

Picosecond time-resolved and steady-state studies of the polarization of the fluorescence of C_{60} and C_{70}

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Abstract

From a measurement of the time-resolved and steady-state fluorescence anisotropies of C_{60} and C_{70} in low-temperature organic glasses, it is concluded that the fluorescence of C_{60} is intrinsically unpolarized, and that the emission transition moment of C_{70} is located in the molecular xy plane. Also for C_{70} , but at higher energies, some transitions occur mainly along the z molecular axis.

1. Introduction

The photophysics of C_{60} and C_{70} have been the subject of many studies in the last five years. One interesting aspect of these molecules is their high symmetry, C_{60} being even one of the few known molecules belonging to the icosahedral point group (I_h).

Previously, based on both theoretical arguments and experimental steady-state anisotropy data, we have proposed that the fluorescence of C_{60} is intrinsically unpolarized [1]. Almost simultaneously, other authors defended the opposite view, i.e. that the fluorescence of C_{60} is polarized [2]. These conflicting views prompted us to carry out picosecond time-resolved experiments on the anisotropy of the fluorescence of C_{60} , in order to further test our proposal. It was observed that the anisotropy of the fluorescence of C_{60} is consistently zero, within ex-

perimental error, even in rigid media at low temperature.

From the point of view of symmetry, C_{70} is again an interesting molecule. It also displays some unusual photophysics, namely a strong delayed fluorescence [3]. The molecule is known to belong to the D_{5h} point group, thus having two equivalent axes (x and y). The electronic transition moment for S_1-S_0 may, in principle, occur either along the z -axis or in the xy plane. In the first case, the fundamental anisotropy of C_{70} may take values between 0.4 and -0.2 , depending on the excitation wavelength. In the second case, the fundamental anisotropy of C_{70} may take values only between 0.1 and -0.2 , depending on the excitation wavelength. Cases where 0.1 is the maximum allowed value are known for planar molecules belonging to the D_{nh} point groups ($n \geq 3$), namely benzene [4,5] and triphenylene [6]. In these, however, anisotropy values cannot be dif-

ferent from 0.1, because all singlet–singlet one-photon transitions are in-plane, whereas in C_{70} out-of-plane ones (i.e. along the z -axis) are also possible. The only available theoretical calculation on the polarization of the electronic transitions of C_{70} [7] predicts the electronic transition moment for $S_1 \leftarrow S_0$ to be in the xy plane. Our experimental results support such a conclusion.

2. Experimental

C_{60} (> 99.9%) and C_{70} (> 99%) were obtained from Stefan Kaesdorf (Munich). Methylcyclohexane, toluene and ethanol were of spectroscopic grade and checked for fluorescent impurities. Apart from some experiments carried out in toluene, two solvent mixtures that give good glasses at low temperature were used: methylcyclohexane–toluene (7:2, v/v), denoted MT, and toluene–ethanol (10:1, v/v), denoted TE.

Details of the experimental procedures for the determination of low-temperature steady-state fluorescence polarization spectra were given previously [1,8]. In brief, fluorescence measurements were performed with either an SLM 8000C spectrofluorime-

ter or an Spex F112 one, in both cases in conjunction with an Oxford cryostat with quartz windows.

Time-resolved picosecond fluorescence intensity and anisotropy decays were obtained by the single-photon timing method with laser excitation. The apparatus consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity dumped Coherent 701-2 dye laser, delivering 3–4 ps pulses (with ≈ 40 nJ/pulse) at a frequency of 3.4 MHz. Intensity decay measurements were made by an alternating collection of impulses and decays with the emission polarizer set at the vertical, horizontal and magic angle positions. Impulse was recorded slightly away from excitation wavelength with a scattering suspension. For the decays, a cut-off filter was used, effectively removing all excitation light. Detection was always done by passing the emission through a depolarizer and then through a Jobin–Yvon HR320 monochromator with a grating of 100 lines/mm. The G factor of the system is unity, and for the calculation of the anisotropy identical accumulation times for both vertical and horizontal components were used, until a total of no less than 25000 counts at the maximum channel was obtained for the vertical component. The detector used was a Hamamatsu 2809U-01 mi-

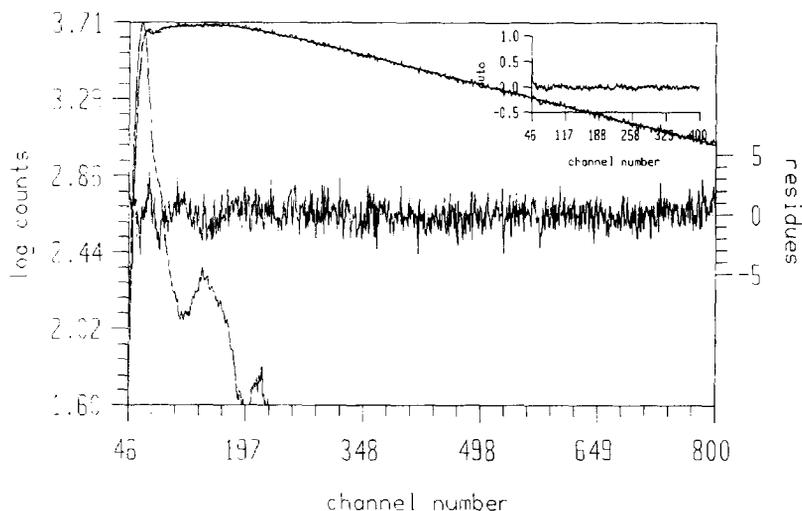


Fig. 1. Fluorescence decay of C_{60} in the MT glass at 110 K. $[C_{60}] = 8 \times 10^{-5}$ M. The excitation and emission wavelengths were 595 and 690 nm. The timescale was 2.77 ps/channel. The Raman scattering can be seen as the first peak in the decay. The decay is well fitted (reduced chi-squared = 1.21) by a sum of three exponentials, one of which, of zero lifetime, accounts for the Raman scattering, the other two having $\tau_1 = 1.09$ ns ($\alpha_1 = 1.25$) and $\tau_2 = 0.10$ ns ($\alpha_2 = -0.25$).

crochannel plate photomultiplier. The instrument response function had an effective FWHM of 35 ps.

Decay data analysis was performed with the Globals Unlimited software package (Laboratory for Fluorescence Dynamics, University of Illinois, Urbana, IL).

3. Results and discussion

3.1. C_{60}

The decay of fluorescence of C_{60} in the MT glass at 110 K is shown in Fig. 1. It is close to single exponential, with a lifetime of 1.1 ns. This value coincides with the lifetimes previously reported by several authors in hydrocarbon solvents [2,9–11], and also measured by us in both methylcyclohexane and toluene at room temperature. It is almost solvent- and temperature-independent, in agreement with an efficient intersystem crossing as the main deactivation path of S_1 [12]. An identical lifetime value was obtained in the TE mixture, both at room temperature and at 100 K. In both solvent mixtures, and owing to the presence of toluene, its intense and polarized Raman bands occurring at ≈ 2900 – 3100 cm^{-1} are clearly seen as a component of zero life-

time. The decay of fluorescence anisotropy (Fig. 2) consists of a fast decay component (less than 1 ps, as obtained from the global analysis of the polarized components), identified as polarized Raman scattering (it is much greater in TE, result not shown, than in MT), followed by a constant plateau, where $r = 0.001 \pm 0.005$ for at least 2.7 ns, i.e. the full time range of the experiment. This result (essentially zero anisotropy) was expected on the basis of previous theoretical reasoning [1], and agrees with the steady-state results obtained in the TE glass at 100 K [1].

Another published report [2] claims, however, that C_{60} has polarized fluorescence. Roy and Doraiswamy [2] only give as experimental evidence the steady-state anisotropy value of 0.006 ± 0.002 recorded in room temperature toluene. Given the low concentration of C_{60} used (10^{-6} M), the weak quantum yield of fluorescence of the compound, the fluidity of the solvent and the possibility of a polarized Raman contribution, and/or of small calibration errors, the reported value is hardly significant. It should also be noted that in the same work the authors report (without details) a depolarized decay of C_{60} in the same solvent and temperature, which they interpret as being an indication that the anisotropy decay occurs on a timescale shorter than their apparatus time resolution. Our results, obtained

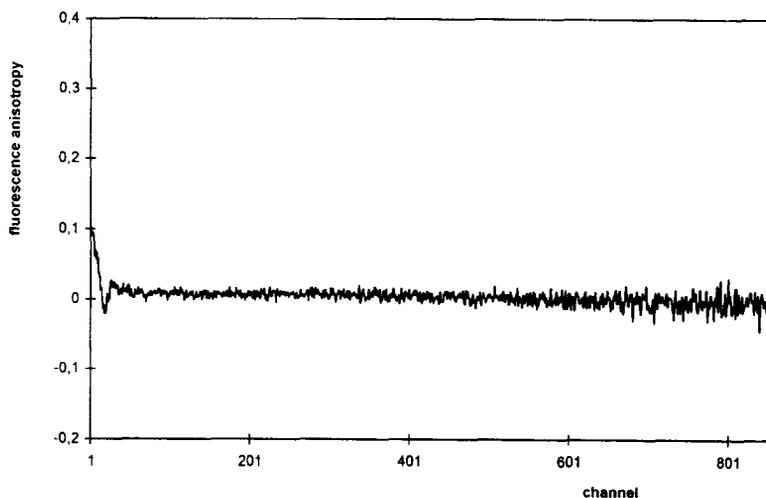


Fig. 2. Experimental fluorescence anisotropy decay of C_{60} in the MT glass at 110 K, computed as $r(t) = (I_{\parallel}(t) - I_{\perp}(t)) / (I_{\parallel}(t) + 2I_{\perp}(t))$, where I_{\parallel} and I_{\perp} are the undeconvoluted polarized components. $[C_{60}] = 8 \times 10^{-5}$ M. The excitation and emission wavelengths were 595 and 690 nm. The timescale was 2.77 ps/channel. It is seen that, after the impulse duration (FWHM = 35 ps, or 13 channels), the anisotropy has a nearly constant value close to zero (0.001 ± 0.005).

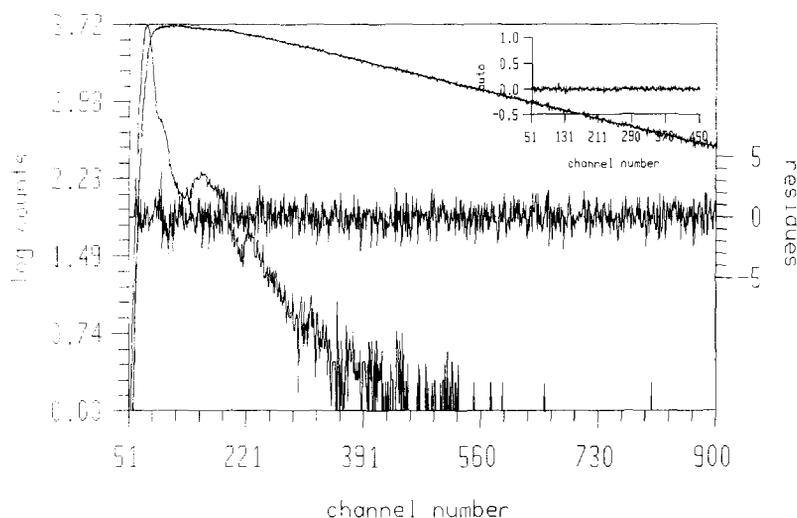


Fig. 3. Fluorescence decay of C_{70} in the MT glass at 110 K. $[C_{70}] = 6 \times 10^{-5}$ M. The excitation and emission wavelengths were 595 and 690 nm. The timescale was 2.77 ps/channel. The decay is well fitted (reduced chi-squared = 1.00) by a sum of two exponentials, $\tau_1 = 0.72$ ns ($\alpha_1 = 1.11$) and $\tau_2 = 0.15$ ns ($\alpha_2 = -0.11$).

in rigid media at low temperature, do not warrant such an interpretation.

3.2. C_{70}

The decay of fluorescence of C_{70} in the MT glass is shown in Fig. 3. The main component, 720 ps, is

close but a little higher than the values reported in the literature for hydrocarbons at room temperature [10,12,13], and also observed by us in the non-degassed solvents (≈ 630 ps). It is almost solvent- and temperature-independent, in agreement with an efficient intersystem crossing as the main deactivation path of S_1 [3,14]. The decay of fluorescence

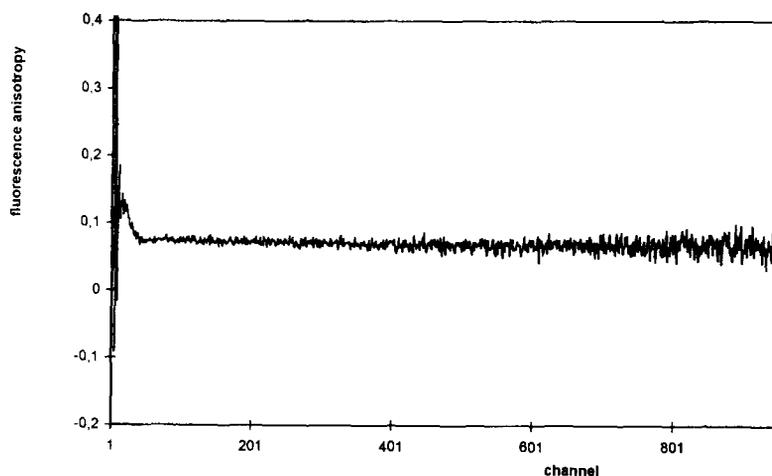


Fig. 4. Experimental fluorescence anisotropy decay of C_{60} in the MT glass at 110 K, computed as $r(t) = (I_{\parallel}(t) - I_{\perp}(t)) / (I_{\parallel}(t) + 2I_{\perp}(t))$, where I_{\parallel} and I_{\perp} are the undeconvoluted polarized components. $[C_{70}] = 6 \times 10^{-5}$ M. The excitation and emission wavelengths were 595 and 690 nm. The timescale was 2.77 ps/channel. It is seen that, after the impulse duration (FWHM = 35 ps, or 13 channels), the anisotropy has a nearly constant value (0.070 ± 0.005).

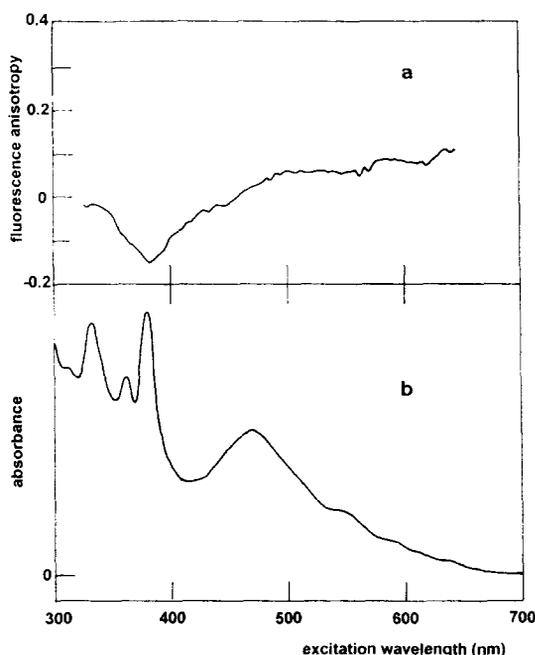


Fig. 5. (a) Steady-state anisotropy of C_{70} in the MT glass at 110 K and (b) absorption spectrum of C_{70} in MT at room temperature, both as a function of the excitation wavelength. $[C_{70}] = 7 \times 10^{-5}$ M. The emission wavelength was 720 nm. The excitation and emission bandwidths were 8 and 32 nm, respectively. A Schott RG695 cut-off filter was employed in the emission. The small oscillations observed in (a) are due to noise.

anisotropy of C_{70} in the MT glass at 110 K is shown in Fig. 4. As for C_{60} , it is constant in the whole time range, but now with a nonzero value: 0.070 ± 0.005 . Given the excitation wavelength used (595 nm) this value is in good agreement with that found from the steady-state excitation polarization spectrum recorded under the same conditions (Fig. 5), 0.08 ± 0.01 . From this spectrum it is also seen that the anisotropy is never above 0.1, even when close to the absorption on-set. It is thus concluded that the first electronic transition of C_{70} is polarized in the xy plane, in agreement with calculations by the tight-binding model [7]. The same set of calculations predicts the 470 nm transition to be z -polarized. As can be seen from Fig. 5, this is not the case, negative values of the anisotropy being attained only for wavelengths

below 460 nm, with a minimum at 380 nm. This minimum, close to -0.2 , coincides with the peak wavelength (378 nm) of a strong absorption band which is therefore z -polarized. Because the tight-binding model does not take into account configuration interaction nor singlet–triplet splitting [15], the observed wavelength mismatch regarding higher excited states is not altogether surprising.

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