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PHOTOPHYSICS OF C_{60}O

by

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
MASTER OF ARTS

APPROVED, THESIS COMMITTEE

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ABSTRACT

Photophysics of C$_{60}$O

by

Angelo F. Benedetto

We present a study of the ground and triplet state properties of C$_{60}$O. UV-vis spectroscopy and a gravimetric analysis are used to produce a quantitative electronic absorption spectrum. Spectrofluorimetry reveals that the fluorescence quantum yield of C$_{60}$O is $8.1 \times 10^{-4}$, which is a factor of 2.5 higher than that of C$_{60}$. Transient absorption spectroscopy is used to study the triplet state of C$_{60}$O, which is seen to exhibit complex decay kinetics. A possible explanation for this behavior involving triplet mediated epoxide ring opening is presented. The intrinsic triplet lifetime is determined to be $6.8 \pm 0.3$ $\mu$s, making C$_{60}$O the shortest lived fullerene derivative studied to date. Additional studies reveal that the decay of C$_{60}$O triplets has a mild temperature dependence corresponding to an $E_a$ value of $4.5 \pm 0.6$ kJ/mol, while self-quenching is seen to play a negligible role. Furthermore, solutions of C$_{60}$O are shown to be unstable with respect to temperature, generating unknown impurities even at room temperature. Mass spectrometric studies failed to unambiguously identify the product contaminant.
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I will end with another well deserved tradition. I wish to thank my family for their continuing support. They stood by every decision I made, which made it easier to make new decisions when the need arose. I'm coming home for Christmas this year, I promise. Dad, warm up the golf clubs and set the alarm; maybe we'll have time for 36.

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CHAPTER 1

INTRODUCTION

With the recent award of the Nobel prize for the 1985 discovery of C\textsubscript{60}, fullerenes are now more than ever a topic of great interest for scientists throughout the world. The discovery of preparative techniques leading to useful quantities of pure fullerenes has expanded this interest to encompass a variety of fullerene derivatives as well, with more derivatives being synthesized all the time. Among the first derivatized fullerenes to be reported was C\textsubscript{60}O, detected by mass spectrometry\textsuperscript{1} and soon afterwards generated, along with higher order fullerene oxides, by electrochemical oxidation of C\textsubscript{60}.\textsuperscript{2} An early stumbling block in the isolation of C\textsubscript{60}O was an inability to separate it using standard chromatographic methods. This was due to an unusual behavior of C\textsubscript{60}O, namely that it efficiently converts to C\textsubscript{60} during chromatography on neutral alumina, a material often used to separate fullerenes.\textsuperscript{3} Soon after this behavior was discovered, C\textsubscript{60}O was isolated by other chromatographic methods as the product of photo-oxidation of C\textsubscript{60}, in quantities large enough to characterize by mass spectrometry, UV-visible spectroscopy, IR spectroscopy and \textsuperscript{13}C NMR.\textsuperscript{3} Yet despite being one of the first reported derivatives, C\textsubscript{60}O has received relatively little attention since its discovery ca. 6 years ago. This may be due to the lack of proposed applications of C\textsubscript{60}O, but given the common occurrence of C\textsubscript{60}O contamination in C\textsubscript{60}, it is surprising that more work has not been done to fully
characterize $C_{60}$O and its behavior compared to that of fullerenes and other fullerene derivatives.

The first report of synthesis by photo-oxidation described a process of 18 hours of UV irradiation, followed by flash chromatography and HPLC, resulting in only a 7% yield of $C_{60}$O.\(^3\) The characterization methods described above suggested that the oxygen was attached to the fullerene cage by way of an epoxide bridge between two carbons which form the shared edge of two adjacent six-membered rings. This location has since become known as a [6,6] bond. An illustration of this structure is presented as Figure 1.1. Since the initial reports, many groups have detected $C_{60}$O as a common contaminant in $C_{60}$, but only the [6,6] closed epoxide structure has been identified, despite some early calculations that suggested that a [5,6] open fulleroid structure, seen in Figure 1.2, might be energetically favored over the epoxide.\(^4\) Recent reports by other groups have disputed this claim, and the matter is still somewhat unresolved.\(^5,6\)
Figure 1.1 The [6,6] closed epoxide structure of C_{60}O.

Not long after the reports of photo-oxidation of C_{60}, Heymann and Chibante reported the very swift creation of fullerene oxides resulting from exposure of fullerenes to ozone. This reaction was up to five orders of magnitude faster than the reported photo-oxidation, and they speculated that formation of C_{60}O in ambient air is due to interaction with ozone. Unlike photo-oxidation, however, ozonation of C_{60} results in not just C_{60}O, but also a host of higher order oxides. The structure of these higher oxides has not yet been adequately determined. Our own research used C_{60}O commercially prepared by photo-oxidation, which does not seem to produce the higher oxides in significant quantities.
Figure 2.2 Proposed [5,6] open fulleroid structure of C_{60}O.

Historically, our lab has been involved in the study of photo-excited states, specifically the relaxation of such states. Many of the proposed applications for fullerenes, including optical limiting and the sensitization of singlet oxygen for medical purposes, depend on fullerene excited states and their properties, so an understanding of fullerene photophysics is fundamental to our understanding of fullerenes in general. Since oxide contamination is very difficult to avoid, we felt it important to understand the photophysics of C_{60}O in general, and specifically how C_{60}O contamination will affect the photophysics of whatever species it is contaminating. To accomplish this, we must first understand the photophysics of fullerenes as a class of molecules.

In fullerenes, photoexcitation initially produces an excited singlet state, but through internal conversion and intersystem crossing, that rapidly and efficiently converts to the lowest lying triplet state.\textsuperscript{8-12} This state has been shown to have by far the longest lifetime of the fullerene excited states, so it is likely that most photophysical or
photochemical processes will be mediated by the triplet state. Given that, it is important to understand the fate of these triplets after they are formed. We have identified several possible deactivation mechanisms for the fullerene triplet state. They are the same photophysical processes that other organic triplets may undergo, and include the following:

Phosphorescence \[ T_1 \xrightarrow{k_{\text{phosph}}} S_0 \]

Unimolecular radiationless decay \[ T_1 \xrightarrow{k_i} S_0 \]

Oxygen quenching \[ T_1 + O_2 \xrightarrow{k_{\text{Q}}} S_0 + O_2^* \quad (1.1) \]

Self-quenching \[ T_1 + S_0 \xrightarrow{k_{\text{s}}} 2S_0 \]

Energy transfer \[ T_1 + S_0 \xrightarrow{k_{\text{e}}} S_0 + T_1 \]

Triplet-triplet annihilation \[ T_1 + T_1 \xrightarrow{k_{\text{T-T}}} S_0 + T_1 \]

The first two processes are both unimolecular decay channels, but in practice phosphorescence is neglected. This is because the radiationless decay of fullerene triplets is much faster than phosphorescence, so their combined rate is essentially the same as the radiationless decay rate. The remaining channels are all bimolecular processes, but some of them may be thought of as pseudo-first-order, depending on conditions. Oxygen, for example, has long been known as a very efficient quencher of organic triplets, and fullerenes are no exception. In a typical experiment, if the concentration of dissolved oxygen is not reduced it will easily be much higher than the concentration of our triplets, and the relative concentration of ground state oxygen in solution will remain largely
unchanged as a result of quenching fullerene triplets. For this reason oxygen quenching is kinetically pseudo-first-order and will contribute to the observed first order fullerene decay constant. Since we are mostly interested in decay channels other than oxygen quenching, we endeavor to eliminate as much oxygen as possible from our sample solutions.

Another pseudo-first-order process is self-quenching, in which an encounter with a ground state molecule causes deactivation of the triplet. The mechanism of this process is the subject of research and speculation, in our lab as well as others. Unlike oxygen quenching, self-quenching cannot be fully suppressed, although its effect can be minimized if low concentration samples are used. This is one of the reasons we are constantly striving to improve the sensitivity of our experimental apparatus, enabling us to examine solutions of concentrations below 1 µM while still maintaining an excellent signal-to-noise ratio.

Energy transfer is the deactivation of one species upon encountering the ground state of another species, resulting in excitation of the second species. In the limit of high quencher concentration and irreversible transfer it too is pseudo-first-order, although it can be eliminated entirely by working with very pure samples, a practice we always attempt to follow in our lab.

Finally, triplet-triplet annihilation results when two excited triplets encounter one another. One of the triplets is deactivated as it transfers energy to the other, promoting that one to a higher excited singlet state, which then rapidly intersystem crosses back to the triplet state, resulting in a net deactivation of one triplet. This is the only truly second
order process we encounter, and while it can never be completely eliminated, we can minimize its contribution to the overall decay by working with very low triplet concentrations resulting from low excitation energies.

With the above kinetic schemes in mind, we have studied the photophysics of \( C_{60}O \), and along the way have also examined some of its ground state properties. We have compared its properties to those of \( C_{60} \) as well as to other simple \( C_{60} \) derivatives, and we have found striking differences between \( C_{60}O \) and the other fullerenes studied to date. Our results indicate that \( C_{60}O \) is a fascinating molecule, with many secrets left to uncover.
CHAPTER 2

EXPERIMENTAL METHODS

2.1 Ultraviolet-Visible Spectroscopy

A number of analytical techniques were used to characterize C₆₀O, both qualitatively and quantitatively. Among these techniques was ultraviolet-visible (UV-vis) spectroscopy, used to study the ground state absorption of C₆₀O in toluene solution. The instrument used for this analysis was a GBC model 918. This instrument uses a 50 W quartz-iodide lamp as its visible source, and a 30 W deuterium lamp as its ultraviolet source, which was automatically switched on when needed. The 918 utilizes a single monochromator in a Czerny-Turner mounting with a holographic grating, and a rotating chopper to generate reference and probe beams. The detector is an R446 photomultiplier tube (PMT), which allows a scanning range of 190-900 nm. We typically scan at 200 nm/minute, using a slit width of 1.0 nm and a data interval of 0.24 nm. When necessary, the slit width can be narrowed to as low as 0.2 nm, or widened to as much as 5.0 nm. The GBC 918 is controlled by an IBM-PC compatible computer operating in a Windows 95 environment. The operating software is Spectral 1.50, Release Version 1.1, which is designed by GBC for this line of spectrophotometers.

Samples can be contained in cells of differing path length, so that a wide range of sample concentrations can be analyzed while remaining in a meaningful absorbance range. Cells of 2 mm and 1 cm pathlength can be held in a standard cuvette holder,
whereas a larger cell of 5 cm pathlength is held in place using a custom made holder. Our standard procedure is to take a baseline with the appropriate cell holder in place. Next, we take a scan of the correct solvent, in these studies toluene, contained in a cell of an appropriate length, with air in the reference beam. This background scan is later subtracted from the scan of the sample solution in the same cell vs. air, resulting in a spectrum that is free of contributions from cell or solvent absorptions. Of course, this correction is not accurate in regions of exceedingly high absorption, such as occurs in toluene at wavelengths below ca. 300 nm. Accordingly, although for the sake of completeness we often scan down to 190 nm, the spectra reported in this work are shown beginning at 300 nm.

Ground state molar absorptivities can be determined, for a sample of known concentration, by applying Beer’s Law:

\[ A = \varepsilon c l \]  

(2.1)

where \( A \) is the base 10 absorbance, \( \varepsilon \) is the molar absorptivity, \( c \) is the concentration of the absorbing species, and \( l \) is the path length. Determining the concentration of a solution without quantitative knowledge of its preparation history or molar absorptivity is not a trivial exercise. The most logical way of going about it is to evaporate all the solvent from a sample, preferably under vacuum, to obtain a clean dry solid. This solid can then be precisely weighed into a volumetric flask, and redissolved to give a solution of known concentration. This method was attempted, but for reasons discussed later, another approach had to be developed.
As an alternative to the method described above, a solution of unknown concentration, obtained as a single HPLC fraction, was loaded into a buret, which was set up to deliver its contents into a small aluminum dish placed on the surface of a hot plate. A small volume of solution was delivered into the dish, which was gently heated to dryness, leaving a residue behind. The dish was allowed to cool and then it was weighed. After a series of such additions, a plot of the weight of the residue vs. the volume added to the dish yielded a line, the slope of which gave the concentration of the solution in mg/mL. Assuming that the solution was pure C$_{60}$O, the known molecular weight was used to give a value in molarity. The validity of this assumption will be discussed later. In all cases where measurement of small masses was necessary, a Perkin-Elmer Autobalance AD-2 was used. This balance was calibrated before each use, and has a nominal accuracy of ±0.01 mg at a full scale of 200 mg.

2.2 High-Performance Liquid Chromatography

The technique of High-Performance Liquid Chromatography (HPLC) is useful for several purposes in our study of C$_{60}$O. Given accurate ground state molar absorptivities at a common wavelength, the absorbance detector lets us judge the purity of a given solution and identify the likely contaminants and their relative concentrations. With the right combination of mobile and stationary phases, we can generate enough separation between these components to enable us to collect “pure” fractions of each substance present in our bulk sample. In our case, we were able to separate the C$_{60}$O component from its main contaminants, C$_{60}$ and C$_{60}$O$_2$, providing us with a much purer sample of
C₆₀O than that with which we started. Some difficulties encountered with this method will be discussed later.

The HPLC system used in this work is equipped with two Waters 510 pumps, allowing for a mixed solvent mobile phase. Typically, we use only one of these pumps, as our mobile phase is pure toluene. The detector is a Waters 996 Photodiode Array (PDA) detector. Our injector is a Waters U6K, equipped with a 2 mL injection loop. Most of the work with C₆₀O made use of a Cosmosil Buckyprep column, 25 cm long with a 4.6 mm inner diameter. A small amount of early work was done on a reverse phase C-18 column, using a mixed mobile phase of toluene and methanol, but this method was only used to compare to earlier work by another research group. The entire HPLC system is computer controlled, using the Millennium 2.0 software package from Millipore, running on an IBM-PC compatible in a Windows 3.1 environment. Typical running conditions specified a mobile phase flow rate of 1 mL/minute, which produced pressures of approximately 1100 psi. Under these conditions, typical retention times for C₆₀ and C₆₀O were ca. 7.5 and 8.5 minutes, respectively. Injection volumes varied in the range of 50 to 500 μL.

2.3 Spectrofluorimetry

The fluorescence quantum yield of C₆₀ in room temperature toluene solution has previously been reported as 2.2 x 10⁻⁴, with very little dependence on excitation wavelength.¹⁴ An effort was made to study the fluorescence behavior of C₆₀O, and to compare it to that of C₆₀, under similar conditions.
All fluorescence excitation and emission spectra were obtained using an SLM Aminco 8100 Series 2 spectrofluorometer, equipped with two single MC200 monochromators, a 450 W quartz-xenon excitation lamp, and two R928 PMT detectors. Both detectors are mounted at right angles to the incident excitation light. One follows a monochromator and is used to record emission spectra; the other measures total fluorescence. The spectrofluorometer was controlled using SLM Aminco 8100 software, designed specifically for this instrument, running on an IBM-PC compatible computer in an OS/2 environment.

Samples were dissolved in toluene solution, held in a 1 cm square quartz cell, and prepared to have a ground state absorbance of 0.15 at an excitation wavelength of 330 nm, the position of maximum absorbance for C₆₀O, within the range of 300-900 nm. For C₆₀, this corresponds to a concentration of \( \sim 3.4 \times 10^{-6} \) M, and for C₆₀O the concentration was \( \sim 3.8 \times 10^{-6} \) M. The solvent used to prepare these solutions was Fisher brand Optima grade toluene, used as received. Spectral bandpasses were set to 8 nm for emission as well as excitation. Schott color glass filters were used to protect the PMT's from scattered excitation light; a 3 mm thick GG400 filter was placed in front of the total fluorescence PMT, while a 2 mm thick GG375 filter was used to protect the PMT behind the monochromator. The same standard conditions were used for all emission scans. The excitation monochromator was set to 330 nm. The emission monochromator was scanned from 400 to 800 nm at a scan rate of 10 nm/second. Ten repetitions of each scan were obtained and averaged automatically by the software.
A check of the instrumental “dark current” response showed exceedingly little light reaching the detectors while no sample cell was in place. Next, a reference spectrum of toluene in the sample cell was recorded, to subtract from subsequent sample spectra. Finally, emission spectra of the C₆₀ and C₆₀O solutions were recorded.

Excitation spectra were obtained in a similar manner. The conditions above were duplicated, with only a few differences. First, the excitation monochromator was not held at one wavelength, but was scanned from 320 to 670 nm at a rate of 10 nm/second. The emission monochromator was set to 690 nm, which corresponds to a major emission peak for C₆₀O. The same combination of filters and bandpasses were used, and each sample was scanned ten times, with automatic averaging as above.

All files were corrected for wavelength dependent instrument response via the Instrument Correction feature of the software. This feature utilizes correction factors, which are generated by the manufacturer and supplied with the software, to compensate for the wavelength dependence of the instrument’s optical elements and detectors.

2.4 Mass Spectrometry

A variety of mass spectrometry methods were used to analyze our C₆₀O samples, some of which proved more effective than others. All methods made use of the same basic equipment. The spectrometer itself is an MAT 95 high resolution, double focusing mass spectrometer from Finnigan MAT. It uses ICIS software on a DECstation 5000 UNIX compatible computer.

The first method attempted was the Direct Insertion Probe (DIP) method, which makes use of a small crucible to hold the sample. The crucible is heated to around 325 °C
to vaporize the sample. This method met with no success, as the temperature was not high enough to completely vaporize fullerene samples. As a result, this approach was quickly abandoned.

The next method used, which also met with only limited success, was Desorption Chemical Ionization. This method consists of dipping a wire into a solution to coat it with solute. The wire is then heated to around 700 °C, which drives off any remaining solvent and vaporizes the analyte. In this case, the temperature was high enough to vaporize the fullerene, but it was so high that it tended to decompose the C\textsubscript{60}O molecules, resulting in an increase in the amount of C\textsubscript{60} detected in a sample, and a corresponding decrease in the amount of C\textsubscript{60}O detected. The exact extent of this decomposition was unknown, but seemed to be quite large.

The method we finally settled on was Atmospheric Pressure Chemical Ionization (APCI) - negative ion mass spectrometry. In this approach, a solution of the analyte, in this case C\textsubscript{60}O in toluene, is sent through a capillary along with a stream of gas, usually N\textsubscript{2}. The capillary is heated to around 250 °C to evaporate the solvent, as the solute/gas stream is passed through a corona to impart charge to the analyte molecules, which are then carried through the rest of the analysis in the usual manner. This approach delivers the analyte in ionic form, but avoids the high temperatures of DCI. Accordingly, the amount of C\textsubscript{60}O destroyed or converted into C\textsubscript{60} is minimized, although not completely eliminated. In fact, unlike most other methods, APCI is relatively gentle to the sample, and thus the usual patterns of sample fragmentation seen in higher temperature methods are not present in an APCI mass spectrum, which consists mostly of unfragmented parent
peaks. This method is therefore useful for qualitatively identifying what components are present in a sample, but as a quantitative tool to judge sample purity it is limited to estimating an upper limit to levels of contamination. Our analyses were performed in the range of 150-2000 mass units, using an instrumental resolving power of ca. 1500, which is sufficient to resolve two peaks separated by 0.5 mass units in the range of 700-750 mass units. This resolution is necessary for properly assigning multiply charged species. The detector is sensitive to the mass-to-charge ratio of the analyte ions, and the masses reported assume that each ion has a charge of one. If a sample molecule picks up two charges, that molecule will be reported as having an apparent mass of half its actual mass. Therefore, in order to determine if a peak at 360 mass units, for example, is actually a species with a mass of 360 or if it is merely a $C_{60}$ molecule which has acquired an extra negative charge, we utilize the natural abundance of $^{13}C$ to perform the following check. We look for peaks due to the presence of $^{13}C$, in this case at 361 and 721 mass units. The peak at 721 will definitely be present, but the peak at 361 might not. If there is a peak at 361 mass units, it is due to the presence of $^{13}C$ in a substance with an actual mass of 360. However, if the peak at 360 is due to a doubly charged $C_{60}$ ion, then there will be no peak at 361 mass units, but there will instead be a peak at 360.5, which is half the value of the $^{13}C$ peak at 721 mass units.

2.5 Transient Absorption Spectroscopy

For several years our research group has investigated the relaxation kinetics of triplet state fullerenes and fullerene derivatives, mostly in the condensed phase. The experimental apparatus which allows us to study these excited triplet states has gone
through a series of revisions, but has always been based on the same underlying principles.

Our sample solution is held in a cylindrical quartz cell with two windows. Attachments to the cell allow for the solution within to be degassed. This is important because oxygen is a very efficient quencher of organic triplet states, and must be rigorously eliminated in order to assure accurate kinetic information. The oxygen quenching constant for C\textsubscript{60} in aromatic solvents has been reported as ca. 1.6 x 10\textsuperscript{9} M\textsuperscript{-1} s\textsuperscript{-1} \textsuperscript{12,15}, which means that if we wish to suppress the oxygen quenching rate to below 100 s\textsuperscript{-1}, we must reduce the concentration of dissolved oxygen in our fullerene solutions to less than 10\textsuperscript{-7} M. This is most easily and efficiently accomplished by repeated freeze-pump-thaw cycles. Experiment has shown that ca. 12 cycles are sufficient to thoroughly degas our samples to the necessary levels, evacuating to pressures below 10\textsuperscript{-4} Torr.\textsuperscript{16}

The design of the cell, illustrated in Figure 2.1, allows the degassed solution to be held under vacuum during the entire data collection process, thus ensuring that oxygen remains excluded. In addition to this feature, some of our cells are water jacketed to allow temperature control of the sample solution. We also designed a cell which allows for mixing of two separate solutions, while both are kept sealed against the atmosphere. With this cell, the concentration of a sample can be varied without the need to degas the solution at each new concentration. Finally, most of our cells have a 5 cm pathlength, but we do have one shorter cell, of 0.5 cm pathlength, useful for studying highly absorbing samples.
Excitation of the sample is accomplished by exposure to the pulsed output of one of two Nd:YAG lasers, frequency doubled or tripled to provide light at either 532 nm or 355 nm. The laser used in the earlier stages of this work was a Lumonics model HY400, which is electro-optically Q-switched to provide pulses of approximately 10-12 ns in length at a repetition rate of up to 10 Hz. At one point during this work, the internal laser optics were modified to give a nearly TEM\textsubscript{00} Gaussian-shaped excitation beam. The excitation laser for the later stages of this work was a MiniLase II-20, from New Wave Research. This smaller unit delivers a beam which is lower in energy, but still powerful enough for our needs. It produces pulses 5-7 ns in length at a repetition rate continuously adjustable up to 20 Hz. The profile of this beam is of a quality comparable to that of the best beam we achieved using the HY400.

In all cases, the excitation beam was expanded or contracted as needed to provide an excitation volume larger than our probe volume. Additionally, the beam was
attenuated, using partial reflections and neutral density filters, to produce appropriate
induced absorbance values. A portion of the excitation beam was diverted onto a
photodiode detector, the output of which was directed into a digitizing oscilloscope to
provide a zero delay trigger reference.

2.5.1 Fixed-wavelength apparatus

A diagram of this apparatus is presented in Figure 2.2. Our probe sources were a
pair of Uniphase model 3501 continuous diode lasers, one centered at 672 nm and the
other at 758 nm. These low power lasers generate approximately 1 mW and are highly
amplitude stable, with nearly Gaussian beam profiles.

The excitation beam and both probe beams travel collinearly through the sample
cell, after which they are spatially dispersed by either a grating or a Pellin-Broca prism.
The excitation beam is trapped, while the two probe beams are directed onto two separate
photoconductive silicon photodiode detectors, sometimes using focusing lenses. These
detectors have active areas of 19.6 mm², and use a standard 9 V battery for bias. Each
detector's output is sent to a separate channel of a Hewlett-Packard model 54504A
digitizing oscilloscope, typically using external 2.6 kΩ termination. The coaxial cable
connections between the detectors and the oscilloscope are kept to under 46 cm, to
minimize cable capacitance and decrease instrumental response time. This set-up
produces an instrument function which is sub-microsecond (ca. 500 ns), but if faster time
response is necessary we can use a lower external termination.
The data collection process is computer controlled and completely automated, after initial parameters are entered and the lasers are properly aimed. The ground states of our fullerene samples typically have very low to negligible absorbance at our probe wavelengths, while the excited triplet states have significantly higher molar absorptivities. The exposure of the sample to the excitation pulse creates a population of singlet excited states, which rapidly convert to the lowest lying triplet state via internal conversion and intersystem crossing. The $T_n \leftarrow T_1$ absorption which follows results in an attenuation of probe beam intensity, which the oscilloscope detects as a drop in signal voltage. As the triplet population relaxes to the ground state, by any of a number of possible channels, the signal returns to its baseline value. The oscilloscope averages
2048 of these waveforms, then transmits them to an IBM-PC compatible lab computer for analysis.

During the automated data collection process, the oscilloscope also collects background waveforms due to probe-only, excitation-only and strictly electronic effects. These backgrounds are used by the analysis software, which then reports the time dependent "induced absorbance" that is attributed solely to the sample under study.

2.5.2 Variable-wavelength apparatus

One drawback of the design outlined above is the limitation of fixed wavelength probe beams. Although the wavelengths chosen were appropriate for C60, there is no guarantee that the triplet state of any other molecule of interest will have an appropriate absorbance at the specific probe wavelength. For this and other related reasons, we developed an apparatus capable of monitoring transient absorption over a wide wavelength range; a diagram is shown in Figure 2.3.
Figure 2.3 A schematic of our variable probe wavelength transient absorption spectroscopy apparatus.

This design is based upon the same principles as the fixed wavelength apparatus, but utilizes a tungsten-halogen bulb as a probe source. We currently use a 12 Volt Welch-Allen lamp with a color temperature of 3240 K, chosen for its high brightness and low noise characteristics. The lamp normally operates at 6 V and 3.35 Amps. After passing through the excited sample volume, the probe light enters a 100 mm focal length monochromator (Instruments S. A. model H-10) with a 1200 grooves/mm, 450 nm blaze diffraction grating. The wavelength of interest is selected and directed onto an amplified
silicon photodiode detector (Hamamatsu model S3887), the output of which is sent to a digitizing oscilloscope (Tektronix model TDS-430A). Custom written computer software analogous to that used in the fixed wavelength apparatus allows for automated data collection and conversion to induced absorbance. It also automatically subtracts "probe closed" backgrounds and normalizes the calculated induced absorbance at each wavelength to the average excitation energy.

The apparatus in its current form has a usable wavelength range of 400 - 900 nm, a spectral resolution of 4 nm, and a time resolution of 500 ns. By taking several hundred averages every 5 or 10 nm within its usable range, this instrument can construct a detailed triplet-triplet absorption spectrum which can be analyzed kinetically. Such an analysis can reveal the presence of time dependent features in a spectrum, which can be an indicator of sample contamination or unusual photoprocesses occurring in the sample.
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Ground State Studies

3.1.1 Ultraviolet-visible spectroscopy

When we begin to study a new fullerene or fullerene derivative, the first step of our procedure is to measure its quantitative ground state UV-vis absorption spectrum. This allows us to determine the concentration of future solutions by simply measuring their absorbance values at a given wavelength and applying Beer’s law (2.1). Acquiring a quantitative spectrum requires that our sample be pure and dry, so that we can create a solution of well known concentration. In the case of C_{60}O, this proved to be a difficult task. Initial attempts to dissolve the C_{60}O in toluene produced solutions with small amounts of undissolved dark particulate which settled to the bottom of the solution. This substance could be brought into solution using ultrasonication, but it was never determined exactly what this substance was. Our commercial supplier (Bucky USA) had reported our sample to be 98.1% C_{60}O, with C_{60} as the major contaminant, but did say that the purification procedure could lead to unwanted chemistry, resulting in unknown contaminants in the final product. In fact, the first sample of C_{60}O we received proved to be insoluble in toluene, and therefore not C_{60}O at all. We believe it was C_{60}O(OH)_x, which our supplier speculated was the result of the C_{60}O reacting with either methanol or trace amounts of water. Accordingly, we suspected that our sample might not be 98%
C₆₀O, and that we would need to purify and dry it ourselves in order to measure an accurate spectrum.

We attempted to do this by using HPLC to obtain a pure solution of C₆₀O, which was then dried by gentle heating (70 °C) in an oil bath. While drying, the sample was kept under vacuum (5 x 10⁻⁵ Torr) and the condensed solvent was collected in a liquid nitrogen trap. The waxy solid left behind was weighed out and dissolved in toluene to give a solution of a slightly browner color than the commercially obtained C₆₀O, but which, like the commercially obtained product, did not fully dissolve in toluene. The calculated molar absorptivity of the sample proved to be lower than expected, although HPLC analysis showed the solution to be 95% C₆₀O, so I assumed the sample had not been thoroughly dried. Accordingly, I repeated the experiment, and left the sample heating under vacuum for several days. This resulted in a lighter colored, less waxy solid, which again gave very low values for its molar absorptivity as compared to C₆₀.¹⁷

The low molar absorptivity combined with the presence of insoluble material in our dried sample led us to believe that we were still not producing pure dry C₆₀O, even though we were starting out with solutions purified by HPLC. We decided that extended heating at even moderate temperatures might be causing changes in our sample, so another method was devised. This gravimetric analysis method, described in the Experimental Methods section, resulted in calculated molar absorptivity values for C₆₀O that were much closer to those for C₆₀, and more reproducible in general. The resulting quantitative electronic absorption spectrum is reproduced in Figure 3.1.
Recent investigations into the room temperature stability of C$_{60}$O solutions suggest that the samples used in our gravimetric analyses were probably less pure than we originally thought. Repeating the gravimetric analyses will likely result in a minor correction of our reported molar absorptivity values, but I estimate that the change will be less than 10%. C$_{60}$O spectra published to date by other groups$^{3,18}$ have not been quantitative, but qualitatively they agree fairly well with ours, although there are some slight differences in the shape of the spectra in the 430-500 nm region. Further experiments will determine if purer samples will produce spectra that agree more closely with previously published work.
3.1.2 Stability studies

HPLC analysis of the commercially obtained \( \text{C}_{60}\text{O} \) showed it to be far less pure than the quoted 98.1%. In fact, the first analysis showed our \( \text{C}_{60}\text{O} \) sample to be only 56.8% pure, with at least three other significant contaminants. This chromatogram is reproduced as Figure 3.2, with retention times and relative peak intensities reported in Table 3.1. All purity levels as reported by HPLC are weighted by the analytes' molar absorptivities at the detection wavelength, but in the case of \( \text{C}_{60} \) and its derivatives, we have always seen a significant ground state absorption at 330 nm, with different derivatives having similar molar absorptivities. Since our transient absorption techniques require samples of high purity, we utilized HPLC in a semi-preparative manner to obtain purified solutions of \( \text{C}_{60}\text{O} \). This resulted in solutions which were ca. 99% \( \text{C}_{60}\text{O} \) with two minor contaminant peaks of less than 0.5% each, one corresponding to \( \text{C}_{60} \) and the other to an as yet unknown substance which eluted under our standard HPLC conditions at ca. 5 minutes. Both of these contaminants are present in the chromatogram of the unpurified \( \text{C}_{60}\text{O} \). The purified \( \text{C}_{60}\text{O} \) was kept as a stock solution, from which to make dilute samples for study. These stock solutions were not routinely shielded from light or oxygen, and were generally kept at room temperature.

Anomalous kinetic behavior of these \( \text{C}_{60}\text{O} \) solutions, detailed later in this text, soon led us to question the purity of our stock solutions. HPLC analysis of a three month old \( \text{C}_{60}\text{O} \) stock solution, which had originally tested as 99% pure, showed that the solution was down to 90% \( \text{C}_{60}\text{O} \), with the major contaminant (7%) being the "5 minute
fraction" as I will now refer to the substance which elutes at 5 minutes under our standard HPLC conditions. This contamination is evident in Figure 3.3, the chromatogram of the above three month old solution. Also visible was a very small C₆₀ peak (0.3%) and another peak which we thought might be C₆₀O₂ (2.3%). Since we knew these solutions had started out very pure, we investigated their stability with regard to ambient light and temperature conditions.
Figure 3.2 HPLC chromatogram of commercially obtained C_{60}O in toluene solution.

<table>
<thead>
<tr>
<th>Retention Time (min)</th>
<th>%Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>2.0</td>
</tr>
<tr>
<td>4.8</td>
<td>16.6</td>
</tr>
<tr>
<td>5.8</td>
<td>2.6</td>
</tr>
<tr>
<td>7.5</td>
<td>10.8</td>
</tr>
<tr>
<td>8.4</td>
<td>56.8</td>
</tr>
<tr>
<td>9.8</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Table 3.1 Result table for chromatogram in Figure 3.2.
Figure 3.3 HPLC chromatogram of three month old C₆₀O solution left exposed to ambient conditions.

<table>
<thead>
<tr>
<th>Retention Time (min)</th>
<th>%Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>7.1</td>
</tr>
<tr>
<td>7.6</td>
<td>0.3</td>
</tr>
<tr>
<td>8.6</td>
<td>90.3</td>
</tr>
<tr>
<td>10.0</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table 3.2 Result table for chromatogram in Figure 3.3.

To see if light would encourage or hinder the formation of the 5 minute fraction, I performed a series of HPLC experiments. First, I injected an older solution of C₆₀O that had become contaminated, and collected only the C₆₀O. I then immediately reinjected the newly collected C₆₀O, and found that there was little to no sign of the 5 minute fraction,
as seen in Figure 3.4. I left the sample at room temperature and did not attempt to shield it from light or air, and 15 minutes later I performed another injection. This revealed that ca. 2% of the solution had transformed into the 5 minute fraction. Fifteen minutes later that had risen to 2.7%, 30 minutes after that it was over 3% and an hour after that it was almost 4%, as shown in Figure 3.5. It was now clear that the 5 minute fraction would form in a C₆₀O toluene solution upon standing at room temperature in ambient illumination. In a separate experiment, I collected a clean C₆₀O fraction into a vial covered in black tape, and kept it at room temperature but shielded from direct light for the course of the experiment. To my surprise, not only did keeping the sample in the dark not inhibit the formation of the 5 minute fraction, it may even have promoted it. After leaving the cleaned sample in the dark for only 15 minutes, the 5 minute fraction accounted for 4.8% of the sample, and in under an hour that value had grown to almost 11%, surpassing the level in the original contaminated solution. The amount of 5 minute fraction continued to grow until after ca. 4 hours it had reached 18.4%. When I analyzed the remainder of the solution almost 20 hours after its initial collection, it contained 22% 5 minute fraction, and a new peak had appeared at 3.4 minutes which accounted for 4.5% of the total area.
Figure 3.4 HPLC chromatogram of freshly purified $C_{60}$O.

<table>
<thead>
<tr>
<th>Retention Time (min)</th>
<th>%Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.5</td>
</tr>
<tr>
<td>8.6</td>
<td>99.5</td>
</tr>
</tbody>
</table>

Table 3.3 Result table for chromatogram in Figure 3.4.
Figure 3.5 HPLC chromatogram of $C_{60}O$, 2 hours after purification.

<table>
<thead>
<tr>
<th>Retention Time (min)</th>
<th>%Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>4.0</td>
</tr>
<tr>
<td>8.5</td>
<td>96.0</td>
</tr>
</tbody>
</table>

Table 3.4 Result table for chromatogram in Figure 3.5.

Although keeping the $C_{60}O$ solutions in the dark does not hinder the formation of contaminants, keeping them cold does seem to have a stabilizing effect. By keeping the collection flasks on ice, a solution of cleaned $C_{60}O$ can be kept stable during the entire HPLC collection process, which often takes several hours. In one instance, I was able to obtain a solution of ca. 99% $C_{60}O$ that maintained its purity level throughout an entire
afternoon. Other attempts have not been as successful and have resulted in solutions of only ca. 95% purity. In all cases, storage of these solutions in a commercial freezer keeps them fairly stable for periods of at least a week. However, since it seems that the 5 minute fraction will form quickly in such solutions even at moderate temperatures, care must be taken to perform experiments on C₆₀O at low temperatures if sample purity is to be maintained.

The fact that temperatures as low as 23 °C are high enough to facilitate formation of the 5 minute fraction helps to explain the difficulties we encountered when trying to get consistent molar absorptivity values using a dry solid sample of C₆₀O. We were heating a solution of C₆₀O to as high as 70 °C for extended periods of time. We assume that this treatment resulted in a solid of very low purity, which therefore resulted in an incorrect assessment of the molar absorptivity of C₆₀O. Even the more accurate values obtained by the gravimetric method were determined with room temperature solutions of C₆₀O, before we fully understood how important it was to keep our samples cold at all times.

3.1.3 Mass spectral analysis

Preliminary mass spectral analysis, shown in Figure 3.6, showed the commercial sample to be at least 70% C₆₀O, with ca. 25% C₆₀, 3% C₆₀O₂, and trace amounts of higher oxides. Attempts to characterize purified samples of C₆₀O suggested to us that even though APCI is a relatively gentle mass spectrometry method, it is still harsh enough to remove oxygen atoms from epoxides, resulting in C₆₀ peaks in spectra of what was supposedly pure C₆₀O, and the possible decrease in apparent amounts of higher order
fullerene oxides. However, all mass spectral work was done before we recognized the relationship between temperature and sample purity in $\text{C}_{60}\text{O}$ solutions. Since we do not yet fully understand the process of contaminant formation in $\text{C}_{60}\text{O}$, the relatively high temperature involved in mass spectrometry might result in unwanted chemistry occurring during analysis, which would lead to an incorrect assessment of sample composition. For this reason, all mass spectrometry results reported here should be considered tentative.

![Mass spectrum of commercially obtained C$_{60}$O.](image)

**Figure 3.6** Mass spectrum of commercially obtained $\text{C}_{60}\text{O}$.

### 3.2 The “5 Minute Fraction”

#### 3.2.1 Factors affecting formation

It has already been stated that the unknown 5 minute fraction will form readily in a toluene solution of $\text{C}_{60}\text{O}$ which is left to stand at room temperature, but will form very slowly, if at all, in a cold solution. It has also been determined that excluding light from
the system does not prevent this formation, and may actually facilitate it. In addition to these experiments, already described above, several more HPLC experiments were performed in an effort to understand the nature of the five minute fraction and the factors affecting its formation.

Since C$_{60}$O solutions did not seem to be transforming completely into solutions of the 5 minute fraction, one possibility was that the C$_{60}$O and the 5 minute fraction were in equilibrium with each other. To see if this was the case, I analyzed a solution of the 5 minute fraction which had been collected as a separate HPLC fraction months earlier and stored at room temperature without exclusion of light or oxygen. This solution proved to be mostly the 5 minute fraction (76%), with a variety of smaller features throughout the 3.5 - 6 minute range, but there was no evidence of C$_{60}$O formation. Since this lack of C$_{60}$O suggested that an equilibrium did not exist, we theorized that the toluene might contain a low level impurity with which the C$_{60}$O was reacting to give the 5 minute fraction. This would explain why the 5 minute fraction quickly formed in a newly cleaned solution of C$_{60}$O, but did not completely replace the C$_{60}$O; there was a limited amount of the contaminant with which the C$_{60}$O could react. When we "cleaned" the sample via HPLC, we were in effect removing the 5 minute fraction while adding more of this unknown reactant by diluting the C$_{60}$O solution with fresh toluene mobile phase. To check this theory, I performed another injection of unclean C$_{60}$O solution, but this time I collected the clean C$_{60}$O fraction into a vial containing additional toluene mobile phase equal to ca. half of the expected volume of the C$_{60}$O fraction to be collected. After 15 minutes, over 2% of the sample had turned into the 5 minute fraction, and 15 minutes
later that had risen to ca. 3.7 %, contrasted with 2.7% contamination in the non-diluted solution after a similar length of time. While this was not absolute proof of the hypothesis, it did suggest that further experiments were warranted.

Accordingly, I performed another injection of the stock C₆₀O solution, this time collecting the clean C₆₀O into a darkened vial containing extra toluene mobile phase. These results were the most dramatic of all, supporting our suggestion that this phenomenon may be due to a reaction with an unknown contaminant in the toluene mobile phase. The level of 5 minute fraction grew to 9.5% in the first 15 minutes, and continued to rise quickly. After 2.8 hours, the sample contained over 31% 5 minute fraction, and after 18.5 hours that number had risen to over 45%. A final check of the sample 5 days later showed that the 5 minute fraction had actually become the major component, accounting for over 52% of the sample.

Finally, to confirm the effect of keeping the reaction shielded from light, I performed another HPLC injection of the stock C₆₀O solution, and collected the pure C₆₀O fraction into a darkened vial containing some extra toluene. I then immediately transferred half of this solution to another vial, identical to the darkened vial, except that this vial was exposed to normal room light. I then periodically analyzed these two solutions for the next 2.5 hours. While the results were not as dramatic as expected, they did support the idea that the reaction was definitely not hindered by the exclusion of light. While the amount of 5 minute fraction seemed to rise in the two samples at about the same initial rate, after 2 hours the dark sample had become almost 12% 5 minute fraction, while the light sample contained only 9.3% 5 minute fraction after 2.5 hours.
Additionally, the percentage of 5 minute fraction did not seem to be climbing as rapidly in the light sample as it was in the dark. The HPLC experiments to study the formation of the 5 minute fraction are summarized in Figures 3.7 - 3.9.

Figure 3.7 The effect of dilution on the formation of the 5 minute fraction. Both of the C₆₀O HPLC fractions above were exposed to ambient light, but only one was diluted with additional toluene mobile phase.
Figure 3.8 The effect of dilution and darkness on the formation of the 5 minute fraction. Both of the C_{60}O HPLC fractions above were shielded from ambient light, but only one of them had been diluted with extra toluene mobile phase.

Figure 3.9 Comparison of two HPLC fractions showing the effect of light on the formation of the 5 minute fraction. The two samples above were both aliquots from the same C_{60}O HPLC fraction. One was shielded from ambient light, and the other was not.
3.2.2 Characterization

The UV-vis spectrum of a toluene solution of the 5 minute fraction of unknown concentration is shown in Figure 3.10, along with the spectra of C_{60}O and C_{60}. For purposes of comparison, these spectra are all normalized to their peak value at ca. 330 nm. While they are all similar, obvious differences can be seen. The absorbance peak of C_{60}O at 424.5 nm is shifted to 433 nm, and the peak at 330 nm is significantly blurred in the 5 minute fraction. When these spectra are compared with that of C_{60}, the differences are even more obvious, the most striking difference being the feature at 424.5 nm in C_{60}O which is completely lacking in the C_{60} spectrum.

![Figure 3.10](image)

Figure 3.10 A comparison of the electronic absorption spectra of C_{60}, C_{60}O, and the 5 minute fraction.
Mass spectral analyses performed on the various HPLC fractions produced ambiguous results. The fraction that was thought to be \( C_{60} \) was found by its mass spectrum, shown in Figure 3.11, to be mostly \( C_{60} \) with some \( C_{60}O \) and a very small amount of \( C_{60}O_2 \). The sample which was supposed to be \( C_{60}O \), shown in Figure 3.12, was mostly \( C_{60}O \) with some \( C_{60} \) and again a small amount of \( C_{60}O_2 \). Both of these samples also contained a small feature at 832 mass units, which would correspond to \( C_{60}O_7 \). The highest order fullerene oxide reported in the literature to date is \( C_{60}O_6 \), and that was in the gas phase.\(^{19}\) When the 5 minute fraction was analyzed, reproduced as Figure 3.13, it showed mostly \( C_{60}O \) with some \( C_{60} \) and an increased amount of \( C_{60}O_2 \). There were also very small features at 695, 768, 812, 832 and 848 mass units. The features at 768, 832 and 848 could correspond to higher oxides, but it is unclear what the other features might represent. From the increase in the level of \( C_{60}O_2 \) in the 5 minute fraction, one might assume that the higher oxides elute earlier than \( C_{60}O \), which comes off our column at ca. 8.5 minutes as compared to 5 minutes. However, Figure 3.14 shows a mass spectral analysis of an HPLC fraction which elutes just after \( C_{60}O \) at 9-10 minutes. This reveals an even greater increase in the level of \( C_{60}O_2 \) relative to \( C_{60}O \) and \( C_{60} \), as well as growth in the features at 768, 784, 848, and even 880 mass units, which would be \( C_{60}O_{10} \), suggesting that higher order fullerene oxides elute after \( C_{60}O \). It is interesting to note, however, that the mass spectral analysis of every fraction except for the \( C_{60} \) fraction showed the major component to be \( C_{60}O \). This led us to believe that one of two scenarios was most likely. One possibility was that the 5 minute fraction was indeed some \( C_{60}O \)
adduct which was formed during or shortly after the HPLC process, but was too fragile to withstand even the relatively gentle conditions of APCI mass spectrometry. This did not seem too unlikely, as we had evidence that some C₆₀O molecules did lose an oxygen atom during mass spectral analysis, and we knew from our commercial supplier’s difficulties that C₆₀O could react with solvent impurities to give other derivatives. The other possibility was that the 5 minute fraction was an isomer of C₆₀O, perhaps arranged as a [5,6] open annulene-like structure (Figure 1.2) as opposed to the [6,6] closed epoxide structure which has been reported as the only structure found experimentally. Although this possibility cannot be completely ruled out, the UV-vis evidence does not seem to support it. Smith and coworkers have reported that the characteristic peak at 424 nm is present in the spectrum of C₆₀O due to the [6,6] closed structure, and that it is also present in analogous cyclopropane derivatives of C₆₀.¹⁸ However, this feature, also seen in the spectrum of the 5 minute fraction, is not present in open annulene-like fullerene derivatives.
Figure 3.11 Mass spectrum of HPLC fraction thought to be C\textsubscript{60}^{-}.

Figure 3.12 Mass spectrum of HPLC fraction thought to be C\textsubscript{60}O.
Figure 3.13  Mass spectrum of HPLC 5 minute fraction.

Figure 3.14  Mass spectrum of HPLC fraction that elutes shortly after C_{60}O.
3.2.3 Stability

As mentioned above, HPLC analysis of an aged solution of 5 minute fraction revealed the presence of several other significant peaks eluting near the 5 minute fraction. Since these peaks were not present immediately after the clean 5 minute fraction was collected, it stands to reason that they correspond to other substances produced from a solution of 5 minute fraction, much as it is formed from a solution of $C_{60}O$. Preliminary HPLC experiments confirm this behavior, as small extra peaks can be seen to appear in a cleaned sample of 5 minute fraction shortly after leaving the sample exposed to ambient room conditions. This observation tends to support the suggestion that the 5 minute fraction is another fullerene derivative, and not just a more stable isomer of $C_{60}O$. A thorough investigation of this behavior has yet to be conducted.

3.3 Fluorescence Studies

3.3.1 Emission spectra

As mentioned earlier, the fluorescence quantum yield for $C_{60}$ has been reported as $2.2 \times 10^{-4}$ when measured over the 400 - 800 nm range.\textsuperscript{14} When the detection range is extended to 1100 nm, this value is more accurately determined to be $3.2 \times 10^{-4}$ in room temperature toluene solution.\textsuperscript{20} Our apparatus limits us to the narrower detection range, so the former value is used to compare the quantum yield of $C_{60}O$ to that of $C_{60}$. This is done by monitoring the total fluorescence of two solutions of similar absorbance and comparing these values directly, after accounting for solvent background and instrumental correction factors. Using this method, the fluorescence quantum yield of $C_{60}O$ is determined to be $8.1 \times 10^{-4}$, which is a factor of 2.5 higher than that of $C_{60}$ and
typical of fullerene derivatives studied so far by other groups. The value quoted above assumes similar near-IR components in the emission spectra of C_{60} and C_{60}O. In the narrow detection range, the shape of the C_{60}O emission spectrum is qualitatively similar to that of C_{60}, as can be seen in Figure 3.15. The two spectra, however, also have obvious differences. The C_{60}O spectrum has a much sharper major feature whose position is seen to be ca. 690 nm. The C_{60} emission spectrum also has a feature in this area, but it is not as sharp and its position, while not as easily determined, does seem to be to the red of the C_{60}O peak. Additionally, the C_{60}O spectrum features a definite shoulder at ca. 760 nm. The presence of this feature in the C_{60} spectrum is much less certain.

Emission Spectra of C_{60} and C_{60}O

![Emission Spectra of C_{60} and C_{60}O](image)

Figure 3.15 Fluorescence emission spectra of C_{60} and C_{60}O.
Figure 3.16 shows the fluorescence emission spectrum of C_{60}O along with the electronic absorption spectrum, shown only in the region of overlapping wavelength. We tentatively assign the S_n→S_0 transition to the major emission feature at ca. 690 nm, and observe that there does seem to be a corresponding absorption in this region, although it is not pronounced.

![Comparison of C_{60}O Absorption and Emission Spectra](image)

*Figure 3.16 A comparison of the C_{60}O absorption and emission spectra.*

### 3.3.2 Excitation spectra

Figure 3.17 shows the excitation spectrum of C_{60}O, along with the UV-vis absorption spectrum. The two are seen to be quite similar, and both show a major peak at ca. 330 nm as well as the distinctive feature at 424.5 nm. The differences between the two spectra might be due to the higher noise in the fluorescence excitation spectrum, or perhaps insufficient instrumental correction. It is also very likely that the two solutions
being directly compared in this figure are of somewhat different purities, due to the chemical instabilities already discussed. All fluorescence work was done with room temperature samples before the value of cooling was fully realized, and no work has yet been done to characterize the fluorescence behavior of the 5 minute fraction as a separate substance.

![C₆₀O Excitation and Absorption Spectra](image)

**Figure 3.17** Fluorescence excitation spectrum of C₆₀O, compared with ground state absorption spectrum.

### 3.4 Triplet State Studies

#### 3.4.1 Triplet-triplet absorption spectrum

Utilizing the variable probe wavelength apparatus described in the Experimental Methods section, a detailed triplet-triplet absorption spectrum was measured for a 14 μM toluene solution of 99% pure C₆₀O. This solution had been purified by HPLC and kept
cold in order to preserve sample purity. A water jacketed cell was used to keep the solution at ca. 2.5 °C during data collection, so as to hinder formation of the 5 minute fraction. The spectrum, reproduced as Figure 3.18, was taken using 355 nm excitation. Data points were collected every 5 nm and excitation energy was kept low to minimize the possibility of UV-light induced sample degradation. Such degradation has been witnessed in degassed solutions of C₆₀O as well as other C₆₀ derivatives exposed to higher energy UV laser pulses. It should be noted that the spectrum presented here is the second of two spectra of this solution, the first of which was taken with wider data point spacing and less averaging several days earlier. Data quality of the later spectrum is higher, and the two are qualitatively very similar, but a very small amount of sample degradation may have occurred despite efforts to prevent it.
Unlike the other C₆₀ derivatives we have studied, the shape of the C₆₀O triplet-triplet spectrum is not constant with probe delay time. In other words, a spectral abstraction of the data at very early times shows a marked difference from an abstraction taken at later times, which is evidence that we are observing more than one transient species. This behavior is illustrated by Figure 3.19, which shows an early and a later time spectrum, both normalized to their peak values. In the later time spectrum, the major peak is slightly blue-shifted, and a definite shoulder has grown in at ca. 820-830 nm. By contrast, no spectral evolution is observed for C₆₀ or its "dihydro" derivatives. A simple explanation of this behavior might be contamination of the sample, but as should be evident we are confident of this sample's purity. An alternate explanation is suggested
by careful comparison of the \( C_{60}O \) spectrum to those of \( C_{60} \) and some other [6,6] derivatized fullerenes.

Figure 3.19 Early and late time \( C_{60}O \) triplet-triplet absorption spectra, normalized to their peak values.

Figure 3.20 shows the triplet-triplet spectrum of \( C_{60} \), as well as the spectra of two "dihydro" fullerene derivatives. As can be seen, both of the [6,6] derivatized dihydrofullerenes show very similar spectra, with a major peak 50 nm to the blue of the major peak of \( C_{60} \), and a very definite shoulder near 830 nm. Current work by other researchers in this lab leads us to believe that the triplet-triplet absorption features in derivatized fullerenes result largely from the substitution pattern rather than the identity of the substituent. This thought has led us to a hypothesis which might explain the unusual behavior seen for \( C_{60}O \). Figure 3.21 is a comparison of the early time \( C_{60}O \)
spectrum to the C\textsubscript{60} spectrum. It shows that, while they do not match exactly, they do share some common features. The major peak of the C\textsubscript{60}O spectrum is less blue shifted than those of the other [6,6] derivatives, and most significantly, neither C\textsubscript{60} nor C\textsubscript{60}O shows the characteristic shoulder at 830 nm. Contrast this with the later time spectrum of C\textsubscript{60}O, presented in Figure 3.22 along with the spectra of the dihydrofullerenes. Clearly this spectrum has more in common with the spectra of the dihydrofullerenes, with its major peak shifting toward the blue, and the appearance of the characteristic shoulder at 830 nm. Since we contend that these features are due to the substitution pattern of the sample, our belief is that the C\textsubscript{60}O is undergoing some change which makes its structure more similar to that of the dihydrofullerenes. The obvious candidate for this is an opening of the epoxide ring due to cleavage of a C-O bond. This would result in a diradical molecule with a structure very like that of the dihydrofullerenes, with a lone electron taking the place of one of the “hydrogens”.
Figure 3.20 Triplet absorption spectra of $C_{60}$ compared to two dihydrofullerenes.

Figure 3.21 Early delay time $C_{60}O$ triplet absorption spectrum compared to $C_{60}$ spectrum.
Figure 3.22 Later time \( C_{60}O \) triplet absorption spectrum compared to that of \( C_{60}H_2 \).

A similar ring opening has already been proposed as a necessary process for the observed rearrangement of [5,6]-open methanofulleroids to [6,6]-closed methanofullerenes.\(^{22}\) Although the two cases are not exactly analogous, there is no reason to believe that such behavior would be impossible or even unlikely in the case of \( C_{60}O \). They both appear to be mediated by the triplet state, as are a number of reports of photochemical C-O bond cleavage in oxiranes of all types. In fact, there is a large body of work detailing the photochemistry of oxiranes and related compounds.\(^{23-29}\) Although for obvious reasons there is no mention of fullerene oxide in these studies, it is clear from these reports that an epoxide ring can undergo C-O or C-C bond cleavage under a variety of experimental conditions. The specific reactions that oxiranes undergo are dependent
on a number of parameters, including temperature, solvent, excitation conditions and the identity of additional nearby substituents. In fact, some reactions of oxiranes will proceed via C-C bond scission under one set of conditions, but via C-O bond scission under another.\textsuperscript{23} While these previous studies suggest that photochemically-activated epoxide ring opening is a very real possibility, they unfortunately do not have definitive value for predicting the ring opening behavior of C\textsubscript{60}O. It should be noted that in the case of the [5,6]-open methanofulleroids, rearrangement only occurs if there are substituents on the methyl carbon, and thus does not occur in the case of C\textsubscript{61}H\textsubscript{2}.\textsuperscript{22} In any case, rearrangement from the [6,6]-closed structure to the [6,5]-open structure has not been seen to occur at all. While none of this disputes the possibility of ring opening in C\textsubscript{60}O, it does suggest that it cannot be assumed to happen without confirming experiments, which have yet to be performed. One such experiment might be to collect data on a solution of C\textsubscript{60}O containing an agent to either inhibit radical formation or quickly react with any radicals formed, and then see if the behavior of the C\textsubscript{60}O is changed. In the latter experiment, a reaction product might be isolated and analyzed. Care would have to be taken, however, that this radical inhibiting agent was not also a triplet quencher, and that it was itself transparent to our measurements. Another set of experiments might determine if there is a solvent dependence to the slower decay component. Since the possibility exists that epoxide ring opening can be accompanied by charge separation, solvents of differing polarity might influence the rate and relative contribution of such ring opening. Of course, fullerenes show very limited solubility in most solvents that are more polar than toluene, so appropriate solvents might be difficult to identify. Finally,
obtaining pure solutions of C$_{60}$O in solvents other than toluene will require a thorough reexamination of our purification methods, as our current method is limited to solvents that are compatible with our HPLC components.

3.4.2 Transient kinetics

Regardless of the cause, it is obvious that the decay kinetics of triplet C$_{60}$O are unlike those of C$_{60}$ or any other fullerene derivative studied in this lab. No sample of C$_{60}$O, regardless of purity or concentration, has ever shown decay which could be accurately modeled as single exponential. Even very low concentration samples of highly pure C$_{60}$O kept at low temperatures show decay kinetics with more than one component. In fact, it was the observation of this behavior which originally led us to the discovery of the 5 minute fraction. Early data led us to believe that our samples were contaminated, but subsequent attempts to clean our samples did not produce the expected single exponential decays evidenced by C$_{60}$ and other fullerene derivatives under similar conditions.

Typical data from our fixed wavelength transient absorption apparatus is presented in Figure 3.23. This scan is from a 4.1 μM solution of C$_{60}$O, of unknown purity, at 23 °C. The most obvious qualitative observation about these data is the very fast decay. As a comparison, the triplet lifetime of C$_{60}$ is on the order of 145 μs$^{30}$, but the C$_{60}$O data clearly indicate a lifetime of under 10 μs. The exact value of the C$_{60}$O triplet lifetime would normally be obtained by fitting such low concentration data to an exponential decay model and extracting a first order decay constant. In the case of C$_{60}$O, however, this model does not accurately represent the triplet decay. This can be clearly
seen in Figure 3.24, which shows the same data from Figure 3.23 plotted on a natural log vertical scale. On such a plot, a simple exponential decay would be fit by a straight line, but this is obviously not the case for this, or any other C₆₀O data.

Typical C₆₀O Kinetic Data

![Graph showing induced absorbance vs. probe delay (μs)]

**Figure 3.23** Single wavelength triplet kinetics of a 4.1 μM solution of C₆₀O in toluene at room temperature.
Figure 3.24 C₆₀O kinetic data from Figure 3.23, plotted on a natural log scale. Note the deviation from linearity due to the presence of two decay components.

Our group uses custom software to model our transient absorption data. This software constructs a model decay utilizing various kinetic parameters entered by the user, then fits the data to the chosen model and calculates the deviation of the data from the fit. It then systematically adjusts the kinetic parameters of the fit to minimize the differences between the data and the constructed fit. Attempts have been made to model the decay of triplet C₆₀O using a number of kinetic schemes, with varying degrees of success. Again, it should be noted that most of the data were collected before we fully understood the importance of keeping our samples cold, so it is very likely that much of the data is contaminated by small amounts of the 5 minute fraction. However, because
even purified C₆₀O kept at low temperatures shows major deviations from single exponential decay, we are confident that this behavior is not due solely to contaminant effects.

All of our kinetic data show at least two components to the decay. The major component is always the very fast decay, followed by a minor, slower component. Some success has resulted from modeling these data as two independent exponential decays (Figure 3.25), although such fits are never perfect. Typically, the fast decay constant equals ca. 150 ms⁻¹, depending on the temperature at which it is determined. The slower decay constant, which represents ca. 10 - 25% of the decay, equals ca. 30 ms⁻¹. Occasionally, the fit can be slightly improved by using a sequential decay model, but in general the resulting kinetic parameters are very similar, especially in the case of the fast decay component. Since this is the case, even though we do not believe that two parallel exponential decays accurately describe the physical processes we observe, we nevertheless can gain valuable information by fitting our data to such a model. If our hypothesis of ring opening in the triplet state is correct, then we assume the fast decay component represents the sum of the ring-opening process and the intrinsic unimolecular decay of the ring-closed triplet state. We further believe that the fast unimolecular decay dominates this process, so we cannot disentangle the two “fast” components, but rather assume that their sum, as modeled by a single exponential decay, describes the intrinsic decay of C₆₀O triplets well enough for our current purposes. We have yet to fully explore the slower component of the decay, but plan to do so soon.
Figure 3.25 Single wavelength triplet kinetics of a 4.1 μM solution of C₆₀O in toluene at room temperature. The solid line is a fit to the data using a sum of two exponential decays.

If we make the above assumptions, we should be able to determine the intrinsic 1/e lifetime of C₆₀O, and thus its unimolecular decay constant, by looking at a series of low concentration data. For each concentration we fit the data to a sum of two exponential decays and extract an observed first order decay constant. By then plotting these observed first order constants versus concentration, we should obtain a straight line using Eqn. (3.1).

\[ k_{\text{obs}} = k_1 + k_{sq} [C_{60}O] \]  

(3.1)
The slope of this line would equal the self-quenching constant for C₆₀O, and the intercept would correspond to the intrinsic first order decay constant. Such a plot is presented in Figure 3.26, however the analysis is problematic.

![C₆₀O Self-quenching](image)

**Figure 3.26** An attempt to examine self-quenching in C₆₀O. Within our error limits, a linear fit through the data has no discernible slope. The line drawn through the data corresponds to the average value of the data points.

A linear fit of the data gives a line with a poorly determined slope, an unsurprising result given the high decay constants and the scatter in the data. In fact, within our error limits the line has no discernible slope at all. Accordingly, at this time all we can say with any confidence about self-quenching in C₆₀O is that it probably plays a very minor role, as we would expect for such a short lived triplet. The line drawn through the data in Figure 3.26 depicts 148 ms⁻¹, the average value of the observed first order decay constant, and corresponds to a unimolecular triplet lifetime of 6.8 ± 0.3 µs.
We likewise examined the temperature dependence of C$_{60}$O triplet decay. Given the tendency of C$_{60}$O to convert to the 5 minute fraction upon heating, the only way we can analyze these data is to make the same assumptions as above. With those assumptions, we can treat the major component as a simple exponential decay, and extract it from a fit of the data to a sum of two exponential decays. If we then plot the natural log of the resulting decay constants versus the reciprocal of the temperature, the data should fit a line whose negative slope is the activation energy of the decay process, according to Eqn. (3.2).

$$k(T) = A \exp \left(-\frac{E_a}{RT}\right)$$

(3.2)

Such a plot is presented as Figure 3.27. From this plot and others like it we can determine a value for $E_a$ of 4.5 ± 0.6 kJ/mol. This is higher than the C$_{60}$ value of 2.5 kJ/mol, but still represents a very small amount of chemical energy.30
Figure 3.27 The intrinsic decay of C_{60}O is dependent on temperature, with an observed E_a value of 4.5 ± 0.6 kJ/mol.

Finally, a study was made of solutions of C_{60} containing small amounts of C_{60}O, to determine if C_{60}O would act as a "quencher" of triplet C_{60}. Many early reports underestimated the C_{60} triplet lifetime, and we speculated that this might have been in part due to unrecognized C_{60}O contamination in C_{60} solutions. In such cases, triplet energy from excited C_{60} can be transferred to ground state C_{60}O molecules upon collision. The excited C_{60}O molecules this creates then decay faster than the energy can be transferred back to other C_{60} molecules via subsequent encounters, so the net effect is an artificial shortening of the observed C_{60} lifetime. If the level of C_{60}O contamination were small, it is unlikely it would be discovered and identified as an independent decay, especially by experiments less sensitive than our own. The results of our experiments show that C_{60}O is a very efficient quencher of C_{60}, with a quenching constant of 3.5 \times 10^9
M⁻¹ s⁻¹. This value, which is more than a third of the diffusion limited rate, is determined by plotting the observed exponential decay constant of C₆₀ versus the level of C₆₀O contamination, as shown in Figure 3.28.

![Quenching of C₆₀ by C₆₀O](image)

**Figure 3.28** C₆₀O has been found to be an efficient quencher of C₆₀ triplet states. The data indicate that C₆₀O quenches C₆₀ triplets at more than a third of the diffusion limited rate.
CHAPTER 4

CONCLUSIONS

We have presented the beginnings of a comprehensive study of C_{60}O, including its ground and excited state behaviors. UV-vis spectroscopy was used to produce a quantitative electronic absorption spectrum which is similar to that of C_{60}, with some important differences which allow us to distinguish one substance from the other. Likewise, the fluorescence behavior of C_{60}O was seen to be similar to that of C_{60}, and the C_{60}O fluorescence quantum yield was determined to be $8.1 \times 10^{-4}$, a factor of ca. 2.5 higher than that of C_{60}. The determination of these values was complicated by an unusual property of C_{60}O, namely an instability with respect to even moderate temperatures. C_{60}O was shown to transform into an unknown substance upon exposure to ambient conditions. The extent of this transformation was seen to depend on various parameters, including temperature and light exposure, and it was hypothesized that C_{60}O might form a weakly bound adduct with an unknown but low concentration contaminant in the toluene mobile phase used during the HPLC purification process. This position is supported by the fact that HPLC can detect the product of this transformation, which has a similar but slightly different electronic absorption spectrum, but even relatively gentle Mass Spectrometric methods cannot discriminate between C_{60}O and the unknown product.

Particular attention was paid to the triplet state of C_{60}O, which was also shown to display unusual behavior. Like other fullerene derivatives, C_{60}O absorbs light to produce excited singlet states which quickly and efficiently convert to the lowest excited triplet
state via internal conversion and intersystem crossing. Unlike other fullerenes, however, these triplet states do not undergo only simple exponential decay down to the ground state, but instead undergo more complex decay, consisting of at least two components. The fastest of these components, which we believe represents mainly the intrinsic unimolecular decay of the triplet $C_{60}O$, dominates the decay and shows $C_{60}O$ to be the shortest lived triplet of any fullerene or fullerene derivative studied to date, with an exponential lifetime of ca. 6.8 $\mu$s. The slower component describes a species with a lifetime of ca. 33 $\mu$s, although this value is less certain than the faster decay. While we do not believe these two components to be unconnected parallel decays of two distinct species, we do believe that we can gain useful information by modeling our kinetic data to the sum of two exponential decays.

This two component decay is also reflected in the triplet absorption spectrum of $C_{60}O$. The shape of such a spectrum is seen to vary with time, a behavior that is not shared by other fullerenes. Careful study of the triplet absorption spectrum has led to the hypothesis that $C_{60}O$ is undergoing triplet mediated opening of the epoxide ring, resulting in a diradical structure which more closely resembles a dihydofullerene. A survey of relevant literature reveals that such ring opening is well known in oxiranes, but is highly dependent on a variety of experimental parameters. A similar ring opening has been proposed for the mechanism of photo-rearrangement in other ring-containing fullerene derivatives. Although we are not suggesting that the epoxide ring is undergoing such a rearrangement, the initial step of such a rearrangement closely resembles the ring opening we have proposed.
Given the fact that triplet C_{60}O has such a short lifetime, it is unsurprising that we found C_{60}O to be a very efficient quencher of C_{60} triplet states, with a quenching constant of 3.5 \times 10^9 M^{-1} s^{-1}, a value which is more than one third the diffusion limited rate under our experimental conditions. We suggest that unrecognized contamination of C_{60}O in solutions of C_{60} may have contributed to erroneous early reports of C_{60} lifetimes. We also report a slight temperature dependence of C_{60}O triplet decay, corresponding to an E_a value of 4.5 kJ/mol. Finally, self-quenching is difficult to quantify in the case of C_{60}O, but it seems to be negligible.

While we have made a good start into the investigation of C_{60}O, it is clear that much remains to be done. The mysterious 5 minute fraction has yet to be identified, as has the effect it has, if any, on the properties of pure C_{60}O. Given the likely presence of the 5 minute fraction in many of our samples, a number of our experiments should be repeated with pure samples, in order to compare the results. Additionally, we are seeking more efficient methods of sample purification, such that we might perform $^{13}$C NMR characterization of a variety of samples, including the 5 minute fraction. Perhaps more important is the elucidation of the complex decay evidenced by C_{60}O triplets. Experiments will have to be designed, along the lines of those already discussed, to confirm or dispute the ring-opening hypothesis. We are very interested in obtaining analogous C_{60} derivatives with a similar ring structure, such as C_{61}H_2, to compare to C_{60}O. The behavior of the higher order fullerene oxides has not yet been examined, even though these species can and have been isolated. Finally, we might extend our studies to include C_{70}O, to see if it shows a drastically reduced triplet lifetime as well.
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