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Intrinsically Unpolarized Fluorescence of C_{60}

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The fluorescence spectrum and the fluorescence steady-state anisotropy of C_{60} in a toluene–ethanol 10 : 1 (v/v) mixture have been obtained at room temperature and at 140 K. At 140 K, where molecular rotation is negligible during the excited-state lifetime, essentially zero fluorescence anisotropy was measured, irrespective of the excitation wavelength. It is concluded, in accordance with theoretical expectations, that the fluorescence of C_{60} is intrinsically unpolarized. C_{60} is the first organic molecule to show this behaviour.

Numerous papers have been devoted to the fullerenes in recent years, with special attention to the photophysical properties of C_{60}, see *e.g.* ref. 1 and references therein. The weak fluorescence of this compound has been observed and characterized,[2–7] but no discussion of its polarization has appeared so far. It is the aim of the present work to show that the fluorescence emitted by C_{60} is intrinsically unpolarized, as shown by experiments performed at low temperature in a rigid solvent and as expected from theoretical considerations.

The polarization of the fluorescence emitted at right angles to the excitation direction is conveniently measured by the quantity anisotropy, r,[8]

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \qquad (1)$$

where $I_{\parallel}$ is the intensity of the fluorescence with vertical polarization and $I_{\perp}$ is the intensity of the fluorescence with horizontal polarization, the excitation being made with vertically polarized light.

For a ground-state isotropic distribution of molecules, the fluorescence anisotropy is a direct measure of the angular correlation between the (one-photon) absorption and the emission transition dipoles[9]

$$r = 0.4\,\frac{3\langle\cos^2\alpha\rangle(t) - 1}{2} \qquad (2)$$

where α is the angle between absorption and emission transition dipoles and $\langle\cdots\rangle$ denotes the ensemble average which is in general a function of time.

If rotation and energy migration do not occur within the excited-state lifetime, the anisotropy in response to excitation by a $\delta(t)$ pulse is constant in time and identical to that obtained for steady-state excitation. In that case, both reduce to the fundamental anisotropy r_0,[9]

$$r_0 = 0.4\,\frac{3\langle\cos^2\alpha\rangle - 1}{2} \qquad (3)$$

where $\langle\cdots\rangle$ is now an average over the angular distribution within the molecular framework. Upper and lower bounds for the fundamental anisotropy are 0.4 (collinear absorption and emission) and −0.2 (orthogonal absorption and emission).

If three mutually perpendicular axes are defined with respect to the molecular framework (molecular frame), these three axes are frequently non-equivalent from the symmetry point of view. In that case, the angle α is unique for a given pair of excitation and emission wavelengths; in particular it is zero for excitation at the 0–0 band of S_1, provided the emitting S_1 retains the Franck–Condon geometry. Hence, the fundamental anisotropy takes its maximum value, 0.4, when exciting at the S_1 0–0 band.

However, if two of the axes of the molecular frame are equivalent, x and y say, and if the absorption and the (several equivalent) emission transition moments occur in the xy plane, then the fundamental anisotropy will have as its maximum value only 0.1.[10,11] This was conclusively shown to be the case for benzene (ground-state symmetry point group D_{6h}) and triphenylene (ground-state point group D_{3h}).[10–12] For the even more symmetrical molecules belonging to the tetrahedral, octahedral and icosahedral point groups, where the x, y and z axes are equivalent, the possibility of intrinsically unpolarized fluorescence arises.

An interesting candidate is the C_{60} molecule, which belongs to the icosahedral (I_h) point group, as convincingly shown by its ^{13}C NMR,[13,14] IR absorption[15,16] and vibrational Raman[16] spectra. The discovery of the weak fluorescence of C_{60}[2–5] prompted us to investigate its fundamental polarization. It was found that the fluorescence of C_{60} had negligible polarization when measured at 140 K in a rigid solvent. It is thus concluded that the fluorescence is intrinsically unpolarized, as expected on theoretical grounds. C_{60} is the first organic molecule to display intrinsically unpolarized fluorescence.

Experimental

Experimental procedures for the determination of low-temperature fluorescence polarization spectra have been described previously.[17] Briefly, fluorescence measurements were performed with an SLM 8000 C spectrofluorometer equipped with single-grating monochromators and an Oxford DN1704 cryostat. In order to suppress the second-order excitation, a Schott OG550 cut-off filter ($\lambda > 600$ nm) was used in the emission. Owing to the extremely weak signals, the sample photomultiplier was set close to the maximum value and 32 nm bandpasses were used when measuring the polarized components.† For each wavelength recorded, the integration time was 10 s. Electronic thermal noise was recorded under identical conditions and subtracted from the polarized components. The uncertainty in the anisotropy was estimated to be ±0.005. Solvent fluorescence was not observed under the conditions used. Intensities were measured in the ratio mode, using Rhodamine 101 as the

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† Identical but noisier results were obtained with 16 nm bandpasses.

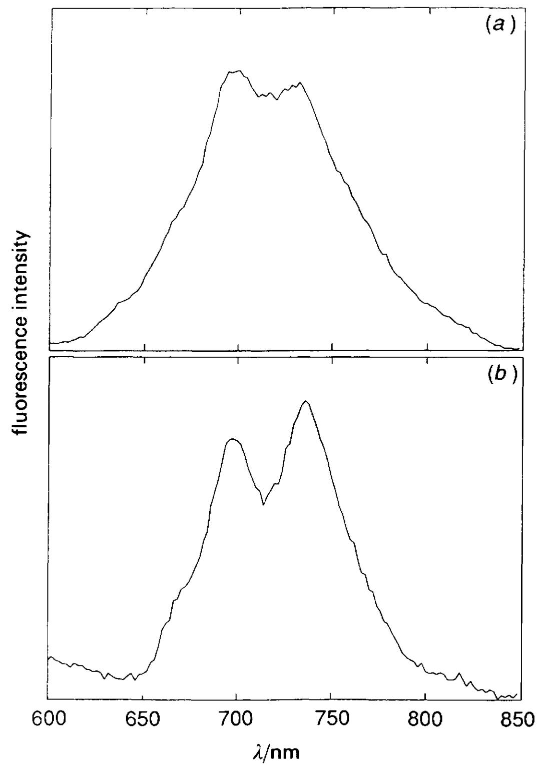

Fig. 1 Fluorescence emission spectrum (16 nm bandpasses) of C_{60} in a toluene–ethanol (10 : 1 v/v) mixture at (*a*) room temperature and (*b*) 140 K. Excitation wavelength = 390 nm.

quantum counter. Solid C_{60} (Kaesdorf, Munich, >99.9%) was dissolved in a toluene (Aldrich, HPLC grade)–ethanol (Merck p.a.) 10 : 1 v/v mixture to yield 2×10^{-4} mol dm^{-3} solutions. The presence of ethanol, while slightly reducing the solubility of C_{60}, was necessary for an optically clear glass to be obtained at 140 K.

Results and Discussion

Fluorescence spectra of C_{60}, recorded at room temperature and at 140 K are shown in Fig. 1: one shoulder at about 663 nm and two peaks at 697 and 736 nm are observed. From a published spectrum[4] obtained in 77 K cyclohexane with better resolution, Negri *et al.*[6] made a detailed assignment of the fluorescence vibronic structure. Apart from the normal narrowing of the vibronic bands upon cooling, the integrated intensity changes negligibly, implying an essentially temperature-independent fluorescence quantum yield, reported to be 2.2×10^{-4} in room-temperature toluene.[7] This is in agreement with the dominant non-radiative path from S_1 being a non-activated intersystem crossing to the T_1 state.[18,19] Previously, excitation dependence of the fluorescence quantum yield of C_{60} had been reported, raising the possibility of the existence of photoprocesses from higher excited states.[4] However, this wavelength dependence was latter shown to be non-existent.[7]

The fluorescence anisotropy at 140 K is shown in Fig. 2 together with the absorption spectrum at room temperature.[‡] As regards the anisotropy, four distinct regions can be defined (A–D in Fig. 2). In regions A (380–410 nm) and C (460–540 nm) the anisotropy is essentially zero, while it is slightly higher than zero in B (410–460 nm) and progressively departs from zero in D (>540 nm). The non-zero value in B is attributed to residual stray light (whose polarization is mainly vertical) which becomes of concern when little exciting light is absorbed, as occurs around the absorption minimum at 438 nm (absorbance =0.05): this has the effect of increasing the amount of stray light and at the same time the fluorescence becomes weaker. In region D, the progressive increase in the anisotropy is due to the combined effect of stray light, increasingly important as the emission wavelength is approached, and polarized Raman scattering by the solvent (*ca.* 3100 cm^{-1}, prominent toluene fundamental), the magnitude of which was found to be comparable to the fluorescence of C_{60}.

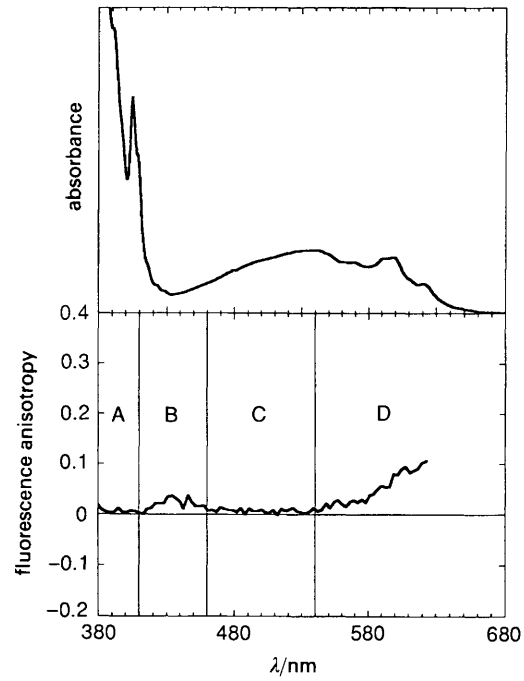

Fig. 2 Absorption spectrum (room temperature) and steady-state fluorescence anisotropy (140 K) of C_{60} in a toluene–ethanol (10 : 1 v/v) mixture. The fluorescence anisotropy is recorded as a function of the excitation wavelength, the emission wavelength being fixed at 740 nm.

Artefacts observed in regions B and D could be reduced by increasing the concentration of the solute; however, 2×10^{-4} mol dm^{-3} is already close to the solubility limit, and higher concentrations were not feasible. The elimination of the artefacts could in principle be achieved by temporal discrimination, as Rayleigh and Raman scattering are essentially instantaneous, while fluorescence is not. It seems, however, that the zero anisotropy repeatedly obtained in the wide and disconnected intervals A and C already provides convincing evidence of the unpolarized character of the fluorescence of C_{60}.

We now address another possible reason for an unpolarized emission, other than the high symmetry of the molecule, *viz.* molecular rotation in the excited state.

At 140 K, the toluene–ethanol mixture used forms a very viscous ($\eta \gg 10^3$ cP, as observed) glass. At lower temperatures, the glass 'cracks' within minutes, but it is stable for several hours at 140 K.

From the Perrin equation,[20] which relates the observed anisotropy r with the rotational correlation time τ_r,

$$r = r_0 \Big/ \left(1 + \frac{\tau}{\tau_r}\right) \qquad (4)$$

where τ is the fluorescence lifetime, one sees that, in order to have $r < 0.005$, as observed, either the fundamental anisot-

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[‡] From the excitation spectrum recorded at 140 K with 2 nm bandwidths, the absorption shows little change when the sample is cooled.

ropy r_0 is close to zero or $\tau/\tau_r \gg 1$. Since the maximum possible value for r_0 is 0.4, it follows that $\tau/\tau_r > 79$, or, with $\tau = 1$ ns,[5,19] $\tau_r < 13$ ps. This value could be observed only for essentially free rotation. Almost free rotation was indeed observed for pure solid C_{60}, but only above the phase-transition temperature, *ca.* 250 K.[21] Immediately below this temperature it is 500 ps[21] and at 100 K it is 50 μs.[22] Factors making free rotation highly unlikely are, besides the low temperature, the strong interaction between toluene and C_{60}[23,24] and the much smaller size of the solvent.[25] Also, the rotational correlation time of C_{60} in a non-viscous solvent (1,1,2,2-tetrachloroethane) at room temperature is 16 ps.[21] The high macroscopic viscosity of the toluene–ethanol mixture at 140 K is thus expected to yield a rotational correlation time of at least hundreds of ns, *i.e.* much higher than the fluorescence lifetime. It is therefore concluded that it is the fundamental anisotropy that is zero, as expected for icosahedral symmetry.

However, the symmetry of the excited state may be different from that of the ground state. It is important to study the effect of a possible symmetry reduction on the polarization.

Analysis of the MCD spectrum of C_{60}[26] shows that the S_1 state belongs to the irreducible representation T_{1g}. The one-photon transition between the ground state (^1A_g) and the orbitally triple degenerate S_1 state is symmetry-forbidden.[1,6] Accordingly, the radiative lifetime computed from the absorption is quite high, *ca.* 1 μs.[7,27] The radiative lifetime obtained from combined fluorescence lifetime and fluorescence quantum yield measurements is of the same order of magnitude,[5] indicating that no significant symmetry reduction occurs in the emitting S_1 state. However, since it is orbitally degenerate in icosahedral symmetry, it must undergo some molecular framework distortion, according to the Jahn–Teller theorem.[28] The question then arises as to whether the instability of the I_h symmetry in the excited state will lead to an effective symmetry reduction (static Jahn–Teller effect) or merely to a dynamic equilibrium between the distorted configurations (dynamic Jahn–Teller effect), thus preserving the initial (icosahedral) symmetry.[28] In view of the large size of the molecule, the excitation of a single electron from S_0 to S_1 is not expected to cause an important modification of the potential-energy surface, in agreement with quantum-chemical calculations showing little activity of Jahn–Teller-active vibrational modes.[6] A weak, dynamic Jahn–Teller effect is therefore expected. EPR studies of the triplet T_1 ($^3T_{2g}$)[29,30] give evidence for a dynamic effect for that state. This effect is equivalent to a pseudo-rotation, owing to the interconversion of the degenerate Jahn–Teller conformers.[29] The rate of interconversion is temperature dependent, but interconversion is still operative at 8 K, albeit slow, as measured by Closs *et al.*[29] Terazima *et al.*, on the other hand, reported static distortions at 3 K, but possibly dynamic ones at 77 K.[30] From the observed anisotropy of the time-resolved EPR signal, it was also proposed that the precursor S_1 state (from which the T_1 sublevels are populated by intersystem crossing) was also in a distorted symmetry.[30]

The existence of Jahn–Teller distortion in the exciting state, even if it reduces the symmetry from the initial I_h, does not change the unpolarized nature of the fluorescence, at least in isotropic media, where distortion is equally likely along any three orthogonal axes. While each excited molecule may or may not still belong to I_h, depending on whether the effect is dynamic or static, the macroscopic ensemble will still have unpolarized fluorescence, because of the original ground-state I_h symmetry.

It is therefore concluded that the fluorescence of C_{60} is intrinsically unpolarized, owing to the high symmetry of the ground state.

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