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Fluorescence of C_{60} and C_{70}

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Abstract: The fluorescence of C_{60} and C_{70} in cyclohexane at room temperature have been measured, providing excitation spectra which completely mimic the corresponding absorption spectra of these compounds. The assignment of the $0 \rightarrow 0$ components in the fluorescence spectra is discussed, the conclusion being that both fullerenes must have very small Stokes' shifts. The presence of oxygen, at least at the concentrations corresponding to air-equilibrated cyclohexane (2.1×10^{-3} M), has no significant influence on the quantum yields of these weak fluorescences.

The availability of C_{60} and C_{70} fullerenes in a high degree of purity has prompted many studies of the reactivity and the properties of their electronic excited states.[1] The fluorescence of fullerenes at room temperature is a matter of discussion. Thus, Arbogast *et al.*,[2,3] using solutions of fullerenes freed of oxygen by bubbling argon, did not detect any fluorescence at room temperature in the case of C_{60} (hexane and benzene solutions) and only a weak and broad fluorescence emission between 650 and 725 nm in the case of C_{70} (hexane and benzene solutions; spectra not shown). Since the emission is so weak and since the fluorescence excited spectrum does not completely mimic the absorption spectra, these authors concluded that the possibility that the emission results from an impurity cannot be ruled out. At the same time, Verhoeven *et al.*[4] observed the fluorescence of C_{70} in a 15%–85% mixture of C_{70} and C_{60} when $(2\text{–}4) \times 10^{-5}$ M solutions of this mixture in dichloromethane, benzene, and cyclohexane were excited at 470 nm at room temperature. The excitation spectrum in benzene solution reflects adequately the corresponding absorption spectrum of C_{70} in the same solvent. In a subsequent publication, this same author reported the emission and excitation fluorescence spectra of C_{70} in *n*-hexane.[5] Wang described the formation of exciplexes of the first singlet excited state of C_{70} with *N,N*-diethylaniline in methylcyclohexane at room temperature.[6] Finally, Kim *et al.*[7] observed the fluorescence of C_{60} and C_{70} at room temperature in toluene solutions carefully degassed. These last authors did not describe the corresponding excitation spectra.

In this publication, we present the fluorescence and excitation spectra of both fullerenes at room temperature in air-equilibrated and in degassed cyclohexane solutions. To corroborate the experimental evidence obtained at room temperature, we will also present fluorescence studies of these fullerenes at 77 K in some selected solvents.

Experimental Section

Materials. The samples of C_{60} and C_{70} were purchased from Fluka and were guaranteed to have a purity higher than 97%.[8] Nevertheless, to eliminate possible fluorescent impurities, these samples were chromatographed in an HPLC.[9] According to the chromatogram obtained, the purity was higher than 99% in both cases. Using a semipreparative column, a small quantity of each compound was isolated, and these samples were identical, in all respects, with the original materials. Cyclohexane (CyH) was obtained from Carlo Erba for fluorescence measurements, and methylcyclohexane (MeCy) and carbon disulfide (CS_2) of spectrophotometric grade were obtained from Aldrich; all of them were used without further treatment.

Photophysics. The absorption spectra were obtained with a Cary 5 spectrophotometer using two matched quartz cells with 1-cm optical paths. The emission and excitation spectra at room temperature were recorded for air-equilibrated and for degassed CyH solutions with an Aminco-Bowman Series 2 spectrofluorometer using a R928 photomultiplier tube. The cyclohexane solutions were 1.7×10^{-5} M for C_{60} and 3.7×10^{-5} M for C_{70}, both being excited at 329 nm. The excitation spectra correspond to lower concentrations, about 4×10^{-6} M. To avoid the presence of oxygen in the solutions, they were handled in a grease-free high-vacuum line, where the emission cell could be evacuated to 8×10^{-6} Torr. Degasification of the solutions was carried out by five freeze–degas–thaw cycles at 8×10^{-6} Torr.

The emission spectra at 77 K were obtained with an SLM 48000s spectrofluorometer using a cooled wide-band rf housing for the R928 photomultiplier tube. Samples of C_{60} and C_{70} in MeCy were near the saturation limit and were contained in sealed quartz tubes of Suprasil quality and 2-mm diameter, which were introduced in the low-temperature SLM accessory, modified to keep the samples in a convenient position for emission measurements. The C_{60} solution in CS_2 were nearly 5 times more concentrated than that in MeCy. Solutions of C_{60} and C_{70} in MeCy were excited at 329 nm, and those in CS_2 at 480 nm.

We tried to obtain spectra of the best possible quality, within our experimental limitations, at room temperature and at 77 K. Due to the high stability of our spectrometers, the quality of the spectra was increased by averaging several scans. All the emission spectra were recorded by setting a Schott KV 550 long-pass 50-mm square filter in the emission channel.

Results and Discussion

The absorption spectra in cyclohexane are represented in Figure 1. They are very similar to those in hexane described by Ajie *et*

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[8] We acknowledge the facilities provided by Fluka AG to dispose of high-purity samples.

[9] A Waters HPLC instrument equipped with a pump (Waters M501), an injector (Waters U6K), a UV/visible detector (Waters M486), and a recorder (Waters M746) was used with a Delta-Pak C_{18} 300-Å reversed-phase column and acetonitrile/toluene (1:1, v/v) as eluent [see: Diederich, F.; Whetten, R. L. *Acc. Chem. Res.* **1992**, *25*, 119–126].

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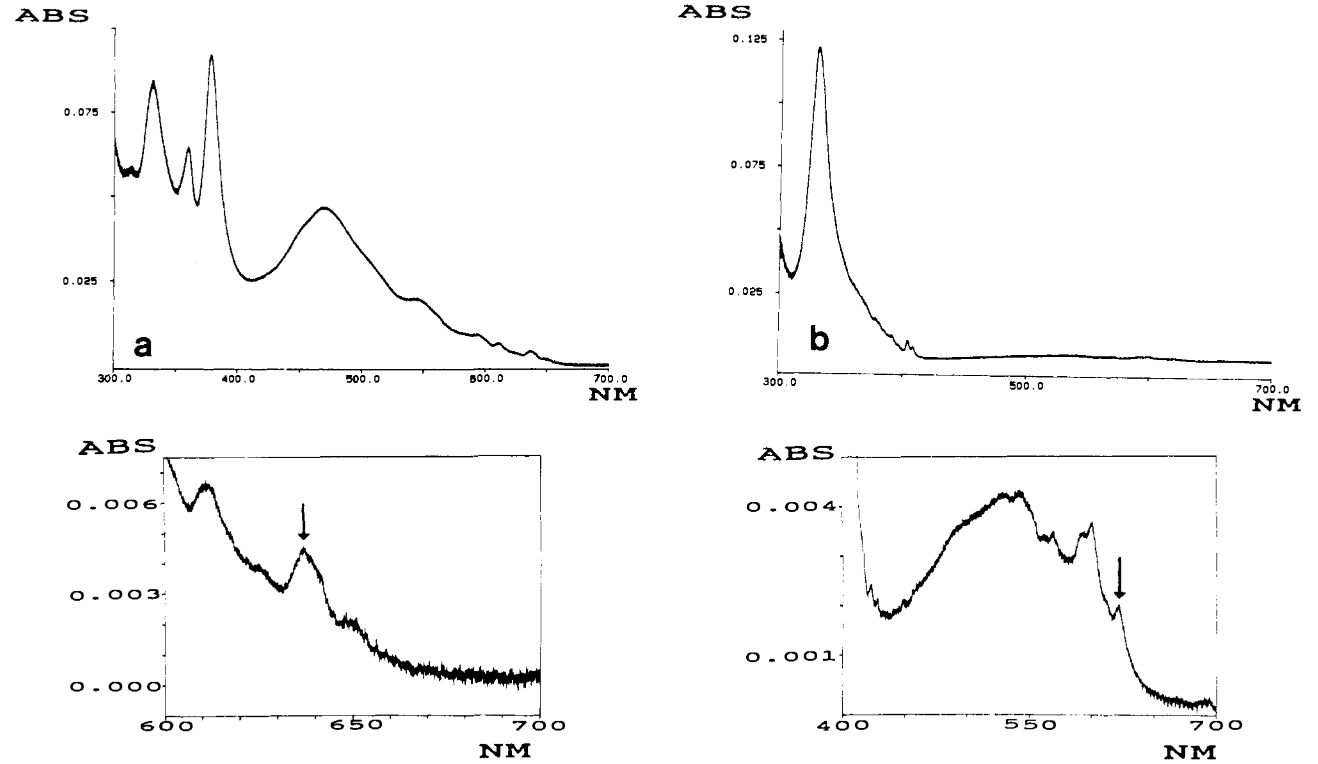

Figure 1. Absorption spectra of fullerenes in cyclohexane at room temperature: (a) C_{70}, (b) C_{60}. For each spectrum, an enlarged view of the red zone is shown framed. A vertical arrow points down to the 0 → 0 component which appears at 637 nm for C_{70} and 622 nm for C_{60}.

Table I. Vibronic Peaks of C_{70} and C_{60} Fluorescence Spectra in "Inert" Solvents

temp	solvent	vibronic peaks, nm	ref
		C_{70}	
77 K	MeCy/3-methylpentane	650, 657, 674, 682, 693, 707, 716	2
77 K	MeCy	651, 658, 676, 683, 694, 708, 717, 728	6
77 K	MeCy	(642), 651, 657, 676, 684, 694, 708, 717	this work
RT	CyH	664, 692, 712	4[a]
RT	CyH	642, 652, 661, 677, 685, 695, 709, 717	this work
		C_{60}	
77 K	MeCy	655, 674, 686, 698, 713, 724, 737, 760	6
77 K	MeCy	654, 674, 685, 698, 713, 724, 736, 764	this work
RT	CyH	(625), (654), (676),[b] 687, (699), (713), 724, 739, (760)	this work

[a] These authors used a large slit (9 nm) for detecting the emission spectra. [b] This shoulder can only be observed using slits no larger than 2 nm. The values in parentheses correspond to shoulders.

al.[10] using samples of high purity (C_{60}, 99.85%; C_{70}, >99%). The excitation and emission spectra of both fullerenes in cyclohexane are shown in Figure 2. The emission spectra are noticeably different from those reported at room temperature in the literature,[2-4] either because solvents (benzene, toluene, ...) which are supposed to strongly interact with fullerenes were used or because the quoted authors were not interested in obtaining well-resolved spectra (wide slits or low average). The emission spectra shown in Figure 2 are the result of three scans recorded with a step of 0.4 nm, a speed of 0.05 nm s^{-1}, and slit widths of 4 and 2 nm for C_{60} and C_{70}, respectively. There is no doubt that these spectra are due to the emission of C_{60} and C_{70} since their excitation spectra show similarities in spectral structure to the corresponding absorption spectra (see Figure 1). The spectra obtained at 77 K in MeCy for C_{60} and C_{70} show the same fluorescence peaks as those reported by Arbogast and Foote[2] for C_{70} in MeCy/3-methylpentane (3:1) matrices and by Wang[6] for C_{60} and C_{70} in MeCy (see Table I).

The fluorescence of C_{70} in cyclohexane at room temperature is unexpectedly structured, to the point that all the vibronic peaks observed in the spectrum of fluorescence at 77 K in MeCy are present. It is logical to assign the peak which appears at 642 nm to the 0 → 0 component; this peak can be seen, as a small shoulder, in the spectrum in MeCy at 77 K (see Figure 3). Consequently, the 0 → 0 component in the absorption spectra of C_{70} cannot be the weak onset at 648 nm[10] but the true first peak at 637 nm (see Figure 1). According to the above results, it is important to notice that C_{70} does not show an appreciable Stokes' shift (only near 100 cm^{-1}).

The fluorescence of C_{60} in cyclohexane at room temperature presents a peak at 687 nm and a large band in the 720-nm zone. Considering that the 0 → 0 component in the absorption spectra appears at 622 nm (see ref 9 and Figure 1), if the 687-nm peak would be assigned to the 0 → 0 component of the fluorescence emission, then the corresponding Stokes' shift would be 1500 cm^{-1}, a value too large for a compound like C_{60} in a solvent like cyclohexane. Moreover, this shift would be inconsistent with the small value obtained for C_{70}. A closer examination of the emission of C_{60} shows a series of shoulders at lower energies than the 687-nm peak (676, 654, and 627 nm; Table I). The shoulders at 676 and 654 nm correspond to two vibronic peaks at 654 and 674 nm recorded for C_{60} in MeCy at 77 K (Table I), but that at 627 nm is not observed at 77 K. The assignment of the shoulder

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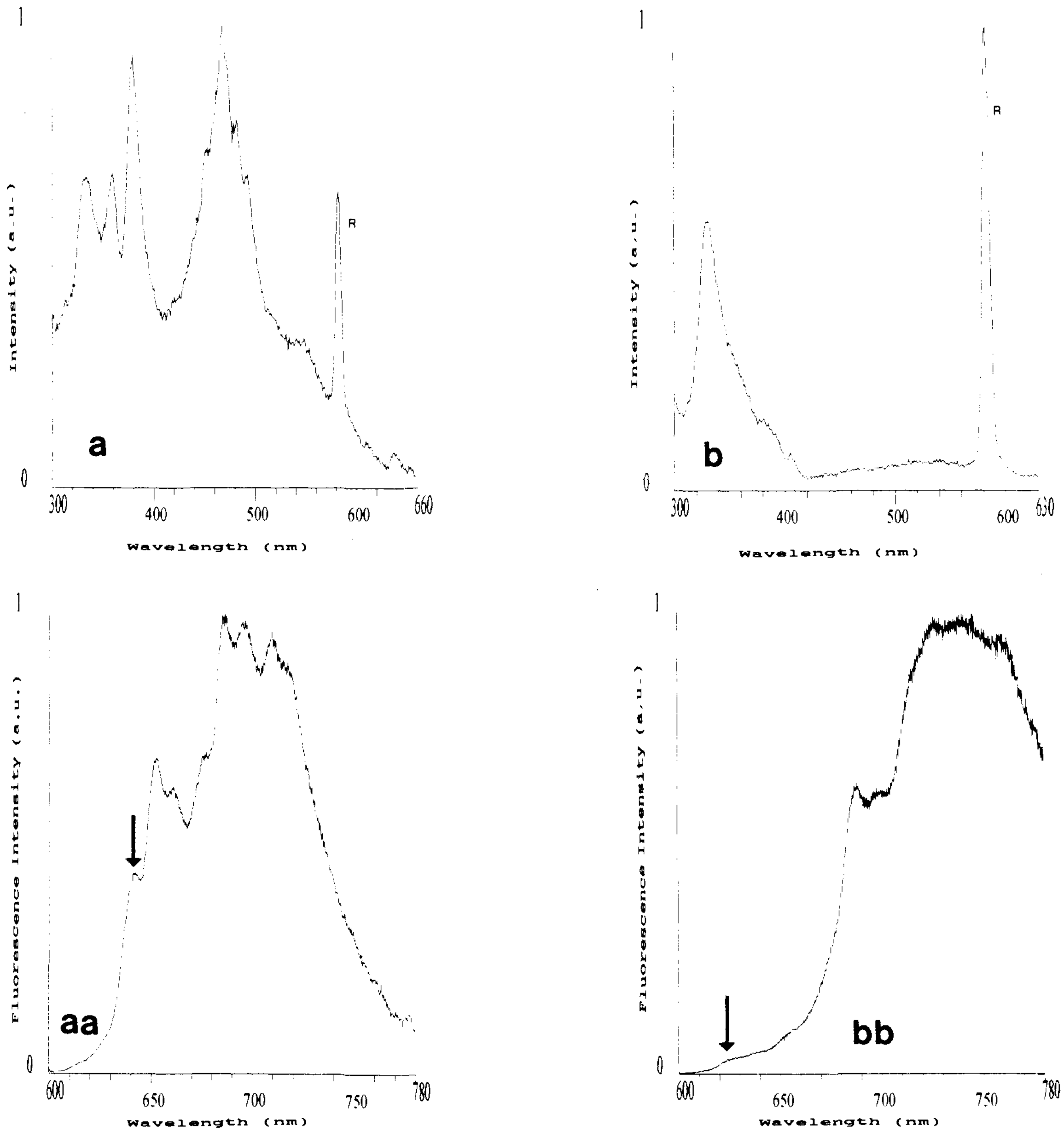

Figure 2. Excitation and emission spectra of fullerenes in cyclohexane at room temperature: (a) C_{70}; (b) C_{60}. In parts a and b (excitation), the peak labeled R corresponds to the Raman peak of the solvent. In parts aa and bb (emission corrected for the sensitivity of the detection system), the vertical arrows point down to the peak tentatively assigned to the 0 → 0 component (see text).

at 654 nm to the 0 → 0 component corresponds to a Stokes' shift (740 cm^{-1}) that is still too large.

These spectra have been reproduced, including the shoulder at 627 nm, with a pure sample of C_{60} provided by Prof. F. Diederich. The fluorescence excitation spectrum monitored at 627 nm completely mimics the spectra monitored at other emission wavelengths. To observe the very weak transition at 627 nm in the spectrum at 77 K, a more concentrated solution of C_{60} should be used. Since the MeCy solution was saturated, we decided to try a carbon disulfide solution because, according to Sivaraman *et al.*,[11] the solubility of C_{60} is 100 times larger in CS_2 than in CyH. The absorption spectrum of C_{60} in CS_2 is very similar to that in CyH: only a very small bathochromic shift is observed; for instance, the 0 → 0 transition changes from 622 nm in CyH to 626 nm in CS_2. In Figure 4, the emission of C_{60} in CS_2 at 77 K is represented: the band in the 627-nm zone is clearly observed. In this solvent, the vibronic structure is less apparent than that in MeCy at the same temperature.

In summary, we propose to assign the shoulder that appears at 627 nm in cyclohexane at room temperature to the 0 → 0 component of fluorescence of C_{60} in cyclohexane. This would correspond to a negligible Stokes' shift. Moreover, our results are consistent with the fact that both C_{60} and C_{70} at room temperature are only weakly fluorescent: we have determined that their quantum yields of fluorescence in cyclohexane are 1×10^{-4} and 3.7×10^{-4}, respectively. Assuming that results obtained in toluene are extrapolable to CyH, then, since in toluene the lifetime of fluorescence of C_{60} is twice the lifetime of C_{70} (1.17,[7] 1.3,[12] and 1.2 ns[13] for C_{60} *versus* 0.66,[7] 0.7,[12] and 0.67 ns[14] for C_{70}), we can conclude that $k^0_F[C_{70}]/k^0_F[C_{60}]$ is approximately 7. An estimation of this ratio using absorption data led to the

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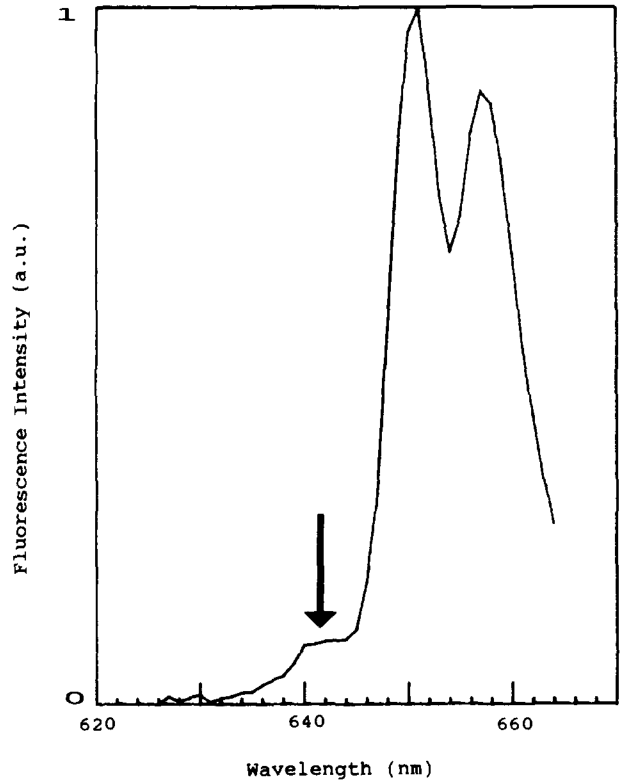

Figure 3. Vibronic components of highest energy in the emission spectrum of C_{70} in cyclohexane. The arrow points down to the tentatively assigned 0 → 0 transition.

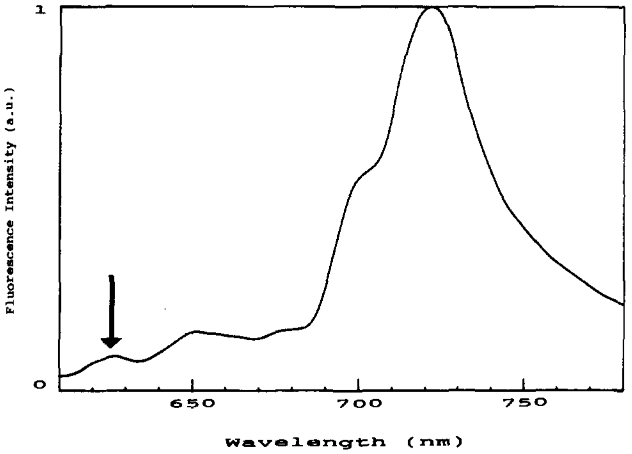

Figure 4. Fluorescence emission spectrum of C_{60} in carbon disulfide at 77 K. The arrow points down to the tentatively assigned 0 → 0 transition.

conclusion, already reached by Hochstrasser *et al.*,[15] that in these compounds, for the calculation of the integrated absorption oscillator strength, it must be assumed that the $S_0 \rightarrow S_1$ transition is simply the 0–0 component. Under these conditions, $k^0_F[C_{70}]/k^0_F[C_{60}] = 4.7(g[C_{70}]/g[C_{60}])$ where g are the degeneracies of the electronic states of fluorescence emission in these fullerenes.

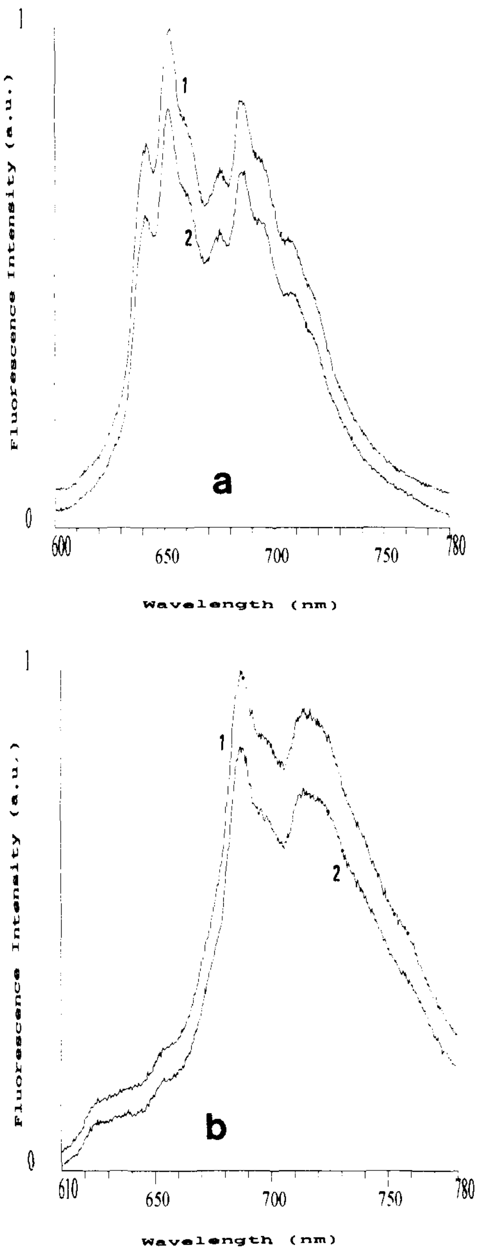

Figure 5. Technical emission spectra of (a) C_{70} and (b) C_{60} in cyclohexane at room temperature. Number 2 corresponds to an air-equilibrated solution, and number 1, to the same solution after degasification at 8×10^{-6} Torr.

Finally, the high efficiency of the production of singlet oxygen by C_{60} has led Arbogast *et al.*[1] to propose that the quantum yield of formation of triplet electronic states in C_{60} is 1.0; nevertheless, the fluorescence of C_{60} can be observed in a nondegassed solution at room temperature. Moreover, as can be seen in Figure 5, the presence of oxygen corresponding to an air-equilibrated solution of C_{60} in cyclohexane, which corresponds to an oxygen concentration of 2.1×10^{-3} M,[16] does not significantly diminish its quantum yield of fluorescence.

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