Electronically Excited C_2 from Laser Photodissociated C_{60}

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Abstract

Spectral and transient emission measurements are made of radiation from products of laser excitation of buckminsterfullerene (C_{60}) vapor diluted in argon at 973 K. The principal radiation is from the Swan band system of C_2 and, at early times, also from a black body continuum. The C_2 radiation is observed only when C_{60} is excited by green (532 nm) and not with IR (1064 nm) laser radiation at energy densities of about 1.5 J/cm^2. Transient measurements indicate that there are two characteristic periods of decay of radiation. The first period, lasting about 2 μs, has a characteristic decay time of about 0.3 μs. The second period, lasting at least 50 μs, has a characteristic decay time of about 5 μs. These characteristic times are thought to be associated with cooling of C_{60} molecules or nano-sized carbon particles during the early period; and with electronically excited C_2 that is a decomposition product of laser excited C_{60}, C_{58}, ... molecules during the later period.

Introduction

It is speculated that fullerenes are possible precursors to the formation of single-wall carbon nanotubes using the laser ablation process .[1] However, the existence of fullerenes is difficult to show directly since in situ C_{60} molecules in the gas phase do not have a characteristic visible emission spectrum. In the laser ablation process, the main radiation observed is that of C_2 Swan bands[2,3]. Arepalli and Scott[1] observed that C_2 Swan band radiation persists for an unusually long period after the laser pulse. Its characteristic decay time is on the order of 8 to 27 microseconds, while the natural lifetime of the $d^3\Pi_g$-state of C_2 is only about 100 ns. Therefore, excited C_2 must continue to be created

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after the initial laser pulse; and whatever is producing it must have a long lifetime. In the laser ablation process, a target of graphite containing a few percent of Ni and Co is irradiated by laser pulses of 532 nm and 1064 nm. These 1.5-J/cm^2-laser pulses, separated by about 50 ns, heat the surface to several thousand degrees and cause the target to ablate. Most of the ablation product is C_3, but some C_2, and possibly some atomic C are also produced. The lifetime of C is very short and within a few tens of nanoseconds recombines to form higher molecular weight carbon molecules. Chemiluminescent decay of C_2 formed from recombination of C would be over very fast – much faster than is observed in the Swan band emission decay. Therefore, another explanation of the persistent C_2 radiation must be found.

It has been known for a number of years[4,5,6] that the C_2 molecule is a dissociation product of fullerenes excited by lasers. The C_{60} molecule may absorb several photons of UV or visible light, putting it in a highly vibrationally excited state. This state is unstable and results in decomposition into C_{58} and C_2. Photodissociation of fullerenes has been observed with mass spectrometry when C_{60} and other fullerenes are illuminated with high intensity laser light[4]. A whole manifold of C_n molecules ($n<60$) has been observed from photofragmentation of C_{60}. Further, C_{58} may absorb photons and decompose into smaller cage molecules, likewise by giving up C_2 molecules. If the original C_{60} had sufficient excitation energy, then the C_{58} may also be excited sufficiently to dissociate by ejecting a C_2 and so on. It was tacitly assumed that the formed C_2 was in its ground state. Fullerenes have been found in abundance in the product of laser ablation of pure graphite[7-8] and has been found as an impurity in laser ablation production of single wall carbon nanotubes. These facts lead us to expect that laser excitation of fullerenes may result in the formation

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of *electronically excited* C_2 molecules leading to Swan band emission. The objective of this work, then, is to investigate C_{60} excitation by lasers and the possibility that photodissociation of fullerenes produces C_2 in electronically excited states.

Experiment

Measurements of the afterglow of C_{60} vapor were made in the same apparatus used for making carbon nanotubes by the laser ablation process at NASA Johnson Space Center.[1] The laser ablation apparatus is similar to the one used at Rice University,[9] and is described in detail elsewhere. [10] The modified apparatus used for the present experiments is shown in Fig. 1. Laser beams are directed along the axis of a 56-mm diameter fused quartz tube that rests inside a tube furnace. A small vial of C_{60} powder (99.9% pure, FOMA International) was placed inside the tube near the observation ports, where the graphite target is normally placed for nanotube production. However, during the C_{60} measurements, the target had been removed and its back-flange support was replaced by a Brewster window to allow the laser pulse to escape the furnace without ablating anything inside the tube. The beam was intercepted externally by an aluminum beam block located approximately 1 meter from the end of the tube. See Fig. 1.

The current configuration uses two 10 Hz pulsed lasers (300 mJ/pulse and 5.0 mm in beam diameter), one operating at 532 nm (green), followed 50 ns later by the second one operating at 1064 nm (IR). Light emitted from the irradiated vapor is transferred via an optical fiber to a Spex 270M spectrograph with a gateable ICCD detector. The light is dispersed by a 300-line/mm grating blazed at 500 nm. All the spectra are intensity calibrated using a standard tungsten lamp with NIST traceable calibration. Time averaged spectra are collected with various gate widths and at different delay times after the laser pulse.

Transient spectral data is collected by a photomultiplier tube (PMT) connected to a transient digitizer having a 10 ns channel width. A 1-mm diameter region is focused on the PMT using a lens and pinhole. An IR blocking filter (KG-5) was used for all measurements. In addition, a notch filter (to remove the 532-nm laser line) and an interference filter centered at 510 nm with 10 nm bandpass were used for some measurements to select the $\Delta v=0$ peak in the Swan band emission.

Results and Discussion

A number of sets of transient and spectral measurements of radiation emitted from the laser-irradiated zone of the mixture of argon and C_{60} vapor were made at various conditions of oven temperature and background pressure. The partial pressure of C_{60} is determined by the oven temperature. The quartz tube was evacuated to a pressure of about one Pascal and flushed with argon before maintaining an argon flow of 100 sccm at a pressure of 66.7 kPa. The oven is then heated slowly to 973 K, thus vaporizing some C_{60} from the vial. From a figure in Ref. 11, at 973 K the vapor pressure of C_{60} is estimated to be about 50 Pa and its density is approximately 10^{15} cm^{-3}, assuming the vapor is in equilibrium with the solid phase. Therefore, the maximum concentration of C_{60} is somewhat less than one part per thousand.

Radiation Measurements

A 1-mm diameter zone of laser irradiated C_{60} vapor at the center of the flow tube is imaged (1:1) on the sensitive surface of a photomultiplier tube. The output of the PMT is processed by a Le Croy transient digitizer with 10 ns bin width and recorded using "Catalysis" software. One thousand scans are averaged. A small zero offset is subtracted before the data is plotted and analyzed. Time zero is taken as the laser Q-switch trigger. As seen in Fig. 2 emission from the zone peaks very rapidly, sometimes saturating the

PMT circuitry at the peak. The emission decreases rapidly for about 2 μs, followed by a slower falloff lasting beyond 20 μs. The bumps noted in the early part of the decay are absent with the 510 nm filter which transmits the Δv=0 band of C_2 Swan system. During early times, the C_2 has shows a decay time of about 300 ns (compared to a radiative lifetime of 100 ns for C_2 Swan bands). At the later times beyond 3 μs, the decay time is much longer, on the order of 5 μs. The decay time results are summarized in Table 1. The differences in decay time for the full spectrum (no filter) with temperature are probably real, but it is difficult to say what the trend is. Obviously, at higher temperatures there should be much more C_{60} in the laser path due to its higher vapor pressure. Also, its internal energy is larger, making it somewhat easier to dissociate.

If the decay of C_2 Swan bands is a measure of dissociation from fullerenes then our decay time of 0.5 μs is about four times shorter than the decay time of C_{60} excited with 15 mJ/cm^2 at 193 nm observed by O'Brien, et al.[4] (30 μs). Their condition is quite different from ours, where our fluence is 100 times higher, and the exciting photon energies are 2.8 and 5.5 times lower. Apparently, the net effect in our experiment is greater excitation of C_{60}.

Spectral details of the radiation zone are recorded by collecting emission from a zone of about 5 mm in diameter using the fiber optic assembly located on the other side of the oven (Fig.1). The spectrum is very weak and we used 500-μm input slit width. The resultant emission is similar to that obtained from the graphite target ablation during carbon nanotube production (Ref.1) and mostly contains C_2 swan bands. The spectral features at 355 and 395 nm are from the aluminum plasma from the beam block. Scattered laser radiation at 532 nm is also seen. The dependence of spectral features on the laser wavelength is noted in Fig. 3, which clearly shows the major role of 532 nm laser beam in

the production of C_2 from C_{60}. When only the IR laser (1064 nm) irradiates the C_{60} vapor no Swan band emission is seen. With only the green laser (532 nm) Swan band emission is seen; but with the IR laser following the green by 50 ns the emission is increased about 50%, indicating that IR may contribute to excitation of C_{60} or daughter molecules. Another possibility is that the IR beam contributes to vaporizing particles and freeing up fullerenes to be excited by next pulse of the green laser 100 ms later.

The recorded spectra at different delay times (0.5, 1, 10, 50 μsec) from the laser trigger are shown in Fig. 4. The changes in relative intensity with time seem to indicate increasing vibrational temperatures. Estimates of the temperature were determined from comparisons of normalized measured spectra with calculated spectra at various temperatures. The "best" visual fit yielded temperatures given in Table 2. It should be noted that these temperature estimates assume that the population of vibrational states is in a Boltzmann distribution. Since we did not have the spectral resolution to do a Boltzmann plot we must interpret the temperature loosely. The intensity of the C_2 spectrum seems to decrease by two orders of magnitude within 50 μs. On the other hand, in the transient data of Fig. 2, one can note a decrease of three orders of magnitude. However, the spatial resolution for the transient study is 1 mm; whereas, it is about 5 mm for the fiber optic data collection which probably averages the overall effect in the radiation zone.

At the earliest measured time (500 ns delay) the spectrum has a significant continuum component underlying the C_2 spectrum. It is apparent that the source of the continuum cools very rapidly, or at least its intensity decreased to negligible values. The continuum could be from carbon particles, including possibly fullerenes. To estimate the mean temperature of the particles during the early time of 0.5-1.0 μs we compared

measured spectra and calculated blackbody spectra for several temperatures as shown in Fig. 5. The blackbody temperature that best matched the measurement is 3600 ±200 K, which is higher than the C_2 vibrational temperature of 2000 ±200 K estimated from the Swan bands. Since the intensity decays very rapidly then average temperatures are weighted toward early times. Highly excited fullerene molecules may be at a temperature equivalent to several thousand degrees.[6] According to figure 12 of Reference 6 a characteristic temperature of 3600 K would represent an internal energy of C_{60} of about 30 eV compared to 2.33 eV photon energy of the 532 nm beam.

To estimate the efficiency of the production of C_2^* by laser excitation of C_{60} we can calculate the number of photons emitted per pulse from C_2^*. For the condition at which laser pulsed from both lasers (532 and 1064 nm) are fired, each having an energy of 0.3 J/pulse we can determine the number of photons emitted per unit volume per pulse based on an absolute calibration of the optical systems. The calibration is approximate because it is difficult to account for soot coatings on the surfaces of the quartz tubes. The intensity is measured and the diameter of the laser beams is taken to be equal to the length of the radiating volume L = 5 mm. The power per unit wavelength radiated from the volume is[12]

$$P = \pi E \ / L \qquad (1)$$

where E is the emission coefficient (equal to intensity) in W/cm^2/nm/sr. The number of photons radiated per unit wavelength and volume is

$$P/h\nu = P\lambda/hc = \pi E\lambda/(hcL) \qquad (2)$$

If we integrate this over wavelength and time, we obtain the total number of photons per pulse of about 10^{13} cm^{-3}. This is about two orders of magnitude lower that the maximum number of C_{60} molecules in the volume. Hence, the efficiency of producing C_2^* is at least

1% and probably greater since the number density of C_{60} may be lower than assumed from its vapor pressure. We can compare this with the number of laser photons available for exciting C_{60}. The laser energy per pulse of 0.3 J represents an average fluence F = 1.53 J/cm^2 over the beam diameter. The fluence of 532 nm photons (energy 2.33 eV) is then

$$F_n = F/h\nu = 4 \times 10^{18}\ cm^{-2} \qquad (3)$$

The cross section for excitation σ is assumed[6] from that given for excitation by 5.6 eV (221 nm) photons to be 10^{-16} cm^2. (It could be lower by an order of magnitude for 532 nm excitation. We get the number of excitations collisions per pulse to be $\sigma F_n = 400$ per molecule of C_{60}. There is quite a bit of disagreement about the energy required to eject a C_2 from C_{60}. However, if we assume a value of 11.6 eV[13], plus a mean excitation energy of 3 eV to excite the C_2 to the $d^3\Pi_g$ state, we would require only 6.3 photons of 532 nm light. Even if the energy required to eject a C_2 from C_{60} is as high as the 20 eV proposed in Ref. 4, the required number of photons would be only 10. Therefore, we have an ample number of laser photons to excite C_{60} and its daughters sufficiently to eject C_2 in electronically excited states. A high level of excitation would lead to temperatures at least as high as measured from the continuum radiation at early times. However, the decay time implied by C_2 emission is not consistent with a relaxation of the internal degrees of freedom represented by the blackbody emission which decays faster.

Conclusions

Vapor of the fullerene C_{60} at 793 K was irradiated by two laser pulses operated at a fluence of about 1.5 J/cm^2 per pulse. Measurements were made of the emission from the region to obtain transient decay of wide and narrow spectral bands. Spectra covering about 400 to 675 nm were also measured in the region. The main radiation observed was C_2 Swan bands and briefly a black body continuum. The major findings are:

1. Excitation of C_{60} vapor by laser radiation produces excited C_2 molecules that can be seen in long lasting Swan band emission spectra.
2. The decay of the C_2 Swan band $\Delta v=0$ emission produced by laser irradiation of C_{60} (about 5 μs) is faster than that seen in nanotube production by the laser ablation process (about 12 to 30 μs). However, it is much longer than the radiative decay lifetime of the C_2 $d^3\Pi_g$-state. It is likely that the decay time depends on the total energy absorbed by the fullerene molecules. The greater the energy, the shorter the decay time.
3. Blackbody emission is seen at very early times, but disappears rapidly. The decay time of the early black body spectra is about 300 ns. The blackbody temperature appears to be about 3600 K at about 0.5 μs after the laser pulses.
4. Swan band spectra indicate that the C_2 temperature increases from about 2000 K to about 3500 K from 0.5 μs to 50 μs after the laser pulses.

Acknowledgments

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Figure Captions

Fig. 1 Schematic of experimental configuration for laser irradiation of C_{60} inside the carbon nanotube production setup.

Fig. 2 Transient spectra of irradiated region at 773, 873 and 973 K.

Fig. 3 Comparison of spectra with different lasers. The spectral features at 355 and 395 nm are from aluminum plasma from the beam block. Scattered 532-nm is also seen.

Fig. 4 Spectra acquired at delay times of 0.5, 1, 10, and 50 μs, showing C_2 Swan band peaks at all delay times. Note the increasing background continuum with increasing wavelength suggestive of blackbody-type radiation.

Fig. 5 Spectrum acquired at a delay time of 0.5 μs and a gate width of with blackbody background compared with calculated normalized blackbody spectra at several temperatures.

Table 1 Summary of radiation decay times from laser irradiated C_{60}

Filter	Oven Temp, K	Time Interval, μs	Decay Time, μs	Dominant Radiation	Time Interval, μs	Decay Time, μs	Dominant Radiation
None	500	4.0 to 21.5	4.8	C_2 Swan	0.7 to 1.7	0.303	Black body
None	600	4.0 to 21.5	6.7	C_2 Swan	0.7 to 1.7	0.278	Black body
None	700	5.2 to 21.6	6.4	C_2 Swan	0.56 to 1.86	0.452	Black body
510	700	4.5 to 17.5	4.6	C_2 Swan	0.66 to 2.12	0.296	Black body

Table 2 Estimated temperature of C_2 Swan band radiation at various delay times.

Time, μs	Temperature, K
0.5	2000 ± 200
1.0	3000 ± 400
10	3000 ± 400
50	3500 ± 500

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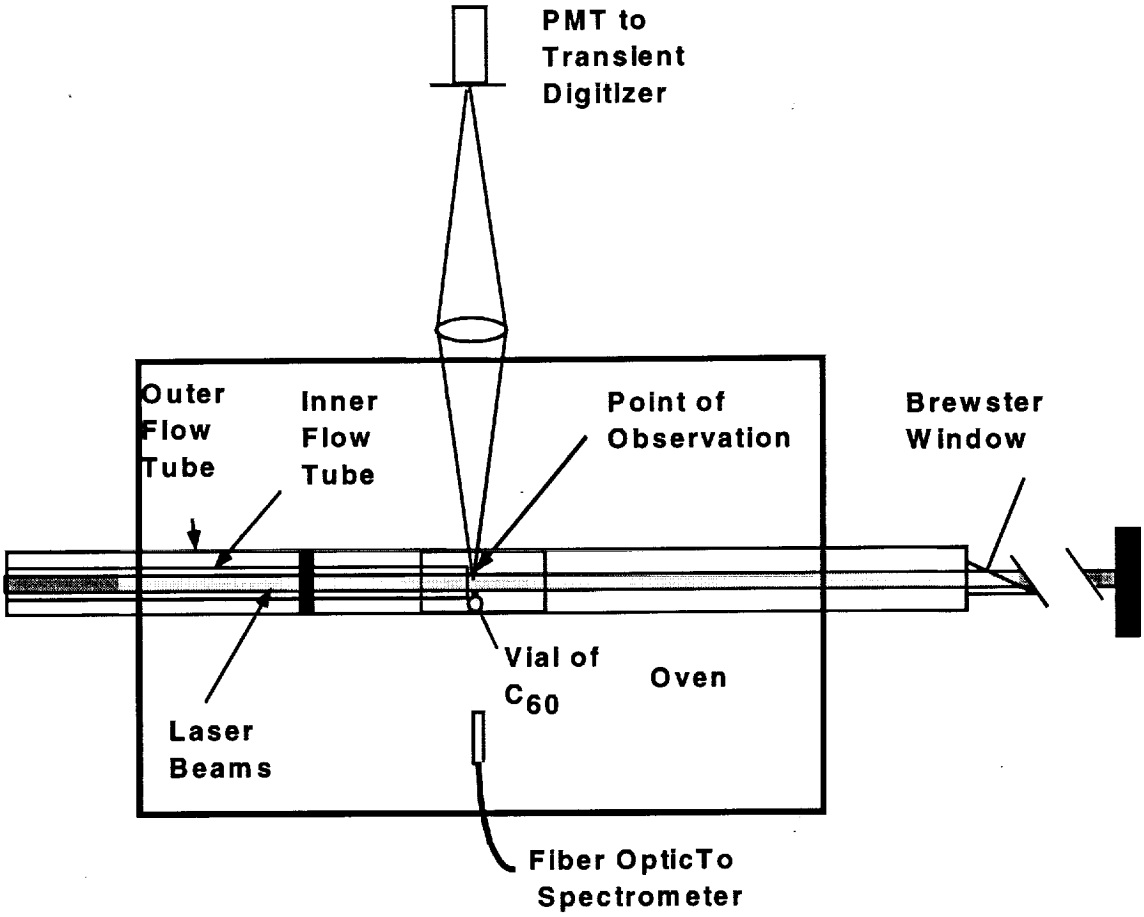
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Figure 1

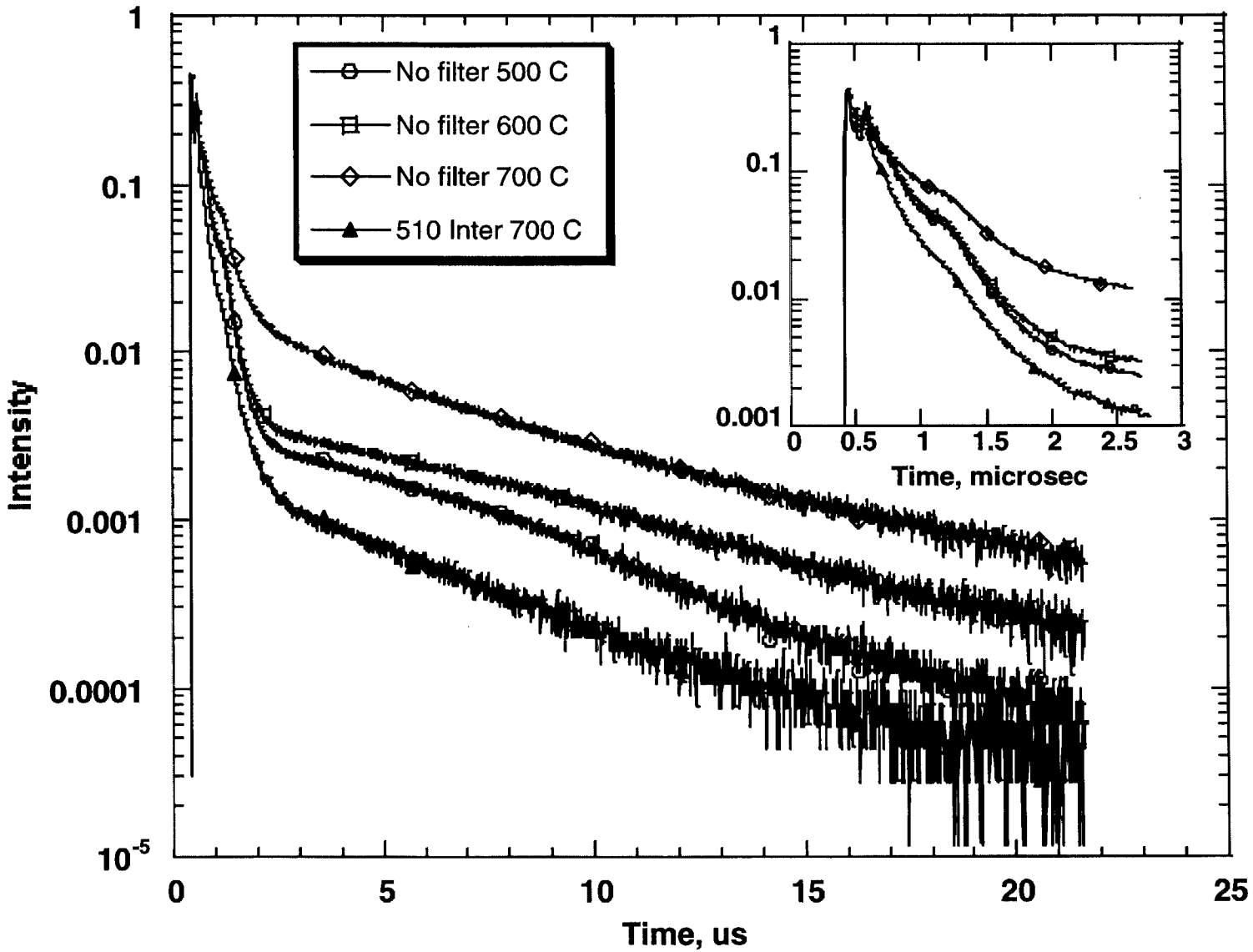
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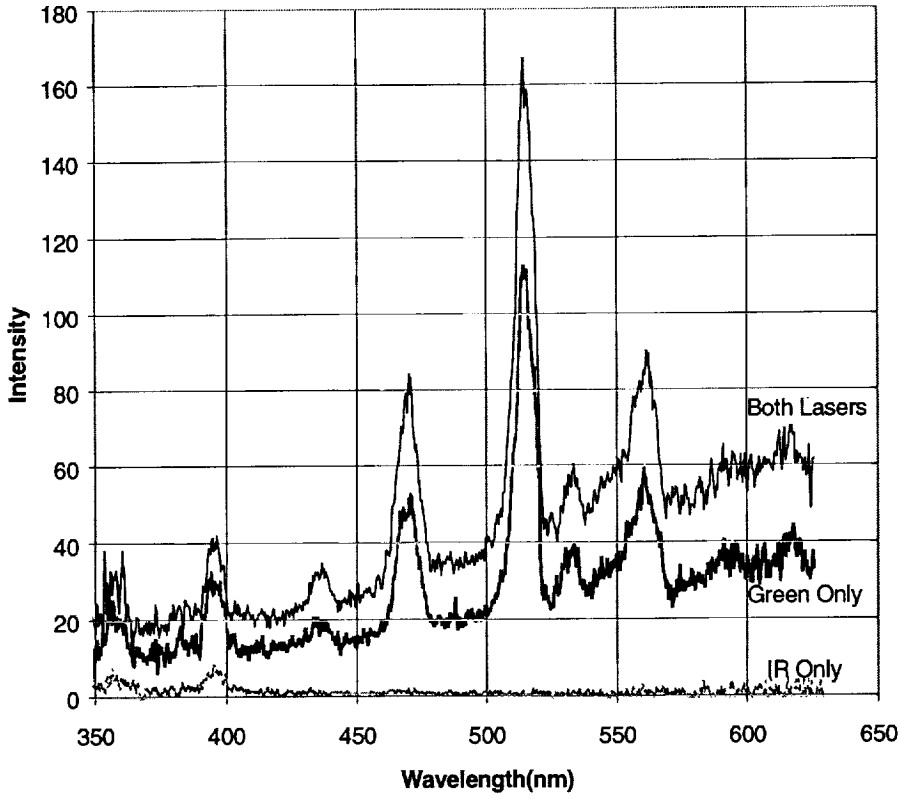
Figure 2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Both Lasers
Green Only
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Figure 4

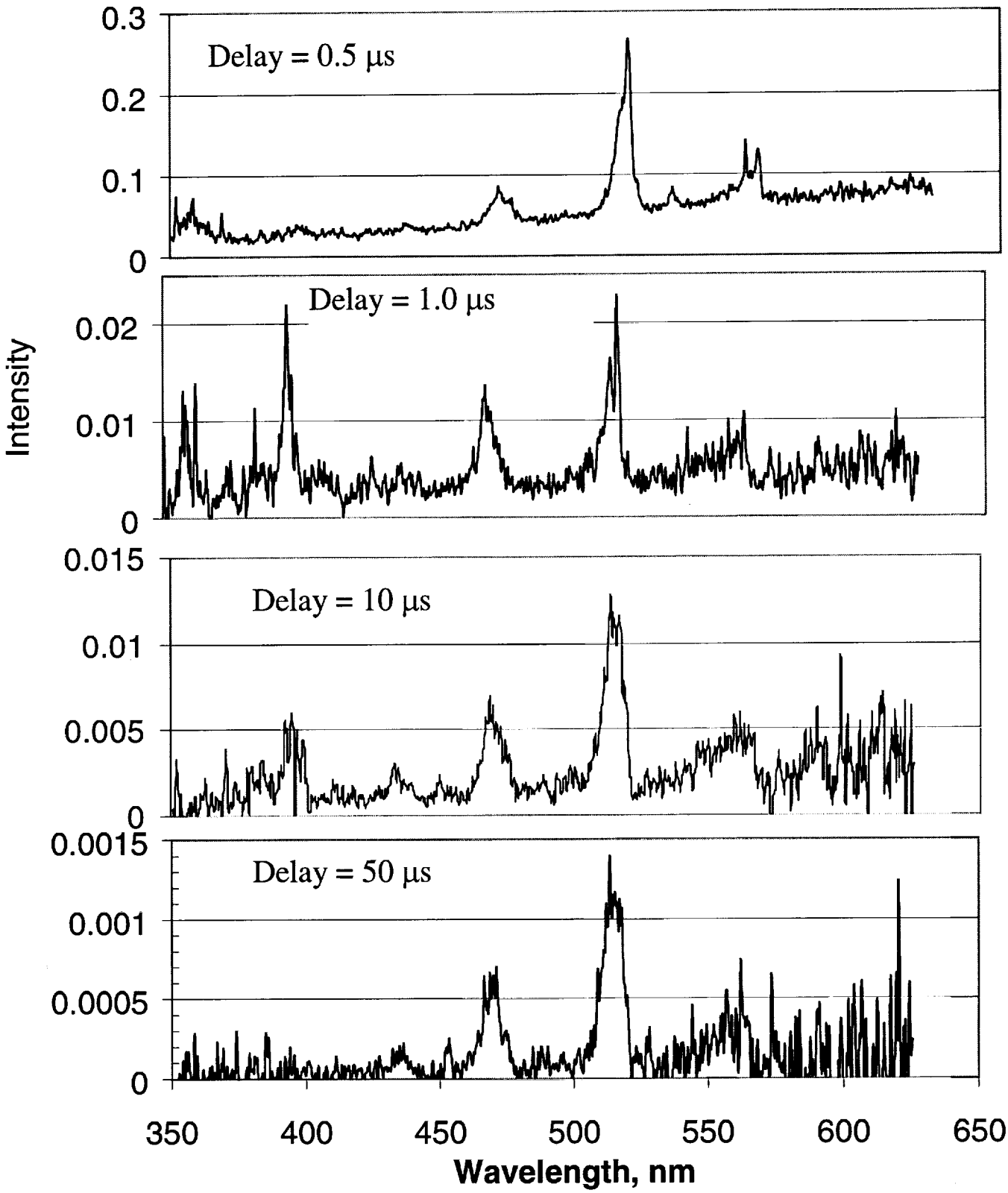
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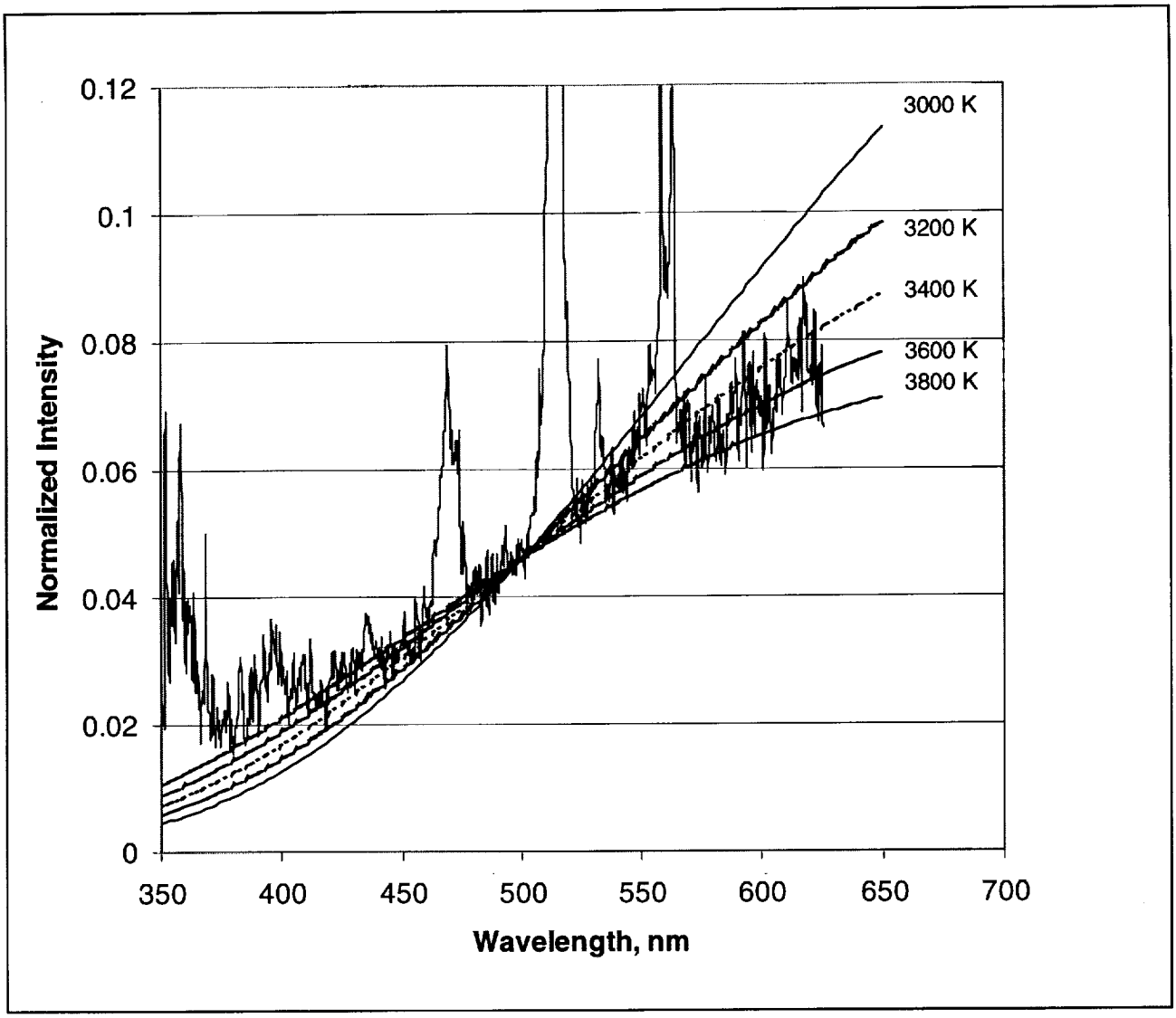
Figure 5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Wavelength, nm
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3200 K
3400 K
3600 K
3800 K

Figure 6