. (Figure 3.23.) The first explanation that comes to mind—energy transfer from a higher-lying \(^{3}\)C_{80} to a lower-lying \(^{3}\)C_{70}—initially seems implausible. One might expect a compound with a singlet onset at 730 nm to have a S_{1} level about 1700 cm\(^{-1}\) lower in energy than the S_{1} level in C_{70}. Moreover, it is well-known that a molecule’s T_{1} level must be lower in energy than its S_{1} level. This is not a function of electron spin; rather, quantum mechanics shows that an antisymmetric (triplet) wavefunction has higher electron correlation, and thus lower energy, than its symmetric (singlet) counterpart.\(^{70}\) Thus, the relative T_{1} levels in Ho_{3}N@C_{80} \{I_{h}\} and C_{70} might be expected follow the pattern of the levels in their singlet manifolds. However, this hypothesis overlooks the fact that the S_{1} – T_{1} energy gaps in the two molecules need not be the same. Given the above assumption that the incar has a S_{1} around 13,700 cm\(^{-1}\),
it follows that a singlet-triplet gap less than, or equal to, 1200 cm\(^{-1}\) in \(\text{Ho}_3\text{N@C}_{80}\{I_h\}\) would enable bimolecular energy transfer between it and \(C_{70}\).

![Figure 3.23. Biphasic transient kinetics observed in degassed mixture of \(C_{70}\) and \(\text{Ho}_3\text{N@C}_{80}\{I_h\}\) (tol) at 298 K.](image)

In an attempt to deconvolute the decay lifetimes of the \(\text{Ho}_3\text{N@C}_{80}\{I_h\}\) and the \(C_{70}\) contaminant, the remainder of the \textit{incar} sample was cast into PMMA. Transient analysis of the degassed film initially gave irreproducible results. Closer inspection revealed that irradiation of the sample induced an irreversible, time-dependent photochemical reaction. An initial kinetic run showed transient absorbance features; after 14 additional minutes of excitation, strong bleaching features appeared at long delays. After the sample was allowed to stand overnight, re-analysis of the same point on the film showed complete disappearance of the positive transients. (Figure 3.24.) This behavior suggests that covalent bonds have formed between the holmium \textit{incar} and the PMMA
matrix—an extremely unusual observation, since few species have been observed to react with this polymer. However, in the absence of additional theoretical and/or experimental data, it is not possible to draw any conclusions about the exact nature of the

![Graph](image)

Figure 3.24. Photoinduced, time-dependent change of Ho$_3$N@C$_{80}$ ($I_h$) transient absorbance in degassed PMMA, at 980 nm and 298 K.

observed change. More to the point, these unstable kinetics ruled out any definitive determination of the triplet lifetime of Ho$_3$N@C$_{80}$ ($I_h$).

3.3.2.4. Emission Spectra

Attempts were made to observe the emission spectrum of Ho$_3$N@C$_{80}$ ($I_h$). The resulting scans showed no evidence of structured fluorescence, regardless of whether InGaAs or PMT detection was used. Excitation scans showed a broad maximum around
364 nm, with a shoulder near 400 nm and a small peak around 443 nm. Additional sharp maxima were observed near 466 and 488 nm. However, with the exception of the shoulder, none of these features corresponded to the *incar*’s ground-state spectrum, making it difficult to ascribe the observed fluorescence to Ho$_3$N@C$_{80}$ \{I$_h$\}.

3.4. C$_{84}$ major isomers

3.4.1. Isomer Assignment via Joint Analysis of Film Samples

Before the properties of the individual major isomers can be discussed, their identities must be determined. The first step in this direction is made by finding photophysical characteristics which differ dramatically between the D$_2$(IV) and D$_{2d}$(II) isomers. It turns out that the kinetic lifetimes of the two species differ dramatically. This was initially noted when the author’s rHPLC work produced a major-isomer-enriched sample, free of C$_4$(a) and other minor C$_{84}$ isomers; this “major” fraction was cast into PMMA and degassed. This film’s transient absorption gave a double-exponential decay, comprised of natural lifetimes ca. 640 and 4 µs.

The second, and final, step in the assignment process is to perform the kinetic analyses on isomer samples that are chromatographically well-separated. Since the elution order of D$_2$(IV) and D$_{2d}$(II) is known, the transient lifetimes seen in these samples can then be directly related to the isomer’s identities. This was not possible with the author’s own samples; due to the aforementioned limitations of the rHPLC procedures, the major C$_{84}$ fraction could not be resolved any further. At this point, samples of D$_2$(IV) and D$_{2d}$(II) were obtained from Dennis and Kanai (Univ. of London).
With totally resolved isomer fractions, one can make assignments by simply reporting the kinetics seen in each, isolated sample. However, inspection of the Dennis fractions showed that this would not be feasible. In the film made from the “D_{2}(IV)” sample, both kinetic components corresponding to the major isomers were seen, indicating incomplete separation. Similar kinetics were also seen in the “D_{2d}(II)” film sample. Even in this situation, assignment would seem like a simple matter of comparing the relative amplitudes of the two isomers’ exponential decays in the two films. Unfortunately, further investigation of the “D_{2d}(II)” film established that its transient absorbance kinetics had four distinct components.

Careful investigation of the “D_{2d}(II)” film kinetics showed that one of the four terms lasted many milliseconds, and was thus due to C_{70} contamination. Three techniques were then applied to circumvent this problem:

a) Transient absorbance observations were made at 570 nm, since this is the region where C_{70}’s ΔA crosses through zero; and

b) The “D_{2d}(II)” film was excited at 705 nm, using a dye laser with Pyridine 1. Since this wavelength is to the red of C_{70}’s absorption onset, this fullerene will not undergo significant excitation; and

c) The transient absorbance of the “D_{2d}(II)” film was monitored at 980 nm, using very long (100,000 μs) timebases. This allowed the amplitude of the C_{70} transient to be determined with maximum accuracy, enabling its subtraction from the other kinetic components.
Further analysis of the kinetics in the "D_{2d}(II)" film showed that, of the three remaining components, one had a natural lifetime on the order of 100 μs. The significance of this result becomes apparent when it is compared with prior data. The unseparated isomeric mixture from the author's earlier work displayed a kinetic term in this lifetime range; the "major" fraction did not show this term, nor did Dennis's D_{2}(IV)-enriched fraction. Moreover, the ground-state NIR absorption of the D_{2d}(II)-enriched sample reveals a shoulder stretching from 1000 to 1200 nm. (Figure) This is clearly inconsistent with the 1050 nm singlet-onset Dennis and Shinohara reported for D_{2d}(II). Furthermore, the C_{5}(a) isomer is known to have a broad singlet onset in this very same region. (Figure) Finally, since C_{5}(a) elutes after D_{2d}(II) in rHPLC, it is likely that the former isomer contaminates fractions of the latter. Therefore, we may conclude that this 125 (±37) μs component stems from C_{5}(a).
Figure 3.25. Normalized transient absorbance traces, at 525 nm, of degassed PMMA films enriched in $D_2$(IV) and $D_{2d}$(II) isomers. Note comparative magnitudes of long and short components. Differing intensities indicate disproportionation of isomers between films, and provide basis for assignment of isomers' triplet lifetimes. Different excitation wavelengths were used to circumvent contamination.

After accounting for all these complicating factors, the remaining kinetic components observed in the two films still displayed different relative magnitudes. (Figure 3.1.4.2.n.). Thus, the transient absorbance traces could be analyzed to determine their origins. The ratios of the multi-hundred-µs-component’s amplitude to the few-µs-component’s amplitude were found for each film at every observation wavelength used; these ratios were then compared. With 532 nm excitation and observation at 525 and 740 nm, these ratios were larger in the “$D_2$(IV)” film than in the “$D_{2d}$(II)” film. Similarly, with observations at 525 and 980 nm, the ratios seen in the “$D_2$(IV)” film (with 532 nm excitation) were larger than the ones seen in the “$D_{2d}$(II)” film (with 705 nm excitation).
(Table 3.1.) Therefore, it is concluded that the long kinetic component belongs to D$_2$(IV), whereas the short component belongs to D$_{2d}$(II).

**Lifetime and amplitude components of D$_2$(IV)-enriched film**

*532 nm excitation:*

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**Lifetime and amplitude components of D$_{2d}$(II)-enriched film**

*532 nm excitation:*

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<th>3rd</th>
<th>4th</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>τ (μs)</td>
<td>A$_1$</td>
<td>τ (μs)</td>
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</tr>
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**705 nm excitation:**

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<th>3rd</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>τ (μs)</td>
<td>A$_1$</td>
<td>τ (μs)</td>
<td>A$_2$</td>
</tr>
<tr>
<td>525</td>
<td>827</td>
<td>1</td>
<td>182</td>
<td>0.538</td>
</tr>
<tr>
<td>570</td>
<td>827</td>
<td>1</td>
<td>182</td>
<td>0.538</td>
</tr>
<tr>
<td>740</td>
<td>620</td>
<td>1</td>
<td>(b)</td>
<td>(b)</td>
</tr>
<tr>
<td>980</td>
<td>816</td>
<td>1</td>
<td></td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3.1. Kinetic components observed in the D$_2$(IV) and D$_{2d}$(II) enriched fractions, at various excitation and observation wavelengths. Their lifetimes (τ), amplitudes (A) and amplitude ratios are listed. (NB: a=poor S/N. b=no third component observed. c=noise.)
3.4.2. $C_{84} \{D_2(IV)\}$

3.4.2.1. Ground State Absorption

In toluene solution at room temperature, the absorption onset of this isomer is seen at 1050 nm, a result consistent with Dennis and Shinohara’s observations. Maxima are observed at 396, 569 and 900 nm; the molar extinction values at these points are 28,000, 4650 and 1500 M$^{-1}$ cm$^{-1}$. Minima are noted at 363, 548 and 876 nm. Shoulders are also seen at 314, 430, 475, 669 and 739 nm. (Figure 3.26.)

![Graph](image_url)

Figure 3.26. Epsilon-scaled ground-state UV-vis absorption spectrum of $C_{84} \{D_2(IV)\}$ (tol) at 298 K.

3.4.2.2. Transient Absorption

The transient absorption spectrum of the $D_2(IV)$ molecule is characterized by maxima around 520, 605, and 740 nm. Minima are observed at about 470 and 565 nm,
with the former feature assigned as a bleaching transient. (Figure 3.27.) The appearance of the 740 nm peak did cause some initial concern, since this is where \( \text{C}_{60} \)'s transient maximum appears. However, the fact that this feature persists far longer than \( \text{C}_{60} \)'s 140 \( \mu \text{s} \) characteristic lifetime means that it is very unlikely to be a result of contamination by the lower fullerene. Moreover, as we shall see later, mass spectrometry turned up no definitive evidence of contamination by \( \text{C}_{60} \).

![Graph showing transient spectrum of degassed \( \text{C}_{84} \{ \text{D}_2(\text{IV}) \} \) (PMMA) at 298 K.]

**Figure 3.27.** Transient spectrum of degassed \( \text{C}_{84} \{ \text{D}_2(\text{IV}) \} \) (PMMA) at 298 K.

As indicated above, the very long kinetics that had been seen before in mixtures of the \( \text{C}_{84} \) isomers were observed once again, and were clearly attributed to the \( \text{D}_2(\text{IV}) \) isomer. Kinetic analysis of the transient absorbance at 740 nm indicated that the triplet state lifetime of this species is about 640 \( \mu \text{s} \). (Figure 3.28.) As noted before, this is an unusually long lifetime for a metastable state. Amongst the fullerenes, \( \text{D}_2(\text{IV}) \) is second
only to C\textsubscript{70} in its kinetic persistence. The latter has been known, for many years, to have a multi-millisecond triplet-state lifetime\textsuperscript{73}, which is currently estimated to be about 23 ms.

![Graph showing transient kinetics of degassed C\textsubscript{84}D\textsubscript{2}(IV) (PMMA) at 298 K.]

Figure 3.28. Transient kinetics of degassed C\textsubscript{84}D\textsubscript{2}(IV) (PMMA) at 298 K.
3.4.2.3. Fluorescence and Singlet Oxygen Luminescence

![Graph](image)

Figure 3.29. Toluene-overtone-corrected emission from C$_{84}$ [D$_2$(IV)] at 298 K. (NB: “fine structure” from 1100-1200 nm is toluene-overtone-correction artifact. Also, rise to blue of 911 nm is filter artifact.)

The emission spectrum of D$_2$(IV) shows two characteristic maxima—a broad peak at 1000 nm, and a smaller, sharper peak around 1277 nm. (Figure 3.29.) The latter, of course, indicates singlet oxygen sensitization, and tells us that the T$_1$ level of D$_2$(IV) lies higher than 7880 cm$^{-1}$. Superposition of the fluorescence trace with the ground-state absorption spectrum establishes, through the mirror-symmetry relationship of the 0-0 bands,$^{44}$ that the S$_1$ level in D$_2$(IV) is $\sim$10,600 cm$^{-1}$. (Figure 3.30.)
Figure 3.30. Superposition of D$_2$(IV)'s fluorescence and absorbance traces, showing singlet onset location.

Careful variation of the oxygen concentration in the solution also permitted determination of the T$_1$→S$_0$ relaxation rate within C$_{84}$ \{D$_2$(IV)\}. To wit: if

\[ T_1 \rightarrow S_0 \quad \text{with rate constant } k_1, \text{ and} \]

\[ O_2 + T_1 \rightarrow ^1O_2 + S_0 \quad \text{with rate constant } k_q, \]

it follows that the fraction of triplet-state molecules giving singlet oxygen is

\[
F = \frac{1}{1 + \left( \frac{k_1}{k_q [O_2]} \right)}
\]

Thus, when F=0.5,

\[ k_1 = k_q [O_2] \]
Since \( k_q \) is known from previous experiments to be about \( 1.7 \times 10^9 \) \( \text{M}^{-1} \text{s}^{-1} \), we can use this to model the data for the luminescence intensity at various oxygen concentrations, and thus obtain \( k_1 \) for \( D_2(\text{IV}) \). The actual asymptotic limit of the luminescence intensity—and, thus, the F=0.5 point—is not known directly, as the rise was still quite pronounced

![Luminescence vs. [O2] graph](image)

**Figure 3.31. Intrinsic T_{1\rightarrow S_0} rate of C_{84}\{D_2(\text{IV})\} from O_2 sensitization at 298 K.**

by the end of the data range. However, this turned out not to be a major problem in practice. By extrapolating with a non-linear curve-fitting routine, the limit can be estimated with a low margin of error (i.e. 2.64 (± 0.05) \( 10^{-2} \) mV) and pronounced goodness of fit \( (R^2 > 0.99) \). (Figure 3.31.)

The result obtained for \( k_1 \), 3.83 (± 0.28) \( 10^5 \) \( \text{s}^{-1} \), corresponds to an intrinsic triplet lifetime of about 2.6 \( \mu \text{s} \)—far faster than the 643 \( \mu \text{s} \) time observed in the PMMA film. Clearly, this acceleration is not a function of oxygen quenching, since this was
accounted for separately in the data analysis. There are two likely contributing factors. One of these is the presence, in the liquid solution, of bimolecular processes that occur independently of contamination. Self-quenching, energy transfer, and triplet-triplet annihilation all fall into this category. These processes would not have been a factor in the solid polymer film. The other factor is the known presence of D_{2d}(II) contaminant in the D_{2}(IV) solution. As we shall see later, the triplet-state energy of D_{2d}(II) lies substantially lower than that of D_{2}(IV). Therefore, it is completely reasonable to expect that energy would be transferred from the main species to the contaminant through collisions between the two molecules.

3.4.2.4. Cryostat Experiments: Variable Temperature Kinetics

The D_{2}(IV) film was placed in the cryostat, and had its transient absorbance kinetics analyzed at 20 Kelvin intervals, from 80 to 320 K. These changes were observed at 525 and 565 nm. Since the former wavelength corresponds to a maximum of D_{2}(IV)’s transient spectrum, and the latter corresponds to a minimum of the spectrum with near-zero ΔA, this facilitated effective deconvolution of the components from the D_{2}(IV) and D_{2d}(II) isomers. Double-exponential fits were performed at each temperature point, to further separate the contribution of each isomer to the overall absorbance decay.

The decay rate of D_{2}(IV)’s transient absorbance changed in a non-linear manner with varying temperature, giving proof that non-Arrhenius triplet kinetics are involved. As in the case of lower fullerenes, this trend was most effectively modeled by a three-component fit, incorporating a constant component (indicative of tunneling T_{1}→S_{0} transitions) and two separate, thermally-activated components. (Figure 3.32.)
“virtual temperatures” in these components correspond to activation energies of 300 cm$^{-1}$ and 2360 cm$^{-1}$. The first of these, due to its low energy, probably reflects vibrationally-induced T$_1$→S$_0$ crossing. The second activation energy, as suggested by its substantially larger value, may correspond to thermal repopulation of the S$_1$ state followed by rapid, radiationless internal conversion.

![Graph showing the rate of C$_{84}$ \{D$_2$(IV)\} (PMMA) decay at various temperatures, with tunneling and thermal decay components shown.]

Figure 3.32. Rate of C$_{84}$ \{D$_2$(IV)\} (PMMA) decay at various temperatures, with tunneling and thermal decay components shown.

3.4.3. C$_{84}$ \{D$_{2\alpha}$(II)\}

3.4.3.1. Ground-State Absorption

As was discussed earlier, there was a noticeable amount of C$_4$(a) contamination present in the D$_{2\alpha}$(II)-enriched fraction. As such, it was not possible to observe the absorption onset directly, or to see if it was consistent with the 1050 nm onset reported
earlier. Otherwise, the absorption features were consistent with what the Nagoya group reported. In toluene solution, maxima are observed at 400 and 622 nm, with extinction values of 38,400 and 5660 M⁻¹ cm⁻¹, respectively. Minima are noted at 369 and 544 nm; their respective extinction values are 31,700 and 4500 M⁻¹ cm⁻¹. Numerous shoulders are also seen; these features are around 465, 500, 581, 663, 739 and 904 nm. (Figure 3.33.)

Figure 3.33. Epsilon-scaled ground-state UV-vis absorption spectrum of C₈₄ \{D₂d(II)\} (tol) at 298 K Note shoulder in 1100-1200 nm region, indicating contamination by C₃(a) isomer.

3.4.3.2. Transient Absorption: Spectrum and Kinetics

The substantial cross-contamination observed in the D₂d(II)-enriched fraction, as discussed earlier, obligated the author to use the "D₂(IV)" film for analysis of D₂d(II)'s photophysics. This substantially complicated the acquisition of the latter's transient absorbance spectrum. The relatively low concentration of D₂d(II) resulted in poor S/N values, which meant that unusually large numbers of shots per wavelength (i.e. 2000 vs.
the usual 200) were needed for clear results. The proportionally longer acquisition times also exacerbated the risk of oxygen contamination skewing the results during the course of the run (through acceleration of the decay components). These difficulties were resolved through both experimental technique and procedural means. To prevent \( \text{O}_2 \)-quenching problems, the cell holding the "D\(_2\)(IV)" film was backfilled with ultra-high-purity \( \text{N}_2 \) (g) immediately after degassing. After positioning the cell, a series of kinetic runs were taken at each wavelength of interest. Each data set was analyzed independently, via a double-exponential fit. Finally, the pre-exponential factor for the short component at each wavelength was multiplied by the y-scale (an additional intensity term covering both components), yielding the deconvoluted amplitudes of D\(_{2d}(\text{II})\)'s \( \Delta A \). This process yields a time-independent transient spectrum for D\(_{2d}(\text{II})\).

In the transient spectrum of D\(_{2d}(\text{II})\), the absorbance changes are positive across the observed range. Maxima are seen at 540, 870 and 980 nm, with a minimum located around 820 nm. (Figure 3.34.) The characteristic lifetime of D\(_{2d}(\text{II})\)'s transient absorbance decay was about 5 \( \mu \text{s} \). The appearance of the 980 nm feature initially set off alarm bells, since C\(_{70}\) has its transient maximum in that region. However, a number of factors indicated that this feature was probably not due to the lower fullerene:
Figure 3.34. Transient absorbance spectrum of C_{84} \{D_{2h}(II)\}, deconvoluted from C_{84} \{D_{2}(IV)\} (PMMA) data.

1) This spectrum originated from a state lasting a few microseconds, not tens of milliseconds. (However, this does not rule out the possibility of C_{70} forming some sort of complex with the higher species, in which the former’s T_{1} state is quenched.)

2) The 980 nm absorption persisted even when 705 nm excitation was used.

3) LDI-TOF-MS analysis of the D_{2}(IV) sample failed to show any clear evidence of C_{70} (or other lower fullerene) contamination. Peaks at 720 and 840 m/z only appeared when very high laser power was used. However, fullerenes in general (and C_{84} in particular) are known to break up, in response to irradiation, by ejecting two carbons at a time. This phenomenon is believed to explain the
Figure 3.35. LDI-TOF-MS of C_{84}[D_{2}(IV)] at a) low, b) medium, and c) high laser power. Note lack of C_{60} & C_{70} in a), and greater C_{84} breakup in b) & c).
presence of the 984 m/z (C₈₂) peak at low power. This higher fullerene is easily resolved from C₈₄ in chromatographic separations; moreover, had C₈₂ been a contaminant in the D₂(IV)-enriched fraction. Under more aggressive irradiation, C₈₄ forms a “fragmentation cascade,” in which its disintegration generates all possible lower species. (Figure 3.35.)

At this point, it is worthwhile to make an observation about the acquisition of the transient spectral data. The characteristic maxima of the two major isomers have both been shown to lie very close to the 532 nm wavelength of the laser pump pulses used. Without the installation of the HNF on the transient spectrometer, these features would have been difficult or impossible to observe. Moreover, knowledge of these features made the task of identifying the isomers, and of confirming their absence of contamination, much easier.

3.4.3.3. Emission and Singlet Oxygen Luminescence Experiments

The emission spectrum of the D₂₆(II) isomer shows the same 1000 nm maximum as the D₂(IV) isomer. This is not an entirely unexpected result, given the extent of cross-contamination in the two fractions. However, there are two notable differences. D₂₆(II) has: 1) a much-more-pronounced shoulder around 1100 nm; and 2) no evident singlet oxygen emission. (Figure 3.36.) This latter result was borne out by oxygen-sensitization experiments with Pd-OEP. The oxygen luminescence decayed more rapidly than it would have in the absence of a quencher (i.e. in 6.5 µs vs. 30 µs). This corresponds to an oxygen quenching constant around 4.5(10⁹) M⁻¹ s⁻¹, or about half of the diffusion rate. Such a result suggests that the T₁ energy of the D₂₆(II) isomer is within approximately 1
kT of the $^1\Delta_g$ level; if the difference were much greater, diffusion-limited quenching would be seen.

![Fluorescence spectrum](image)

**Figure 3.36.** Toluene-overtone-corrected fluorescence spectrum of aerated C$_{84}$ \{D$_{2d}$(II)\} (tol), showing absence of apparent $^1\Delta_g$ O$_2$ emission.

Assignment of the S$_1$ energy for the D$_{2d}$(II) isomer is more complicated than the D$_2$(IV) isomer’s assignment; in addition to the aforementioned contamination issues, the peak corresponding to the fluorescence maximum is only resolved as a vague shoulder in the absorption spectrum. An estimation of the absorption peak’s location was made via analysis of the derivative of the ground-state spectrum. After normalizing the corresponding point’s intensity to the emission peak, the S$_1$ energy was estimated to be 10,575 cm$^{-1}$—virtually identical to the energy found for the D$_2$(IV) isomer. (Figure 3.1.4.2.n.)
3.4.3.4. Cryostat Experiments: Variable Temperature Kinetics

For the reasons noted above, the D$_{2d}$(II) kinetics were extracted from the data obtained in the variable temperature analysis of the D$_{2}$(IV)-enriched film sample. When the rates of the D$_{2d}$(II) decay were plotted as a function of temperature, there was a general trend of acceleration; however, this appeared shallow and flat on a linear scale. (Figure 3.38.a) Arrhenius plotting of, and non-linear fits to, the data suggest that there are two kinetic components:

1) a relatively large tunneling term; and

2) a thermal term, with a 650 cm$^{-1}$ activation energy, which manifests itself around 195 K. (Figure 3.38.b)
This gap is larger than one would expect for direct coupling between T₁ and a low-frequency vibrational mode, and lower than would be anticipated for a pure electronic transition. Consequently, it is proposed that the activation energy is indicative of a proximity effect. In other words, vibronic interaction between T₁ and a nearby electronic level (perhaps T₂) leads to accelerated decay of the former state. This proposal is consistent with both the rapid decay of D₂(II), and the minimal influence of temperature on its kinetics. However, the scatter of the data results in a poor R² value, indicating unreliability of the fit. This is reflected in the large uncertainty (±37%) associated with the activation energy. Thus, one would need better S/N ratios, from a sample with more—and more-pure—D₂(II), before the energetic assignments could be made definitive.
Figure 3.38. Rates of $C_{84} \{D_{2d}(II)\}$ (PMMA) decay at various temperatures, and a 2-component fit, on: a) linear plot, and b) Arrhenius plot.
3.5. $C_{84}$ minor isomer: $C_{84} \{C_5(a)\}$

3.5.1. Ground-State Absorption

The long-wavelength absorption onset of the $C_5(a)$ isomer presented experimental difficulties, since this feature lies in the same area (between 1000-1200 nm) as the C-H overtone bands of most commonly used organic solvents. The very high intensity of these bands, coupled with the very low magnitude of the isomer’s absorbance, made the latter extremely difficult to observe. The fact that we wished to dissolve this isomer in a 1:1 mixture of methylcyclohexane and decahydronaphthalene—so it could be frozen into a cryogenic glass—only complicated matters further. To address this dilemma, we chose to redissolve the $C_5(a)$ in the all-deuterated counterparts of these two cycloaliphatic solvents. By doing this, the vibrational overtones were redshifted by a factor of $\sqrt{2}$, moving them out of the way of the absorption onset region. While the attempts to make this solution into a cryogenic glass were unsuccessful (as mentioned earlier), solvating the isomer in the hydrocarbon mixture gave a ground-state absorbance spectrum that had substantially more detail than the comparable toluene-based spectrum. (Figure 3.39.) For example, the maxima seen at 625 and 850 nm appeared only as shoulders in the toluene spectrum. The maxima in the bifurcated main peak were determined to be at 389 and 406 nm. Minima were also seen at 354, 398, 601, 800 and 994 nm. Finally, shoulders were manifested around 315, 454, 547, and 731 nm. (Figure 3.39.)
Figure 3.39. UV-Vis-NIR spectrum of $C_8d \{C_8(a)\}$ (1:1 methylecyclohexane-$d_{14}$: decahydronaphthalene-$d_{18}$) at 298 K.

There was still residual C-H contamination observable in the spectrum at 1197, 1229 and 1264 nm. Nevertheless, the deuteration held this down to a sufficiently low level to permit detailed observation of the singlet onset. The $C_8(a)$ absorption was seen to begin at 1185 nm. When the decreased broadening is taken into account, this observation is consistent with the 1200 nm result reported for the CS$_2$ solution of the compound.$^{72}$ Of particular note is the reproducible, periodic structure observed in this region. On top of the main peak corresponding to the $S_1 \leftarrow S_0$ transition, one can see clear sub-peaks manifested clearly at 1003, 1029, 1053, and 1076 nm, along with less-clearly-resolved shoulders to the red. (Figure 3.40.) The spacing between these feature is about 220 cm$^{-1}$. This suggests that the first singlet transition is being modulated by a low-frequency
vibration of the C$_{84}$. The most likely candidate would seem to be the totally-symmetric A, or breathing, mode.

Figure 3.40. NIR spectrum of C$_{84}$ {C$_{6}$} (1:1 methylcyclohexane-d$_{14}$: decahydronaphthalene-d$_{18}$), showing absorption onset, and vibronic progression of S$_{1}$→S$_{0}$ transition.

3.5.2. Transient Absorbance Kinetics

As mentioned above, the transient absorbance lifetime of the C$_{6}$ isomer in degassed PMMA is estimated to be 125 (±37) μs. This observation is consistent with the author’s prior observation that a kinetic component with a ca. 100 μs lifetime disappeared from the earliest-eluting (major isomer) fraction of C$_{84}$ after repeated rHPLC runs. Also, it is remarkable to note that the three most abundant C$_{84}$ isomers, with such similar π-π interaction properties, should have triplet-state lifetimes that differ so markedly.
3.5.3. Transient Absorbance Spectrum

Before the C₅(a) sample was transferred from toluene into the glass-forming solvents, it was degassed, and had its transient spectrum taken. This was done in a piecewise manner, in order to keep the slit width (and, thus, the signal strength) as close to optimum as possible. In addition, the number of steps in each "piece" of the spectrum was varied, in an attempt to gain better resolution in the regions of the spectrum where peaks occurred.

![Graph showing transient absorbance spectra](image)

**Figure 3.41.** Overlaid transient absorbance spectra of degassed C₅(a) (tol) and D₂(IV) (PMMA). Note similarities between two traces.

In the resulting transient absorbance spectrum (Figure 3.41.), the general profile of the spectrum, along with the locations of the maxima and minima (Table 3.2.), are disquieting in their apparent similarity to the D₂(IV) results. Further investigation
muddies the issue, as there are differences between the two spectra. For example, the D$_2$(IV) spectrum manifests a bleaching feature that is not present in the other isomer’s transient response. Also, some C$_s$(a) extrema are consistently redshifted with respect to

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<th>Maxima (nm):</th>
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<tr>
<td>C$_s$(a)</td>
<td>D$_2$(IV)</td>
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<td>750</td>
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Table 3.2. Locations of extrema in transient absorbance spectra of C$_s$(a) and D$_2$(IV) (tol) at 298 K.

their D$_2$(IV) counterparts. Moreover, two of the zero-slope points in the C$_s$(a) transient spectrum that are closest to D$_2$(IV)’s corresponding features (680 & 648 nm, respectively) are very weak, and lie within the noise limits of the spectrometer’s resolution. Nevertheless, there is enough of a shared resemblance between these two isomers’ transient spectra to suggest that there are contamination problems in the C$_s$(a) fraction. Since the C$_s$(a) isomer elutes immediately after the two main isomers, and since D$_2$(IV) is the more-abundant of the two main isomers, it follows that whatever cross-contamination did occur probably happened during the separation process. A definitive answer to the question of whether this actually happened would require making a PMMA film of the C$_s$(a) fraction and examining its kinetics. However, since it is solvated in a mixture comprised largely of decadeuteronaphthalene (a very high-boiling, non-volatile solvent), the C$_s$(a) would also have to be extracted into toluene through additional chromatography. Given all the problems with residual contamination the author had encountered with the HPLC equipment, it was felt that such a separation attempt would be ill-advised. Therefore, the study of the C$_s$(a) isomer was halted at this point.
CHAPTER IV. CONCLUSIONS

4.1. Summary of Results

4.1.1. C\textsubscript{60} Variants and Derivatives

The behavior of n-C\textsubscript{60} (aq) is dominated by its colloidal nature, as demonstrated by the Rayleigh scattering and Beer's law deviations observed in its ground state spectrum. While fullerene molecules on the periphery of the sol particles do enter the triplet state (as the colloid's unsaturated singlet-oxygen sensitization shows), the transient attenuation of n-C\textsubscript{60} (aq) is primarily thermal in origin. Luminescence from the colloid (both fluorescence and \(1\Delta_g\) \(O_2\) emission) is redshifted, which indicates the lowering of electronic energy levels by the polarizable C\textsubscript{60} environment surrounding the emitting species.

BAA exhibits transient absorption which is blueshifted by its derivatization. This absorbance change is also quenched by oxygen addition, indicating that its T\textsubscript{1} level is substantially higher-lying than 7880 cm\textsuperscript{-1}. Faint 1277 nm luminescence also confirms the occurrence of this process. While quenching of singlet oxygen by BAA is also observed, this process occurs at no more than 6% of the diffusion-limited rate, indicating that it is an "uphill" process.

4.1.2. C\textsubscript{80} Isomers

The C\textsubscript{80}\{D\textsubscript{5d}\} isomer lacks appreciable transient absorption; this is apparently due to a combination of negligible quantum yield and small triplet-state epsilons. It does quench singlet oxygen emission, albeit at about 1/3\textsuperscript{rd} of the diffusion limit; this suggests that the T\textsubscript{1} state of C\textsubscript{80}\{D\textsubscript{5d}\} is within 1 kT (~ 300 cm\textsuperscript{-1}) of 7880 cm\textsuperscript{-1}. 
The Ho$_3$N@C$_{80}$ ($I_h$) isomer's transient absorption properties were largely obscured by C$_{70}$ contamination. Oxygen quenching experiments demonstrated that the incar's T$_1$ energy lies above 7880 cm$^{-1}$. While it was proven that Ho$_3$N@C$_{80}$ ($I_h$) quenches C$_{70}$'s transient absorbance, further experiments showed apparent energy transfer from the incar to C$_{70}$; this makes it difficult to say where the T$_1$ level of Ho$_3$N@C$_{80}$ ($I_h$) lies in relation to 12,600 cm$^{-1}$. In film experiments, laser irradiation caused an irreversible, photoinduced reaction between Ho$_3$N@C$_{80}$ ($I_h$) and PMMA.

### 4.1.3. C$_{84}$ Isomers

This research has clearly demonstrated that the isomers of C$_{84}$ have dramatically different triplet-state properties. The energy levels of the D$_2$(IV) and D$_{2d}$(II) T$_1$ states are significantly different. The other energy levels within the isomers' triplet state-manifolds, as well as the vibronic interactions within and between those states, also differ markedly.

While the T$_1$ level of D$_2$(IV) lies above the energy of singlet oxygen, D$_{2d}$(II)'s T$_1$ state lies below 7880 cm$^{-1}$. Moreover, while D$_2$(IV) shows both vibronic and electronic transitions in its triplet manifold, D$_{2d}$(II)'s kinetics are suggestive of a proximity effect. Furthermore, the lifetimes associated with these states range over two orders of magnitude, from the second-longest on record (the 643 µs of the D$_2$(IV)), to the 127 µs of C$_s$(a), to one of the shortest (the 5 µs of the D$_{2d}$(II) isomer). This is a remarkable change, given the subtle cage geometry differences that bring about these substantially varying lifetimes.

### 4.2. The Future of Higher Fullerene Research: New Approaches and Proposals

The widely varying triplet-state properties of higher fullerene isomers, which have been established in the author's work, hold potential for future photophysical
experiments and applications. However, this promise is still severely curtailed by the
great difficulties involved in their chromatographic separation. In addition to the severe
challenge the separation of higher fullerene isomers presents, their relatively low
abundance in Huffman-Krätschmer soot makes the isolation of usable quantities difficult.
Crystallization of higher fullerenes from a supersaturated solution does allow one to
bypass large-scale HPLC extraction;\textsuperscript{77} however, this process is inefficient, as it does not
remove a high percentage of these larger fullerenes from the starting solution. For further
progress to be made in the study of higher fullerenes, these issues must be addressed.

4.2.1. Flash Vacuum Pyrolysis (FVP) of Polyaromatic Hydrocarbons

The origin of the isomeric separation problem is the unselective nature of higher-
fullerene synthesis. Since any fullerene $\geq C_{76}$ has a wide range of possible cage
arrangements, the Huffman-Krätschmer and flame methods, which use atoms and C\textsubscript{2}
radicals as their reactants, will inevitably create a substantial fraction of these isomers. If
the creation of higher fullerenes is to be more constrained, a different “carbon source”
must be used, one that has more of the product’s internal complexity, and offers fewer
degrees of freedom to the cage-forming process.

Scott et al. at Boston College have established a methodology that may lead to
such selective higher-fullerene-isomer synthesis. In an 11-step process, they created a 3-
armed, planar, halogenated PAH (C\textsubscript{60}H\textsubscript{27}Cl\textsubscript{3}). When subjected to FVP—which is simply
vacuum distillation through a heated tube\textsuperscript{78}—at 1373 K and 10 mTorr, this polyaromatic
species “curled up,” losing hydrogen and chlorine to form $C_{60}$. No other fullerenes were
generated in this process.\textsuperscript{79} This suggests that Scott’s procedure may be very useful in
generating isomers of $C_{84}$. Since 84 is evenly divisible by 3, it is feasible to generate a
“three-armed” precursor for each of the isomers. (Of course, to generate isomers lacking 3-fold symmetry, one would have to synthesize different structures for the PAH’s arms.\textsuperscript{80}) Furthermore, since this methodology appears to give only the desired fullerene product, it would be ideal for creating the various C\textsubscript{84} isomers of interest. However, the poor overall yield for Scott’s total synthesis (between 0.1 and 1\%) makes it unlikely that it could be used for bulk synthesis. Moreover, while the FVP step is the main source of inefficiency, the high temperatures and low pressures used indicate that the procedure was well-optimized for this unimolecular reaction.\textsuperscript{81} Nevertheless, the small quantities of fullerene generated by this technique are already adequate for photophysical work. The PAH precursors can be generated in gram quantities, and one only needs milligram amounts of fullerene for optical measurements.

\textbf{4.2.2. Host-Guest Chemistry}

One potential solution to both problems has been developed by Shoji, Tashiro and Aida at the University of Tokyo. For some time, researchers have sought to exploit the strong interactions between fullerenes and porphyrins for separation purposes. Previously, this had been done indirectly, by derivatizing porphyrins onto silica to form an HPLC stationary phase.\textsuperscript{82} Shoji et al. sought to utilize fullerene-porphyrin interactions more directly, through synthesis and application of a complexing system. Connecting two zinc-porphyrin molecules to one another, though a pair of ether-linked alkyl chains, creates a dimer that engages in host-guest chemistry with fullerenes. Lengthening the alkyl chains imparts greater affinity for higher fullerenes. Once the dimer-fullerene complex has formed, it can be extracted via chromatography with an alumina column; treatment with 4,4’-bipyridine then disrupts the complex and frees the fullerene. The
Tokyo group also found that the dimer’s fullerene affinity was reduced with symmetric alkyl derivatization of the porphyrins\textsuperscript{83} (probably due to steric effects). This result, while undesirable, hints at two general modifications to the procedure that could be helpful in addressing the isomer separation problem. One approach would be to derivatize the porphyrins in an asymmetric manner. This would constrain fullerenes to adopt specific “angles of attack” in order to complex with the dimer. Now, the isomers of any given higher fullerene will differ in structure (and, thus, in shape). Thus, some isomers would fit into an asymmetric dimer more readily than others. Consequently, there would be differences in the dimer’s affinity for specific isomers. The other approach would be to change the structure of the dimer’s porphyrins to alter their $\pi$-$\pi$ interactions with the fullerene. This could be done in two ways:

1) Aromatic side groups, e.g. phenyl or pyrenyl moieties, could be functionalized onto the porphyrin rings; and/or

2) The metallation of each porphyrin ring could be altered individually. For example, one could link a zinc porphyrin to a palladium porphyrin.

4.2.3. \textbf{Isocratic CS$_2$ Separations and Two-Detector SMB}

As mentioned earlier, SMB has the potential to improve isomeric separations of higher fullerenes. If this is to be implemented, three practical problems—two of which deal with the use of CS$_2$—must be addressed:

1) One should be able to monitor the progress of the separation during the course of the run, which is not possible with the setup the author used;

2) The toxic, flammable vapors from the solvent must be contained and suppressed; and
3) Some means of *in situ* solvent recycling must be implemented, as both financial and safety considerations oblige limits on the amount of eluent used.

As the solvent control considerations are the most pressing, these will be considered first. The very high vapor pressure (300 Torr at 293 K) of CS$_2$ obligates one to use it in a sealed environment, and to prevent accumulation of gases. This would be done by following procedures similar to those employed in an inorganic lab. All equipment for the separation would be mounted in an electrically grounded glove box. This box would be modified by the replacement of its oxygen-scavenging catalyst chamber (which would be poisoned by CS$_2$) with an exhaust hose, routed directly into a hood. A dry-gas source would continuously flush the box with N$_2$, purging solvent vapor, water vapor, and oxygen from the system. Check valves would seal off these lines in the event of a gas-flow disruption. By creating an inert, atmospheric-pressure environment around the HPLC, these measures would minimize mixing of CS$_2$ vapor and oxygen in the event of a leak in the box. Part of the glove box's floor would have slightly elevated platforms to hold the HPLC equipment and bottles; the remainder would be completely covered with a few cm of vermiculite. Septum-sealed bottles would be used at the reservoir, waste-collection, and sample-collection points. Each bottle would take two needle-terminated lines—one for solvent, the other for gas. Wherever possible, the lines and hardware would be made of titanium, as CS$_2$ has a tendency to irreversibly contaminate other materials. An autosampler would be used for collection, to minimize the risk of needle sticks. This device would be equipped with two solenoid valves. One valve would route the eluent from the detector to either the waste bottle or the selected sample bottle; the other valve would route the gas from either one of those bottles into a
condenser. The re-distilled solvent, along with the displaced gas, would then flow back into the reservoir through its “return” line. These measures would certainly be expensive, and may strike some as extreme. However, after considering the low toxicity limit (10 ppm), low explosive limit (1%), and flash-back behavior of CS$_2$, along with the very real dangers of a lab fire, the author feels this setup is the minimum that would allow isocratic CS$_2$ separations to be conducted safely.

To monitor the progress of an SMB separation in progress, one must use a two-detector, two-valve setup. Simultaneous, electronic actuation of a pair of four-way switching valves swaps the columns around either side of a central UV-vis absorption unit. (Figure 4.1.n.) In addition to providing data on the progress of the separation, this first detector gives ample warning of pre-elution. A second, identical UV-vis unit is kept at the end of the flow path. By watching the chromatogram generated by the second detector, the operator can determine when to switch column order, and take spectra of fractions (both pre- and deliberately-eluted) as they leave the system.

The chief disadvantage of this setup lies is that it subjects the first detector’s flow cell to high pressure. However, with a sufficiently low flow rate, the pressure at that point in the system can be held to 1600 psi, which a typical UV-vis unit could tolerate. As regards complexity, this SMB system has 14 “systemic” connections (i.e. after the injector and before the last detector); there are 10 such connections in “standard” SMB. As long as precautions are taken to keep line lengths similar, to cut tubing cleanly, and to swage fittings securely, the plumbing of the two-detector SMB system should not pose insuperable problems.
Figure 4.1. Two-valve, two-detector SMB system for continuous monitoring of separation during run.

4.3. Closing Remarks

It has been pointed out that the unusually pervasive, and pronounced, nature of the redshifts observed in the aqueous C$_{60}$ colloid may indicate that some other mechanism, in addition to a fullerene solvent effect, may be involved. The fact that the lowest-energy "camel" peak in the n-C$_{60}$ (aq) absorption spectrum is 5 nm redder than the corresponding C$_{60}$ (s) maximum tends to support this view. It has been proposed that the sol particles have two distinct, crystalline phases; this hypothesis has been advanced as a potential explanation for the bathochromic shifts observed in the C$_{60}$ colloid. If the
behavior of bulk C₆₀ is dominated by fcc/hcp structure,¹ however, it is hard to see how
the coexistence of other A-type lattices—which are, by definition, less closely
packed⁸⁶—would intensify redshifts. Perhaps the sub-micrometer scale of the sol
particles precludes the long-range disorder seen in the macroscale, and thus magnifies the
effects of close-packing. Another aspect of the colloid's redshifting is that it seems to
clash with others' observations. It is difficult to reconcile the bathochromic shift of ¹Δ₈
O₂'s emission with the hydrated environment Andrievsky et al. claim for the sol particle
interior. Additionally, the solvent-effect hypothesis conflicts with the aforementioned
group's assertion that hydration prevents direct interaction of fullerene molecules in the
sol.⁸⁷ However, the flocculent nature of Andrievsky's colloids (as seen in TEM images)²⁸
suggests there may be consequential preparation differences between the n-C₆₀ (aq)
samples in Houston and in Kharkov.

The interaction of C₈₄'s isomers with oxygen is interesting, in light of potential
biomedical applications. Since the D₂(IV) isomer sensitizes singlet oxygen and has a very
long-lived triplet state, it could possibly form the basis for a PDT agent. Following the
same line of reasoning, one could also employ D₂d(II) (and/or other C₈₄ isomers) as
parent compounds for antioxidant agents. However, as the previous discussion
demonstrated, the ability of these, and other, biocompatible fullerenes to interact with
singlet oxygen may—or may not—be relevant to their actual performance in vivo. To
make matters worse, there is uncertainty about the significance of ¹Δ₈ O₂ in PDT.²⁴
Finally, there is disagreement on whether singlet oxygen primarily poisons through
attacks on fatty acids,⁶⁶,⁸⁸ nucleic acids⁶⁵ or proteins.⁸⁹ In short, the confusion
surrounding this issue must be resolved, if fullerenes are to play a significant medicinal
role. Since superoxide anion has an absorption peak around 220 nm, with an extinction coefficient (ca. 2500 M$^{-1}$ cm$^{-1}$)$^{90}$ similar to those seen in fullerene triplets, transient absorption spectroscopy could play a role in answering the questions concerning ROS. One would only need to find a probe source with sufficient intensity in the UV.

If nothing else, this research has demonstrated the utility of transient absorption methods as a sensitive assay of the composition of a fullerene mixture. This initially seems surprising, in light of instrumental design principles. Ground-state absorption measurements require the monitoring of small light intensity changes; observation of short-lived, subtle shifts in absorbance only exacerbates the difficulties involved. However, these problems are ameliorated by the differences in the fullerenes’ transient spectra, triplet quantum yields and lifetimes. Even trace amounts of cross-contamination in a sample are sufficient to dramatically alter the kinetic and spectral properties of a solution. Thus, as fullerenes gain importance in the industrial realm, transient analytical techniques will be employed along with these compounds.

Before leaving the subject of higher fullerenes entirely, there are two very fundamental questions that must be posed:

1) Why do different masses of higher fullerene have such different degrees of intersystem crossing?

2) Why should the minor changes in symmetry between higher fullerene isomers of a given mass have such extreme effects on their triplet-state lifetimes?

Approaching an answer to the first conundrum will require a more quantitative approach to the measurement of the isomers’ quantum yields. This would necessitate higher-purity samples than the ones available for this experiment. As for the second question, its
solution must lie in the molecules’ conformational changes in the aftermath of the exciting pulse. More importantly, this issue is deeply enmeshed within the non-adiabatic processes that form the background of our photophysical measurements. Perhaps, by investigating the higher fullerenes, we will shed some light upon these “dark” phenomena—and, with them, our understanding of molecules in general.
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