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On the applicability of the Kasha–Vavilov rule to C₆₀

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Abstract—Via full correction for the instrumental response function, the fluorescence excitation spectrum of C₆₀ in methylcyclohexane between 240 and 580 nm is shown to match the absorption spectrum. This proves that, in contrast to earlier reports, also after UV excitation into higher S_n states, deactivation proceeds virtually completely via the S₁ state, in accordance with the Kasha–Vavilov rule.

INTRODUCTION

DURING recently emerging investigations regarding the photophysical properties of C₆₀ and C₇₀, different research groups have occasionally reported data that cannot be reconciled. A typical example is provided by the scatter in the reported singlet excited state lifetimes for both C₆₀[†] and C₇₀[‡]. The topic we would like to discuss here, however, is whether C₆₀ and C₇₀ undergo significant deactivation avoiding the S₁ state after UV excitation into higher singlet excited states. Recent literature led to some contradiction on this point regarding both C₆₀ and C₇₀. Some groups have reported excitation wavelength-dependent singlet oxygen quantum yields using C₆₀ as a sensitizer [$\Phi(^1\text{O}_2) = 0.76$ (355 nm), $\Phi(^1\text{O}_2) = 0.96$ (532 nm)] [10] and wavelength-dependent triplet quantum yields [$\Phi_T = 0.77$ (337 nm), $\Phi_T \approx 1.0$ (510 nm)] [11] for C₆₀. Wavelength-dependent fluorescence quantum yields [$\Phi_f = 3.8 \times 10^{-6}$ (370 nm), $\Phi_f = 1.9 \times 10^{-5}$ (405 nm)] have also been reported [12]. Other groups, however, reported excitation wavelength-independent singlet state lifetimes (for 265, 355 and 532 nm excitation), $\Phi_T \approx 1$ (for 248, 337 and 351 nm excitation) [7] and $\Phi(^1\text{O}_2) \approx 1$ (340 and 530 nm excitation) for C₆₀ [13].

While it had been reported that C₇₀ also shows an excitation wavelength-dependent fluorescence quantum yield [$\Phi_f = 6 \times 10^{-5}$ (370 nm), $\Phi_f = 1.3 \times 10^{-4}$ (378 nm) and $\Phi_f = 2.2 \times 10^{-4}$ (471 nm)] [12, 14], and thus does not obey Kasha–Vavilov's rule, this has been convincingly contradicted by using time resolved photoacoustic calorimetry ($\Phi_T = 0.97$ for 337, 464 and 510 nm excitation) [11], transient absorption ($\Phi_T \approx 1$ for 248, 337 and 351 nm excitation) [7] and by careful correction of the fluorescence excitation spectrum [9].

In a recent report [11] it was concluded on the basis of the available data for C₆₀ and C₇₀ that: "it appears that C₇₀, in contrast to C₆₀, obeys Kasha's rule and relaxes efficiently to S₁ from higher S_n".

In 1950 Kasha stated that in most aromatic molecules emission occurs from the lowest excited electronic state of a given multiplicity (i.e. from S₁ or T₁), the most well known exception being azulene which shows fluorescence from S₂.

The statement that fluorescence quantum efficiency is independent of the excitation wavelength (for non-ionizing radiation) is known as Vavilov's law, and is also called the Kasha–Vavilov rule [15, 16]. Both empirical rules imply that internal conversion (from S_n to S₁ or from T_n to T₁) is so fast that other processes like fluorescence, intersystem crossing, or phosphorescence cannot compete significantly.

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[†] Values reported for C₆₀ are (in ps): 1200 ± 120 (TA), 33 (TA), <1000 (TA), 650 ± 100 (TA), 1300 ± 200 (TA), 1170 ± 20 (F), 1450 ± 150 (TA) (used techniques are specified—transient absorption: TA, fluorescence: F), and appeared in, respectively: Refs [1], [2], [3], [4], [5], [6], [7].

[‡] Values reported for C₇₀ are (in ps): 115 (TA), 670 ± 67 (TA), 700 ± 50 (TA), 660 ± 20 (F), 627 ± 20 (F), 450 ± 50 (TA) (used techniques are specified—transient absorption: TA, fluorescence: F) and appeared in, respectively: Refs [2], [8], [5], [6], [9], [7].

Although C_{60} displays much weaker fluorescence than C_{70} we now decided to test the Kasha–Vavilov rule for C_{60} , as we did earlier for C_{70} [9], by comparing its absorption spectrum with a carefully corrected excitation spectrum employing an excitation range extending from the visible as deeply as possible into the UV.

EXPERIMENTAL

C_{60}^* was purified using literature procedures [17]. Purity was checked by UV–vis and HPLC (silica, *n*-hexane) and was >99%.

Fluorescence and excitation spectra were recorded on a SPEX Fluorolog 2 instrument equipped with a red sensitive GaAs photomultiplier (RCA C31034, Peltier cooled) of which the spectral response extends to ≤ 900 nm and is known to be quite flat from the UV to about 860 nm. The fluorescence spectrum (see inset of Fig. 1A) was measured on a dilute solution ($[C_{60}] = 3.8 \times 10^{-4}$ M in methylcyclohexane, integration time 10 s) in a 1 cm fused silica cell using 490 nm (excitation-path) and 570 nm (emission-path) cutoff filters. An excitation wavelength of 500 nm was used. Excitation and emission bandwidths of 9 nm were employed and no corrections were applied to the fluorescence spectrum.

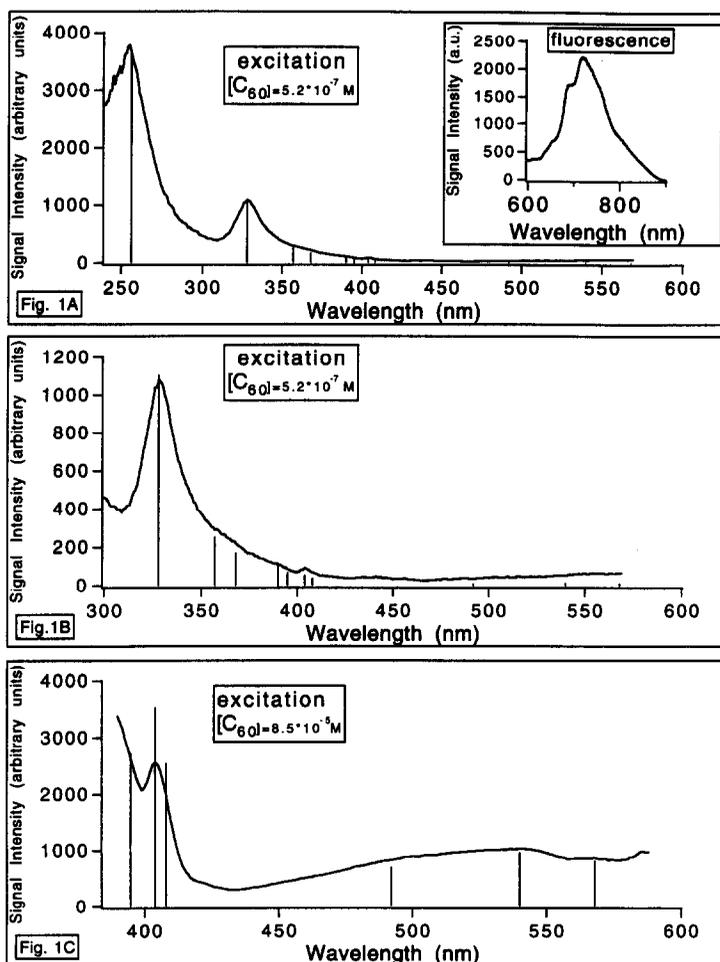


Fig. 1. Three excitation spectra in different wavelength ranges of C_{60} in methylcyclohexane (detection wavelength: 720 nm). Bar graphs show scaled extinction coefficients from the literature indicating that the fluorescence quantum efficiency is independent of wavelength. The inset in Fig. 1A shows the room temperature fluorescence of C_{60} in methylcyclohexane.

* We thank D. Heymann for the generous gift of crude soot, from which the sample used in this study was obtained.

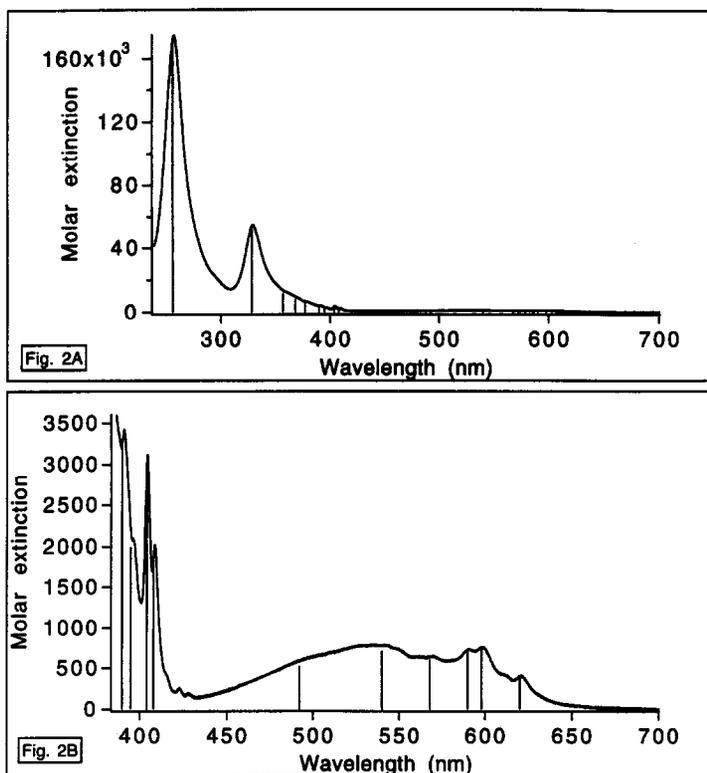


Fig. 2. Absorption spectra of C_{60} in methylcyclohexane. Bar graphs indicate extinction coefficients from the literature.

The fluorescence excitation spectra in methylcyclohexane (see Fig. 1) were measured on solutions sufficiently dilute to maintain an absorbance less than 0.2 over the excitation wavelength range ($[C_{60}] = 5.2 \times 10^{-7}$ M (240–580 nm) and $[C_{60}] = 8.5 \times 10^{-5}$ M (390–580 nm)) in 1 cm fused silica cells with bandwidths of 4.5 nm (excitation-path) and 28.8 nm (emission-path) and an integration time of 10 s. The fluorescence was monitored at 720 nm using a 665 nm cutoff filter. Correction of the excitation spectrum was achieved primarily by ratioing the emission signal and the signal of a Rhodamine B quantum counter (effective range 220–590 nm), which is operated by the light derived from the excitation beam via a quartz-plate beam splitter. Additional correction factors to compensate for the optical path difference between sample and quantum counter were determined by measuring the apparent excitation spectrum of a concentrated Rhodamine B solution (in front face geometry). Fluorescence measurements were conducted at room temperature.

Absorption spectra were recorded with a Cary 3 spectrophotometer (bandwidth 0.5 nm).

RESULTS AND DISCUSSION

Figure 1A shows an excitation spectrum from 240 to 580 nm using a very dilute solution of C_{60} in methylcyclohexane. Bar graphs indicate scaled extinction coefficients from the literature [18]. This spectrum shows that the maxima at 256 and 328 nm are reproduced and thus produce fluorescence with the same quantum efficiency (Φ_f). Figure 1B shows an expansion of the >300 nm region of Fig. 1A. It is clear that shoulders at 357, 368, 376, 390 and 395 nm also show the same Φ_f . At the concentration used ($[C_{60}] = 5.2 \times 10^{-7}$ M) to record excitation spectra 1A and B the absorption in the visible region drops to $A(1 \text{ cm}) < 0.002$ and the fluorescence signal to noise ratio becomes too small for reliable measurements. The noise level in this wavelength range reaches a signal intensity of circa 50 c.p.s. Increasing the concentration to $[C_{60}] = 8.5 \times 10^{-5}$ M allowed us to record the 390–580 nm region (Fig. 1C). From this it is clear that the shoulder at 390 nm shows the same Φ_f as the maxima at 492, 540 and 568 nm.

Unfortunately the sharp absorption maxima at 404 and 408 nm are not well reproduced, which is due to the large bandwidth used (4.5 nm). The inset in Fig. 1A shows the room temperature fluorescence of C₆₀ in methylcyclohexane with maxima at 655, 688 and 720 nm, in agreement with the fluorescence reported in literature [12].

For comparison the characteristic UV-vis absorption of C₆₀ is shown in Fig. 2A and B. The similarity between the excitation and absorption spectra is emphasized by indicating literature extinction coefficients in *n*-hexane [18] as bar graphs in all spectra. Clearly, upon UV excitation fluorescence is produced with an efficiency identical (within an experimental accuracy of ±10%) to that produced by vis excitation.

These results prove that after UV excitation into higher S_n states deactivation proceeds virtually completely via the S₁ state. In contrast to earlier reports [11, 12, 14], we thus find no indication of an upper excited state process. In conclusion our experiments prove unambiguously that C₆₀ obeys the Kasha–Vavilov rule (under our experimental conditions).*

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* Using high laser powers and subsequent multiphoton absorption or photodissociation, deviations from Lambert–Beer's law, impurities and photochemical reactions could cause apparent deviations from this behaviour.