Fluorescence Spectra and Quantum Yields of Buckminsterfullerene (C_{60}) in Room-Temperature Solutions. No Excitation Wavelength Dependence[†]

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Abstract: Noise-eliminated fluorescence and fluorescence excitation spectra of C_{60} in room-temperature hexane and toluene solutions are obtained with the application of principal component analysis. Fluorescence quantum yields of 2.0×10^{-4} and 2.2×10^{-4} are determined for C_{60} in hexane and toluene, respectively. Fluorescence spectra and fluorescence quantum yields are excitation wavelength independent for different bands of the absorption spectrum, indicating no competing decay pathways to the rapid internal conversion relaxation of the upper excited singlet states. The excited- state properties of C_{60} are discussed on the basis of these results, and a comparison is made between experimental and calculated fluorescence radiative rate constants.

Introduction

The development of methods for mass production of C_{60} and other fullerenes has prompted great scientific interest in these molecules.[1-5] Particularly, the photophysical properties of C_{60} and C_{70} have been the subject of several recent publications.[6-14] While the absorption spectra of C_{60} are determined at both room and low temperatures, emission properties of C_{60} are still a matter of debate. Emission spectra have been reported for C_{60} solid at cryogenic temperatures[11] and for C_{60} in a solvent glass at 77 K.[11,12] In room-temperature solutions, weak fluorescence was observed[12,14] and a rather noisy fluorescence spectrum in toluene with excitation at 525 nm has been reported.[14] Under such conditions, the fluorescence quantum yield of C_{60} was estimated to be $\sim 2 \times 10^{-4}$. No quantum yield data are available for C_{60} in room-temperature solutions at other excitation wavelengths. However, in methylcyclohexane glass at 77 K, the fluorescence quantum yield of C_{60} was reported to be excitation wavelength dependent, exhibiting a 5-fold increase from 3.5×10^{-6} to 1.9×10^{-5} for a change of excitation wavelength from 370 to 405 nm.[12] The dependence was rationalized by proposing an unknown photochemical reaction in competition with relaxation of the upper excited states through internal conversion. Obviously, it is interesting to examine fluorescence properties of C_{60} in room-temperature solutions at different excitation wavelengths in order to better understand the proposed-excited state mechanism.

In this paper, we report a systematic fluorescence study of C_{60} in room-temperature hexane and toluene solutions. Noise-eliminated fluorescence and fluorescence excitation spectra of C_{60} are obtained through applications of principal component analysis. It will be shown that fluorescence spectra and quantum yields of C_{60} in the room-temperature solutions are essentially excitation wavelength independent, indicating no competing decay pathways other than internal conversion for the upper excited singlet states.

Experimental Section

Buckminsterfullerene (C_{60}) (Aldrich) was purified through silica gel column chromatography. 9-Cyanoanthracene (Aldrich 99%) was used as a fluorescence standard after repeated recrystallization from ethanol. Hexane and toluene (both from B&J, spectrophotochemistry grade) were used as received because no interference of possible impurities in the wavelength region of interest was found on the basis of absorption and emission spectroscopic measurements of the solvents.

Emission spectra of C_{60} were recorded on a SPEX Fluorolog-2 photon-counting spectrometer equipped with a 450-W Xe lamp and a Hamamatsu R928 photomultiplier tube. The excitation and emission slits were 1.25 and 2.5 mm, respectively, corresponding to spectral resolutions of 5.7 and 9.4 nm. A 495-nm color glass sharp-cut filter (Schott, GG-495) was placed before the emission monochromator to eliminate the overtone of the excitation Raman. A 10-mm square cell was used for fluorescence measurements with solution optical density smaller than 0.1. For fluorescence excitation spectra, a 10-mm square cell was used for the longer wavelength band (>400 nm) with a dilute solution 10^{-4} M (OD < 0.1 at λ_{exc}), and a cell of 2-mm path length was used for the shorter wavelength bands with a more dilute solution 10^{-5} M (OD < 0.5 at λ_{exc}). The 2-mm cell was oriented about 45° with respect to the exciting and the monitored beams to avoid innerfilter effects. Absorption spectra of C_{60} solutions in the concentration range from 10^{-5} to 4×10^{-4} M are essentially identical, indicating no effect from possible C_{60} aggregates.

For the determination of fluorescence quantum yields as a function of excitation wavelength,[15] fluorescence spectra of C_{60} were measured at a series of excitation wavelengths in the ratio mode of the fluorescence spectrometer that automatically corrects exciting light intensities to a great extent (rhodamine-B as quantum counter). The exciting light

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[†] This paper is dedicated to Professor Jack Saltiel on the occasion of his 55th birthday.

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intensities were further corrected using predetermined excitation correction factors. Fluorescence excitation spectra of C_{60} were corrected in a similar fashion.

The fluorescence quantum yields in toluene were also corrected for the difference in solvent index of refraction (n) on the basis of the following equation:[16]

$$\frac{\Phi_F(\text{toluene})}{\Phi_F(\text{hexane})} = \frac{F_A(\text{toluene})}{F_A(\text{hexane})}\frac{n_{\text{toluene}}^2}{n_{\text{hexane}}^2} \tag{1}$$

where F_A is the ratio between the area under the fluorescence spectrum and the optical density at the excitation wavelength.

Absorption spectra of C_{60} were obtained on a computer-controlled Shimadzu UV2101-PC UV-vis spectrophotometer. Data processing based on principal component analysis was accomplished using an IBM-compatible 486 50-MHz personal computer.

Results and Discussion

Principal Component Analysis. As one of the most useful methods in factor analysis,[17-22] principal component analysis can be applied to deduce a noise-eliminated average spectrum from a data matrix consisting of repeatedly measured weak experimental spectra.[23,24]

For a data matrix **D** composed of m experimental spectra as rows and n intensities at n wavelengths as columns, the analysis results in a representation of **D** by an eigenvector matrix **V**,[17]

$$\mathbf{D} = \mathbf{E}\mathbf{V} \tag{2}$$

where **E** is a diagonal matrix consisting of m eigenvalues e_i ($e_i > e_{i+1}$). Only k ($k \leq m$) eigenvectors are significant for a k-component problem, namely that an experimental spectrum D_i in the data matrix can be regenerated linearly by k eigenvectors V_p ($p = 1, k$) within experimental noise limits,

$$D_i = \sum_{p=1}^{k} a_{pi} V_p + R_i \tag{3}$$

where a represents combination coefficients and R_i is a residual vector. In our C_{60} case, $k = 1$, and the noise eliminated spectrum is represented by the first eigenvector which corresponds to the largest eigenvalue. The other eigenvectors consist primarily of spectral noise.[23,24]

Fluorescence and Fluorescence Excitation Spectra. Fluorescence spectra of C_{60} were measured as a function of excitation wavelength in room-temperature hexane and toluene solutions. Because of weak signals (averaging 1500–3000 counts at the fluorescence band maximum), multiple spectra were recorded at each excitation wavelength for noise elimination using principal component analysis. For C_{60} in toluene, 40 fluorescence spectra at $\lambda_{exc} = 320$ nm were obtained to generate a spectral data matrix. Each fluorescence spectrum consisted of 250 points, from 600 to 849 nm with 1-nm increments. Principal component analysis of this 40 × 250 data matrix yielded a set of eigenvalues (the largest three: 0.247, 0.811×10^{-5}, and 0.384×10^{-5}) which are clearly consistent with a one-component system. The noise-eliminated fluorescence spectrum as the first eigenvector corresponding to the largest eigenvalue is shown in Figure 1. Also shown in Figure 1 is the second eigenvector, which consists primarily of noise in the experimental spectra. A similar treatment was performed for a fluorescence spectral data matrix (80 × 250) generated by exciting C_{60} at 520 nm. The noise-eliminated fluorescence spectrum as the first eigenvector from principal component analysis is identical to the spectrum from 320-nm excitation (Figure 1). The fluorescence spectra corrected for nonlinear instrumental response are shown in Figure 2. While the uncorrected spectra are in reasonable agreement with the weak fluorescence band reported earlier,[14] our results are more accurate because of the noise elimination.

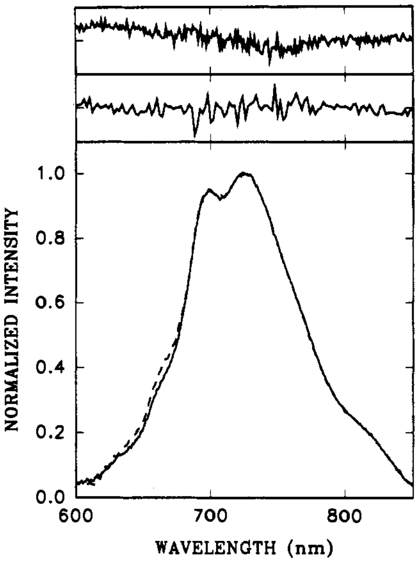

Figure 1. Uncorrected fluorescence spectra of C_{60} in room-temperature toluene determined from principal component analysis noise-elimination method, $\lambda_{exc} = 320$ nm (—) and $\lambda_{exc} = 520$ nm (- - -). The top inserts are spectral noise as represented by the corresponding second eigenvectors.

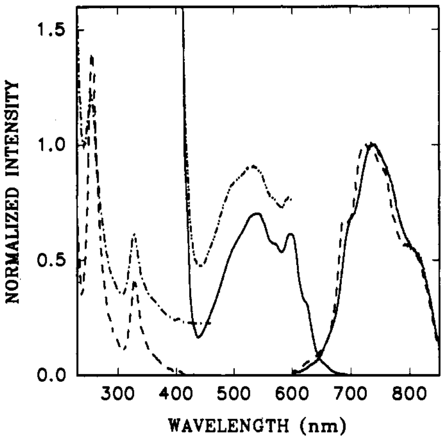

Figure 2. Absorption and fluorescence spectra (in toluene, —; in hexane, - - -) and fluorescence excitation spectra (in toluene, - . . -, in hexane, - . -) of C_{60}. All emission spectra are corrected for nonlinear instrumental response.

Since the absorption and fluorescence spectra of C_{60} and C_{70} are different, the excitation wavelength independence of experimentally determined fluorescence spectra indicates that influence due to possible C_{70} contamination, if any, is negligible.

For C_{60} in hexane, fluorescence spectra were obtained by exciting into the UV absorption band. Principal component analysis of a 40 × 250 spectral data matrix generated with 280-nm excitation yielded the corrected spectrum shown in Figure 2. It is quite similar to the fluorescence spectrum obtained in toluene.

Fluorescence excitation spectra of C_{60} in room-temperature hexane and toluene solutions were determined in a similar fashion through principal component analysis of excitation spectral data

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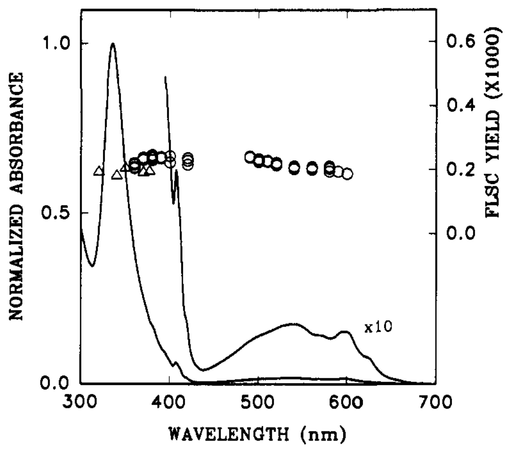

Figure 3. Fluorescence quantum yields of C_{60} in room-temperature toluene (○) and hexane (△) solutions as a function of excitation wavelength. Absorption spectra of C_{60} are also shown for a better illustration of the data.

matrices generated with fluorescence monitored at 720 nm. The corrected excitation spectra (Figure 2) are in excellent agreement with the absorption spectra of C_{60}, including fine structures such as the small peak at 404 nm.

Fluorescence Quantum Yields. Fluorescence quantum yields of C_{60} in room-temperature hexane and toluene solutions were determined as a function of excitation wavelength using a hexane solution of 9-cyanoanthracene ($\Phi_F = 1.0$)[25] as a standard. While there are small variations in observed fluorescence yields for different excitation wavelengths, the changes are within 10% of the average values 2.0×10^{-4} and 2.2×10^{-4} for C_{60} in hexane and toluene, respectively, and the variations reveal no specific trend. Therefore, we conclude that the fluorescence quantum yields of C_{60} in these solutions are excitation wavelength independent not only within individual absorption bands but also for different bands of the absorption spectrum (Figure 3). The determined fluorescence quantum yields are in surprisingly good agreement with an earlier rough estimate for C_{60} in toluene, $\sim 2 \times 10^{-4}$ at $\lambda_{exc} = 525$ nm.[14]

It seems that the excited-state processes of C_{60} in low-temperature glass and in room-temperature solutions are different, assuming that the reported[12] strong excitation wavelength dependences of C_{60} fluorescence yields in methylcyclohexane at 77 K are real. While the much smaller fluorescence yield at a shorter excitation wavelength (370 nm) was rationalized[12] by proposing an unknown photochemical reaction which is fast enough to compete with internal conversion of the higher excited states, such a mechanism can hardly explain the differences between the results in room-temperature solutions and in a 77 K glass. It is unlikely that the proposed photochemical reaction becomes slower in a room-temperature solution. It is also surprising that the fluorescence yields of C_{60} in a low-temperature glassy matrix[12] are smaller than the yields in room-temperature solutions by a factor of 10–50. More experimental investigations for a systematic determination of C_{60} fluorescence quantum yields as a function of excitation wavelength at low temperatures are required in order to further address the issue.

The excitation wavelength dependence of intersystem crossing yield as determined from singlet oxygen generation has also been reported.[8a] However, the difference for the two different excitation wavelengths, 335 and 532 nm, is small (~25%). Despite the fact that our results over the entire absorption spectrum carry uncertainties of as much as 20%, there is no evidence in support of a corresponding dependence of fluorescence quantum yields on excitation wavelength.

Table I. Photophysical Parameters of C_{60} in Room-Temperature Toluene Solution

ref	τ_F (ps)	k_F/n^2 (s^{-1})
6	33^a	2.9×10^6 d
7	650 ± 100^b	1.5×10^5 ^{d}
14	1170 ± 20^c	8.35×10^4 ^{d}
26	$1200^{a,b}$	8.2×10^4 ^{d}
this work (eq 4)		$1.59 \times 10^6/g_e$
this work (with the assumed absorption band)		$7.16 \times 10^5/g_e$

[a] From the decay of singlet transient absorption. [b] From the rise time of triplet transient absorption. [c] From time-correlated single photon counting. [d] Calculated on the basis of our Φ_F value of 2.2×10^{-4} in toluene.

Radiative Rate Constant. Several reported fluorescence lifetime measurements of C_{60} in room temperature solutions using transient absorption[6,7,26] and time-correlated single photon counting[14] methods yielded rather different results (Table I). Based on our fluorescence quantum yield data presented above, fluorescence radiative rate constants from these lifetime results are listed in Table I. They are compared with theoretical values from the Strickler–Berg equation,[27]

$$k_F/n^2 = 2.880 \times 10^{-9} \langle \tilde{\nu}_F^{-3} \rangle_{AV}^{-1} (g_0/g_e) \int (\epsilon/\tilde{\nu}) d\tilde{\nu} \qquad (4)$$

$$\langle \tilde{\nu}_F^{-3} \rangle_{AV}^{-1} = [\int I_F(\tilde{\nu}) d\tilde{\nu}]/[\int \tilde{\nu}^{-3} I_F(\tilde{\nu}) d\tilde{\nu}] \qquad (5)$$

where g represents state degeneracies. For C_{60}, $g_0 = 1$. Since we have determined the fluorescence spectrum of C_{60}, a direct calculation of k_F based on eqs 4 and 5 becomes possible. By using the extinction coefficient of 940 cm^{-1} $(mol/L)^{-1}$ at the first absorption band maximum, determined in a toluene solution, $k_F/n^2 = 1.59 \times 10^6/g_e$ s^{-1} is obtained with the entire first absorption band included in the calculation. Different g_e values have been suggested based on different quantum chemical calculations.[28-30] By adopting a g_e value of 3,[7,14,28] $k_F/n^2 = 5.3 \times 10^5$ s^{-1} is obtained. As listed in Table I, experimentally determined fluorescence radiative rate constants vary widely. Considering that the fluorescence lifetime determined from time-correlated single photon counting[14] is close to several transient absorption results,[7,26] we believe that the 33-ps lifetime reported in ref 6 is probably over-estimated. Therefore, our calculated radiative rate constant is at least several times larger than those determined experimentally (Table I). It has been proposed[7] that the larger calculated rate constant for C_{60} could be due to an over-estimation of the transition probability by including the entire first absorption band, namely that the broad absorption band could be a superposition of more than one transition. However, no attempt has been made to separate these different transition.

The proposal is apparently supported by our spectroscopic results. The fluorescence bandwidth at half maximum (fwhm), 2350 cm^{-1}, is less than half of that (5000 cm^{-1}) of the first absorption band. The difference becomes clear when absorption and fluorescence spectra are plotted on the wavenumber scale (Figure 4). Also shown in Figure 4 is the absorption band for the lowest excited state obtained by assuming a mirror-image relationship between absorption and fluorescence. The assumed band and the structured portion of the observed absorption spectrum agree remarkably well. With the assumed absorption band and $g_e = 3$, $k_F/n^2 = 2.39 \times 10^5$ s^{-1} is obtained, which is in

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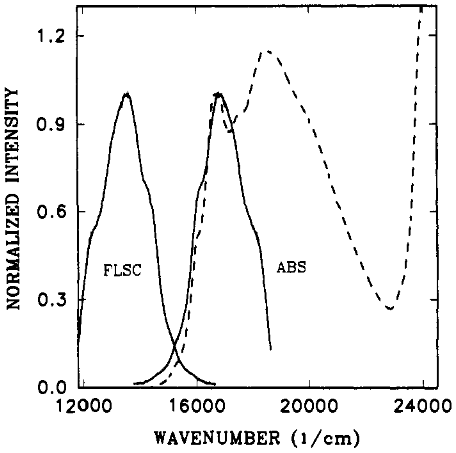

Figure 4. Absorption and corrected fluorescence spectra of C_{60} in room-temperature toluene solution are plotted on the wavenumber scale. Also shown is the assumed first absorption band as the mirror image of the fluorescence spectrum.

better agreement with the experimental radiative rate constants (Table I).

In addition to the uncertainties in fluorescence lifetime data, the accuracy of the Strickler–Berg equation (eq 4) can also be a factor contributing to the remaining disagreement between experimental and calculated radiative rate constants. The equation was originally derived for strongly allowed transitions.[27] Although it has been successfully applied to some weakly allowed systems such as polyenes,[31] application of the equation to accurately predicting the radiative rate constant for weak transitions in the spherical aromatic molecule C_{60} may require further theoretical justification. However, on the basis of the results discussed above, it is probably safe to conclude that for C_{60} in room-temperature toluene the fluorescence lifetime is in the range of 650 ps to 1.2 ns and the fluorescence radiative rate constant is in the range of 1.8×10^5–5.3×10^5 s^{-1}.

Photostability. Contrary to a recent suggestion[32] that C_{60} is unstable to irradiation, the photostability of C_{60} in room-temperature solutions is high at all excitation wavelengths. Absorption and fluorescence spectra obtained with a solution irradiated in the emission spectrometer for up to 10 h (450-W Xe lamp and 1.25-mm slit) are essentially identical to the spectra from a fresh solution. The high photostability is also contrary to the possibility of an efficient photochemical reaction from the upper excited states of C_{60}.

In conclusion, the photophysical parameters reported here indicate that the behavior of the excited singlet states of C_{60} in room-temperature solutions should be considered to be normal, or at least not as complicated as has been perceived. The absorption to the lowest excited singlet state is likely only responsible for the structured portion of the first absorption band. Fluorescence of C_{60} is from the lowest excited singlet state, and there is no competition from other decay pathways, at least in room-temperature solutions, with the internal conversion relaxation of the upper excited singlet states of C_{60}.

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