13 June 1997

ELSEVIER

Chemical Physics Letters 271 (1997) 361–366

CHEMICAL
PHYSICS
LETTERS

A study of thermally activated delayed fluorescence in C_{60}

Filipa A. Salazar, Aleksandre Fedorov, Mário N. Berberan-Santos

Centro de Química-Física Molecular, Instituto Superior Técnico, 1096 Lisbon Codex, Portugal

Received 14 March 1997; in final form 15 April 1997

Abstract

The existence of thermally activated delayed fluorescence in C_{60} is demonstrated by the study of the temperature dependence (291–353 K) of the fluorescence intensity of C_{60} degassed solutions. The determined singlet–triplet energy gap, 35 ± 2 kJ/mol, agrees with the value calculated from previously reported fluorescence and low temperature phosphorescence spectra for this molecule (35 kJ/mol). The estimated quantum yield of triplet formation, 0.8 ± 0.1, agrees with previous determinations. The fluorescence lifetime of C_{60}, also measured, $\tau = 1.1$ ns, does not change appreciably with excitation wavelength, degassing nor with temperature, in the range 243–343 K. © 1997 Elsevier Science B.V.

1. Introduction

Thermally activated delayed fluorescence (TDF) [1], occurs whenever, after $S_n \leftarrow S_0$ molecular photoexcitation, there is an intersystem crossing to the triplet manifold ($S_1 \rightarrow T_1$), followed by a second intersystem crossing back to the singlet manifold ($S_1 \leftarrow T_1$), fluorescence emission ensuing (Scheme 1).

TDF is significant only if the two following conditions are met [2]: (i) reasonably high probability of $S_1 \rightarrow T_1$ intersystem crossing, i.e., high quantum yield of triplet formation Φ_T, and, (ii) reasonably high probability of subsequent $S_1 \leftarrow T_1$ back intersystem crossing, i.e., high quantum yield of singlet formation, Φ_S. In fact, the steady-state intensities ratio of delayed fluorescence (DF) to prompt fluorescence (PF) is given by [2]

$$\frac{I_{DF}}{I_{PF}} = \frac{\Phi_{DF}}{\Phi_{PF}} = \frac{1}{1/\Phi_S \Phi_T - 1} . \qquad (1)$$

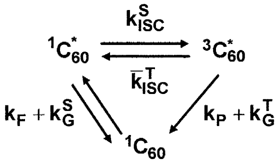
From the theory of nonradiative transitions, it is known that high values of k_{ISC}^{S} are favoured by a small ΔE_{ST}(S_1–T_1 gap). The same holds for k_{ISC}^{T}, approximately given by [1,3]

$$k_{ISC}^{T} = \bar{k}_{ISC}^{T} \exp\left(-\frac{\Delta E_{ST}}{RT} \right), \qquad (2)$$

where $\bar{k}_{ISC}^{T}$ is the average rate constant for the adiabatic $S_1 \leftarrow T_1$ intersystem crossing, and the exponential factor is the fraction of triplets whose total internal energy (electronic + vibrational) is equal or larger than the electronic energy of S_1. TDF is therefore only possible for molecules with small ΔE_{ST} and even then at not too low temperatures.

Although known for many years [1] (and references therein), the phenomenon of TDF remains rare, with a few unambiguous observations in some dyes [1], aromatic ketones [4], aromatic thiones [5], aromatic hydrocarbons [6–9], and, more recently, in the fullerene C_{70} [2]. In most of the cases studied, including the classic one, eosin [1], it is exceedingly weak, in the sense that $\Phi_{DF} \ll \Phi_{PF}$. We have recently observed strong TDF ($\Phi_{DF} \gg \Phi_{PF}$) in the fullerene C_{70} [2], for which Φ_{DF}/Φ_{PF} can in principle be as high as 167 in the high temperature limit

PII S0009-2614(97)00469-7



Scheme 1.

(the maximum value measured was 50, at 70°C). The same study enabled the revision of the published values of ΔE_{ST} and of Φ_T, the last one obtained from a new kinetic analysis.

The known photophysical properties of C_{60}, namely the quantum yield of triplet formation close to one [10–13], the small S_1–T_1 gap [10,14,15] and the relatively long intrinsic phosphorescence lifetime [12], although not as favourable as in C_{70}, should also predispose C_{60} for TDF. However, and apart from the expected weaker TDF, there are three additional experimental difficulties with the study of C_{60}: (i) The weak fluorescence intensity (2 to 3 times lower than that of C_{70}, already weak); (ii) The low solubility in most solvents [16,17] (iii) The absence of detectable phosphorescence in hydrocarbon solvents for temperatures higher than a few kelvin [15,18–20]. This last fact precludes the use of the Parker plot [1], the only steady-state method of analysis left being that based on the dependence of the total fluorescence intensity with temperature [2].

In this work, we report the observation of TDF in C_{60} ($\Phi_{DF} \approx \Phi_{PF}$), and give values of ΔE_{ST}, Φ_T and $\bar{k}_{ISC}^{T}$, obtained from the kinetic analysis previously developed [2]. The value of ΔE_{ST} found, 35 ± 2 kJ/mol, is compatible with that calculated from previously reported fluorescence [18,19,21–24] and low temperature phosphorescence spectra [18] for this molecule, 35 kJ/mol. The value of Φ_T found, 0.8 ± 0.1, is in reasonable agreement with previous determinations.

2. Experimental

C_{60} ($> 99.9\%$) was purchased from Stefan Kaesdorf (Munich). USP light oil, a mixture of long-chain alkanes of moderate viscosity (31 cP at 20°C, 13 cP at 40°C, 4 cP at 80°C), was passed through an activated silica column to remove fluorescent impurities. Purity of both materials was controlled by UV–VIS and luminescence spectroscopies. Taking advantage of the high boiling point of the solvent, solutions of C_{60} (ca. 10^{-5} M) were degassed at room temperature with a turbomolecular pump, under vigorous stirring (final pressure: ca. 3×10^{-8} atm), and the respective cells sealed afterwards. Luminescence spectra were obtained in a Spex Fluorolog F112A fluorimeter. Excitation wavelength was usually 330 nm. A UG-11-S bandpass filter and an LG-625-S cut-off filter were used in the excitation and emission, respectively. Temperature was controlled to within ± 0.5°C. At each temperature, fluorescence intensities were measured in the presence (I_{PF}) and in the absence ($I_{PF} + I_{DF}$) of oxygen. Time-resolved picosecond fluorescence intensity decays were obtained by the single-photon timing method with laser excitation. The set-up consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity dumped Coherent 701-2 dye (rhodamine 6G) laser, delivering 3–4 ps pulses (with ca. 40 nJ/pulse) at a frequency of 3.4 MHz. Intensity decay measurements were made by alternated collection of impulse and decays with the emission polarizer set at the magic angle position. 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. Usually no less than 5000 counts were accumulated at the maximum channel. A timescale of 2.76 ps/channel was used. The detector employed was a Hamamatsu 2809U-01 microchannel 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, USA).

3. Results and discussion

3.1. Fluorescence spectrum and fluorescence decay

Fluorescence spectra of degassed solution of C_{60} in USP light oil, taken at different temperatures, are shown in Fig. 13. The observed variation is attributable to the increasing contribution of delayed fluorescence as the temperature increases, as observed for C_{70} [2]. The effect is reversible, i.e., an equivalent intensity decrease is observed upon cooling of the heated samples.

The fluorescence decay of C_{60} in the same solvent, as a function of temperature (243, 293, 318, and 343 K), was measured for both aerated and degassed solutions. The decay at 293 K of an aerated solution is shown in Fig. 2.

A single exponential decay is observed, with a lifetime of 1.1 ns. This value is identical to the previously reported lifetime for C_{60} obtained with 595 nm excitation [25], and agrees with literature values [26,27]. Within experimental error, the lifetimes were also constant for both aerated and degassed solutions in the whole temperature range (243–343 K). The insensitivity towards oxygen can be explained on the basis of the combined effect of the high viscosity of the solvent and of the short lifetime of C_{60}. From a simple Stern–Volmer equation, assuming a diffusion-controlled quenching and an oxygen concentration similar to dodecane (2×10^{-3} M) one obtains for the aerated solution at the highest temperature (343 K) a quenching rate constant $k_q \cong 3 \times 10^9$ $M^{-1}\,s^{-1}$, hence $1 \geqslant \tau_0/\tau \geqslant 0.993$, and the lifetime is therefore practically insensitive to oxygen.

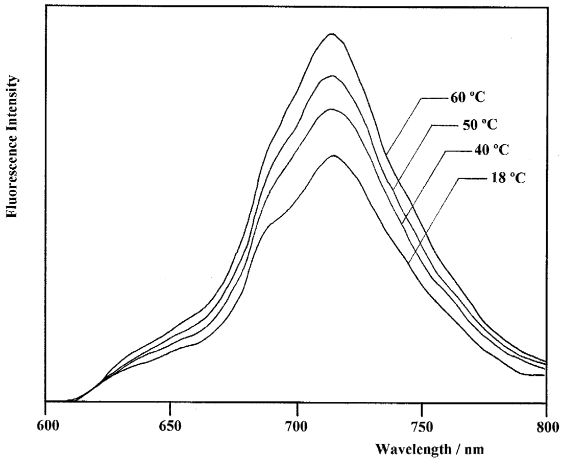


Fig. 1. Fluorescence spectrum of a degassed solution of C_{60} in USP light oil at 18, 40, 50 and 60°C. $[C_{60}] = 1.2 \times 10^{-5}$ M. The intensity of non-degassed solutions is independent of temperature, and is entirely due to prompt fluorescence. The rise with temperature observed in the degassed solution results from the increasing contribution of delayed fluorescence to the total intensity. Excitation and emission slits were 18 and 4.5 nm, respectively.

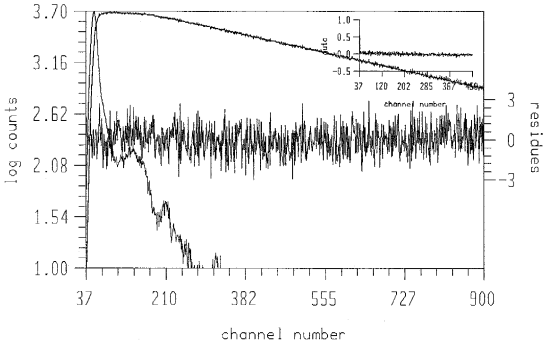


Fig. 2. Fluorescence decay of C_{60} in USP light oil at room temperature. $[C_{60}] = 1.2 \times 10^{-5}$ M. Excitation and emission wavelengths were 330 and 695 nm. The time scale was 2.76 ps/channel. The decay is well fitted (reduced chi-squared = 1.07, random residuals and negligible autocorrelation) by a single exponential, $\tau = 1.1$ ns.

The insensitivity towards temperature, already observed in the temperature range 100–293 K [25], is in agreement with an efficient and non-activated intersystem crossing as the dominant decay path of S_1 [10].

3.2. Analysis of delayed thermal fluorescence kinetics

The standard method of analysis of the delayed thermal fluorescence problem, due to Parker [1], is to measure the steady-state delayed fluorescence (DF) and the steady-state phosphorescence (P) intensities, as a function of temperature, and then to determine ΔE_{ST} from a plot of $\ln(I_{DF}/I_P)$ vs. $1/T$. In the present case such an approach is unfortunately not feasible owing to both the low solubility and the extreme weakness of the phosphorescence of C_{60} in hydrocarbons (recorded up to now only for relatively concentrated solutions at 1.2 K [18]).

An alternative approach is however possible, and ΔE_{ST} can in principle be obtained from the temperature dependence of the ratio I_{DF}/I_{PF}, because Eq. (1) can be rewritten as [2],

$$\ln\left[\frac{I_{PF}}{I_{DF}} - \left(\frac{1}{\Phi_T} - 1\right)\right] = \ln\left(\frac{k_P + k_G^T}{\bar{k}_{ISC}^T \Phi_T}\right) + \frac{\Delta E_{ST}}{RT}. \tag{3}$$

Provided $(k_P + k_G^T)$, often dominated by k_G^T, is essentially temperature independent, a plot of the l.h.s. vs. $1/T$ should be linear. However, the correct value of Φ_T (also assumed temperature independent) is required for a linear least-squares fit. In effect, the shape of the plot is a very sensitive function of Φ_T in the high temperature domain, not being, in general, a straight line. Continuous variation of this parameter in the search for maximum linearity yields its best value and, simultaneously, ΔE_{ST}. The method based on Eq. (3) yields therefore ΔE_{ST} and Φ_T, and, with lesser accuracy, $\bar{k}_{ISC}^T$.

3.3. Singlet–triplet energy gap

We now describe the application of the method to C_{60} dissolved in liquid USP light oil. Firstly, the assumed temperature independence of certain parameters was checked by the measurement of the fluorescence quantum yield of non degassed solutions (where, owing to quenching of the triplet by molecular oxygen, delayed fluorescence is negligible): It was temperature independent, from 291 K up to 353 K, in agreement with a non thermally activated dominant decay channel ($S_1 \rightarrow T_1$ intersystem crossing). The phosphorescence lifetime does not appear to change much with temperature: Reported values are 0.4 ms at 1.2 K [18], 0.3–0.4 ms at 77 K [28], and 0.25 ms and 0.13 ms (both extrapolations to zero concentration) in degassed benzene at room temperature [29,30].

Secondly, the possibility that the delayed fluorescence is due to triplet–triplet (T–T) annihilation is ruled out by the low concentration used, relatively low phosphorescence lifetime of C_{60}, and the high viscosity of the solvent. No concentration effect was indeed found experimentally.

Thirdly, to exclude the possibility of thermal or photochemical reactions of C_{60} that might affect the fluorescence intensity, the degassed solutions were submitted to a complete thermal cycle, in order to check the reversibility of the intensity upon cooling. Aerated solutions did not change significantly their intensity upon heating. Further evidence for the absence of decomposition in other fluorescing products is provided by the already mentioned invariance of the fluorescence lifetime with temperature.

Using the kinetic analysis method described above, for 1.2×10^{-5} M solutions and for temperatures from 18°C to 80°C, Fig. 3, one obtains a singlet–triplet gap of 35 ± 2 kJ/mol from the slope of the best straight line.

From the accepted spectroscopic assignment of ca. 650 nm as the 0–0 band of the $S_1 \leftarrow S_0$ and $S_1 \rightarrow S_0$ transitions in similar solvents (cyclohexane [31], decalin–cyclohexane 3:1 v/v [18]), the determined range of values of ΔE_{ST} (33–37 kJ/mol) places the 0–0 band of the phosphorescence in the range 789–810 nm, which is compatible with the reported value for the phosphorescence 0–0 band of C_{60} in the same decalin–cyclohexane mixture at 1.2 K, 798 nm [18]. The values reported in the literature for rare gas matrices, 783 nm [19] and 787 nm [20], are expected to be blue shifted, owing to the weaker solute–matrix interactions [20]. The estimated gas-phase value is 774 nm [20]. In this way, and in contrast to what is observed for C_{70} [2], it is possible

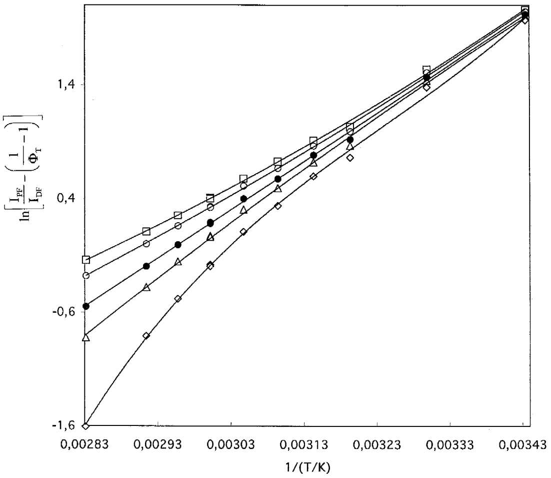


Fig. 3. Fit of I_{PF}/I_{DF} versus $1/T$, according to Eq. (3), for temperatures from 18 to 80°C. The effect of Φ_T on the linearity is apparent: $\Phi_T = 1.00$ (□), 0.90 (○), 0.78 (best value, ●), 0.70 (△), 0.60 (◇). Excitation and emission slits were 18 and 4.5 nm, respectively.

that the wavelength of the phosphorescence origin does not shift with temperature. The range of values allowed by the experimental error is however substantial, and, in the absence of the phosphorescence spectrum in the same temperature range, more definite conclusions cannot be drawn.

3.4. Intersystem crossing rate constants

The direct intersystem crossing rate constant is $k_{\mathrm{ISC}}^{\mathrm{S}} = \Phi_{\mathrm{T}}/\tau_{\mathrm{F}} = (8 \pm 1) \times 10^{8}\ \mathrm{s}^{-1}$. The fit according to Eq. (3) yields an intercept from which, using the measured phosphorescence lifetime at low temperature, 0.4 ms [18], a value of $\bar{k}_{\mathrm{ISC}}^{\mathrm{T}} = (9 \pm 4) \times 10^{8}$ s^{-1} is calculated. A much higher phosphorescence lifetime, obtained from time-resolved Raman spectra, has also been reported for oxygen free films of C_{60}, 55 ± 5 ms [32]. Interestingly, this value is close to the reported phosphorescence lifetime of C_{70} [2,28]. Calculation of $\bar{k}_{\mathrm{ISC}}^{\mathrm{T}}$ with the higher phosphorescence lifetime yields $\bar{k}_{\mathrm{ISC}}^{\mathrm{T}} = (7 \pm 3) \times 10^{6}\ \mathrm{s}^{-1}$. From the available experimental data, a wide range of values is therefore possible for $\bar{k}_{\mathrm{ISC}}^{\mathrm{T}}$. Note that for C_{70}, it has been found that $\bar{k}_{\mathrm{ISC}}^{\mathrm{T}} = 10^{7}\ \mathrm{s}^{-1}$, and $k_{\mathrm{ISC}}^{\mathrm{S}} = 2 \times 10^{9}\ \mathrm{s}^{-1}$ [2].

3.5. Triplet quantum yield

The plot shown in Fig. 3 yields the best straight line for $\Phi_{\mathrm{T}} = 0.78$. From Fig. 3 it can be seen that values of Φ_{T} below 0.7 or above 0.9 produce curved lines. Reported quantum yields of triplet formation for C_{60} are 0.88 ± 0.15 [13] and 0.93 ± 0.07 [12]. With our data, the assumption of unit quantum yield yields a slightly curved plot (Fig. 3). The recovered values from a straight line fit ($\Phi_{\mathrm{T}} = 1$) are $\Delta E_{\mathrm{ST}} = 30.4$ kJ/mol and $\bar{k}_{\mathrm{ISC}}^{\mathrm{T}} = 10^{8}\ \mathrm{s}^{-1}$. The singlet–triplet energy gap thus obtained seems too small.

Direct application of Eq. (1) to the raw experimental data already allows the estimation of a lower bound for Φ_{T} [2]. That equation can be rewritten as

$$\Phi_{\mathrm{T}} = \frac{1}{1 + I_{\mathrm{PF}}/I_{\mathrm{DF}}} \frac{1}{\Phi_{\mathrm{S}}}\,; \tag{4}$$

Because Φ_{S} is smaller or equal to unity, a lower bound for Φ_{T} is

$$\Phi_{\mathrm{T}}^{\min} = \frac{1}{1 + I_{\mathrm{PF}}/I_{\mathrm{DF}}}\,. \tag{5}$$

$\Phi_{\mathrm{T}}^{\min}$ is the closest to Φ_{T}, the closest Φ_{S} is to one, that is, the highest the temperature. At 80°C, $I_{\mathrm{DF}}/I_{\mathrm{PF}} = 0.867$, and therefore, from Eq. (5), $\Phi_{\mathrm{T}}^{\min} = (1)/(1 + 0.867) = 0.54$. On the other hand, from the experimentally determined value $\Phi_{\mathrm{T}} = 0.8 \pm 0.1$ and from Eq. (1), one obtains for the high temperature limit ($\Phi_{\mathrm{S}} = 1$), that $(I_{\mathrm{DF}}/I_{\mathrm{PF}})_{\max} = 4_{-2}^{+5}$. In this way, the global fluorescence quantum yield ($\Phi_{\mathrm{F}} = \Phi_{\mathrm{PF}} + \Phi_{\mathrm{DF}}$) of C_{60} can in principle be, at most, 10 times higher than that of prompt fluorescence.

4. Conclusion

The existence of considerable thermally activated delayed fluorescence in C_{60}, with $\Phi_{\mathrm{DF}} \approx \Phi_{\mathrm{PF}}$, was demonstrated by the study of the temperature dependence (291–353 K) of the fluorescence intensity of C_{60} degassed solutions. The determined singlet–triplet energy gap (35 ± 2 kJ/mol) agrees with the value calculated from previously reported fluorescence and low temperature phosphorescence spectra for this molecule in a similar solvent, and is higher than that reported for C_{70} (26 ± 2 kJ/mol). The estimated quantum yield of triplet formation, 0.8 ± 0.1, reasonably agrees with previous determinations. The fluorescence lifetime of C_{60}, also measured, $\tau = 1.1$ ns, does not change appreciably with degassing nor with temperature, in the range 243–343 K.

Acknowledgements

Aleksandre Fedorov was supported by Junta Nacional de Investigação Científica e Tecnológica.

References

[1] C.A. Parker, Photoluminescence of Solutions, Elsevier, Amsterdam, 1968.
[2] M.N. Berberan-Santos, J.M.M. Garcia, J. Am. Chem. Soc. 118 (1996) 9391.
[3] F. Tanaka, M. Okamoto, S. Hirayama, J. Phys. Chem. 99 (1995) 525.
[4] M.W. Wolf, K.D. Legg, R.E. Brown, L.A. Singer, J.H. Parks, J. Am. Chem. Soc. 97 (1975) 4490.

[5] A. Maciejewski, M. Szymanski, R.P. Steer, J. Phys. Chem. 90 (1986) 6314.
[6] J.L. Kropp, W.R. Dawson, J. Phys. Chem. 71 (1967) 4499.
[7] J.C. Fetzer, M. Zander, Z. Naturforsch. 45a (1990) 727.
[8] B. Nickel, D. Klemp, Chem. Phys. 174 (1993) 297.
[9] B. Nickel, D. Klemp, Chem. Phys. 174 (1993) 319.
[10] J.W. Arbogast, A.O. Darmanyan, C.S. Foote, Y. Rubin, F.N. Diederich, M.M. Alvarez, S.J. Anz, R.L. Whetten, J. Phys. Chem. 95 (1991) 11.
[11] J.W. Arbogast, C.S. Foote, M. Kao, J. Am. Chem. Soc. 114 (1992) 2277.
[12] L. Biczok, H. Linschitz, R.I. Walter, Chem. Phys. Lett. 195 (1992) 339.
[13] R.V. Bensasson, T. Hill, C. Lambert, E.J. Land, S. Leach, T.G. Truscott, Chem. Phys. Lett. 201 (1993) 326.
[14] R.R. Hung, J.J. Grabowski, J. Phys. Chem. 95 (1991) 6073.
[15] Y. Zeng, L. Biczok, H. Linschitz, J. Phys. Chem. 96 (1992) 5237.
[16] R.S. Ruoff, D.S. Tse, R. Malhotra, D.C. Lorents, J. Phys. Chem. 97 (1993) 3379.
[17] N. Sivaraman, R. Dhamodaran, I. Kaliappan, T.G. Srinivasan, P.R.V. Rao, C.K. Mathews, Fullerene Sci. Technol. 2 (1994) 233.
[18] D.J. Heuvel, I.Y. Chan, E.J.J. Groenen, J. Schmidt, G. Meijer, Chem. Phys. Lett. 231 (1994) 111.
[19] W.-C. Hung, C.-D. Ho, C.-P. Liu, Y.-P. Lee, J. Phys. Chem. 100 (1996) 3927.
[20] A. Sassara, G. Zerza, M. Chergui, Chem. Phys. Lett. 261 (1996) 213.
[21] Y. Wang, J. Phys. Chem. 96 (1992) 764.
[22] F. Negri, G. Orlandi, F. Zerbetto, J. Chem. Phys. 97 (1992) 6496.
[23] Y. Sun, P. Wang, N.B. Hamilton, J. Am. Chem. Soc. 115 (1993) 6378.
[24] A. Sassara, G. Zerza, M. Chergui, J. Phys. B: At. Mol. Opt. Phys. 29 (1996) 4997.
[25] A. Fedorov, M.N. Berberan-Santos, J.P. Lefèvre, B. Valeur, Chem. Phys. Lett. 267 (1997) 467.
[26] T.W. Ebbesen, K. Tanigaki, S. Kuroshima, Chem. Phys. Lett. 181 (1991) 501.
[27] D. Kim, M. Lee, Y.D. Suh, S.K. Kim, J. Am. Chem. Soc. 114 (1992) 4429.
[28] M.R. Wasielewski, M.P. O'Neil, K.R. Lykke, M.J. Pellin, D.M. Gruen, J Am. Chem. Soc. 113 (1991) 2774.
[29] N.M. Dimitrijevic, P.V. Kamat, J. Phys. Chem. 96 (1992) 4811.
[30] M.R. Fraelich, R.B. Weisman, J. Phys. Chem. 97 (1993) 11145.
[31] S. Leach, M. Vervloet, A. Desprès, E. Bréheret, J.P. Hare, T.J. Dennis, H.W. Kroto, R. Taylor, D.R.M. Walton, Chem. Phys. 160 (1992) 451.
[32] L. Akselrod, H.J. Byrne, C. Thomsen, A. Mittelbach, S. Roth, Chem. Phys. Lett. 212 (1993) 384.