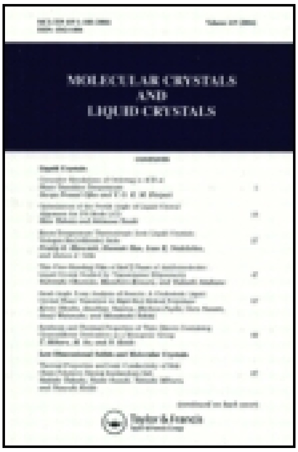

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Optically Detected Magnetic Resonance (ODMR) Study of Isolated C_{70} Molecules and C_{70} Films

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OPTICALLY DETECTED MAGNETIC RESONANCE (ODMR) STUDY OF ISOLATED C_{70} MOLECULES AND C_{70} FILMS

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Abstract The X-band ODMR of C_{70} molecules isolated in a toluene/polystyrene (C_{70}:T/PS) glass and C_{70} films is compared to that of C_{60}. As C_{60}:T/PS, the C_{70} glasses exhibit only a triplet pattern at $g \approx 2$, clearly due to an exciton delocalized over the molecule; however, it is strikingly asymmetric and narrower, due to the larger size of C_{70}. The ODMR of both C_{60} and C_{70} films includes a narrow photoluminescence-enhancing polaron resonance and full- and half- field narrow and broad triplet exciton patterns. As in the glasses, the narrow pattern is due to the exciton delocalized over the molecule and is narrower in C_{70}. The broad pattern is tentatively assigned to a triplet localized on a face adjacent to a neighboring molecule. In contrast to C_{60}, the ODMR of C_{70} films is detectable up to 295 K, apparently due to the slower rotation.

INTRODUCTION

Since their availability in macroscopic quantities,[1] the optoelectronic properties of isolated molecules and films of soccerball-like C_{60} (radius R = 7.065 Å)[2] and rugbyball-like C_{70} (major and minor axes a = 7.80 Å and b = 6.94 Å, resp.)[3] have been extensively studied. Experimental measurements have included absorption,[4-6] photoinduced absorption,[7-10] photoluminescence (PL),[9,11-14] light-induced ESR,[12,15-17] optically (i.e., PL) detected magnetic resonance (ODMR),[12,18,19] and photoinduced absorption detected magnetic resonance (ADMR).[19,20] They have shown that in C_{60} isolated in a toluene/polystyrene glassy matrix (C_{60}:T/PS) at least 99% of the photogenerated singlet excitons intersystem cross into a low-lying triplet exciton at 1.53 eV.[16] The lifetimes of these triplets were found to vary from ~130 μs to ~50 ms in C_{60}[9,15,18] and ~500 ms in C_{70}[18] glasses, resp. In C_{60}:T/PS, the only observable ODMR was the triplet exciton powder pattern. The ODMR of films,[12] however, was strikingly similar to that of π-conjugated polymers,[20-23] including a narrow polaron resonance at $g \approx 2.0025$ and full- (due to $\Delta m = 1$ transitions) and half-field (due to $\Delta m = 2$ transitions) patterns of two distinct triplet excitons. Interestingly, in a comparative ODMR and ADMR study of C_{60}:PS and C_{70}:PS glasses by Wei et al.,[18] the ADMR of the latter appeared to be very similar to the ODMR of C_{60} films, while the full-field triplet exciton pattern of the ODMR was PL-quenching. As indicated above, the various studies show that the spectra and dynamics are very sensitive to the environment of the Fullerene molecule. In addition, C_{70} exhibits striking clustering effects in various solvents.[14]..This paper therefore describes the ODMR of both C_{70} films and C_{70}:T/PS glasses in carefully controlled configurations. In particular, we show below that at dilute (0.3 mol%) C_{70} in T/PS no C_{70} precipitates are visible, and the ODMR spectra are quite similar to those of C_{60}:T/PS. However, while the low temperature intensities of the narrow delocalized and the broad localized triplets are comparable in C_{60}, the broad localized triplet exciton is much weaker in C_{70}. Finally, in contrast to C_{60} films, where no ODMR is observable above 100 K, the ODMR of C_{70} is observable up to room temperature, probably as a result of the slower rotational dynamics.

EXPERIMENTAL PROCEDURE

Texas Fullerene Corp.[24] 99% pure C_{70} powder was dissolved in Toluene and processed into films and C_{70}:T/PS as described elsewhere for C_{60}.[12] As the former is apparently more susceptible to clustering and precipitation, special effort was made to obtain C_{70}: T/PS in which the Fullerene molecules would probably be indeed isolated from each other. The X-band ODMR spectrometer, enabling the detection of signals $\Delta I/I \geq 5\times10^{-7}$ in samples with a PL yield $\eta \geq 0.1\%$, has been described previously.[12,20-23]

RESULTS AND ANALYSIS

C_{70}:T/PS

Figure 1 and its insets display the total PL-detected ODMR of C_{60}:T/PS and C_{70}:T/PS and the respective PL spectra excited at 488 nm. The PL yields were 0.12 and 0.05%, resp. While the ODMR of the two glasses is qualitatively similar, two features of C_{70}:T/PS should be addressed: (i) The splitting between the two peaks (singularities) is ~110 G, as compared to ~160 G in C_{60}:T/PS. As the resonance is clearly due to a triplet exciton $^3C_{70}$ delocalized over the

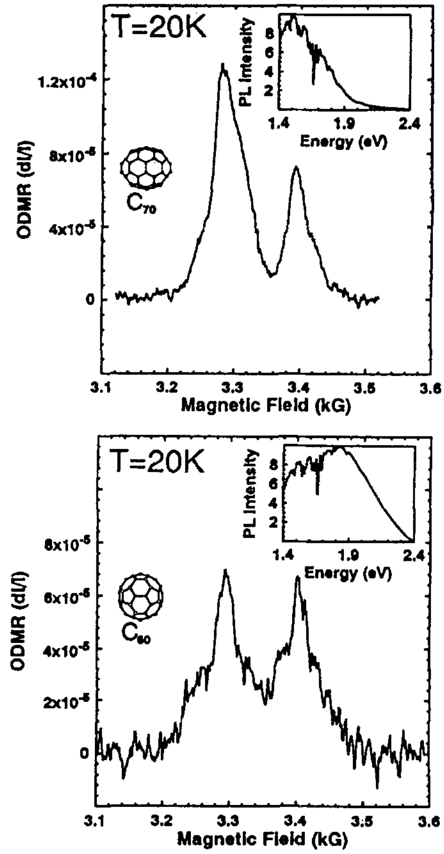

Figure 1. *The full-field X-band total PL-ODMR of (a) C_{60}:T/PS and (b) C_{70}:T/PS glasses. Insets: The respective PL spectra.*

molecule, the narrower pattern in C_{70} is consistent with its larger size. The resulting zero-field splitting (ZFS) parameters are $D \approx 0.0051$ and $E \leq 6\text{x}10^{-4}$ cm^{-1}, in agreement with the dimensions of the molecule given above. (ii) The pattern of C_{70}:T/PS is strikingly asymmetric, as the lower-field peak (singularity) is much more intense than the higher field, and each is strongly asymmetric. The nature of these asymmetries is not clear at present, since the powder patterns of triplets with well-defined ZFS parameters, whether axially symmetric or not, are expected and usually observed to be approximately symmetric about $g = 2.002$. However, some speculative scenarios which might result in these asymmetries are suggested in section IV below.

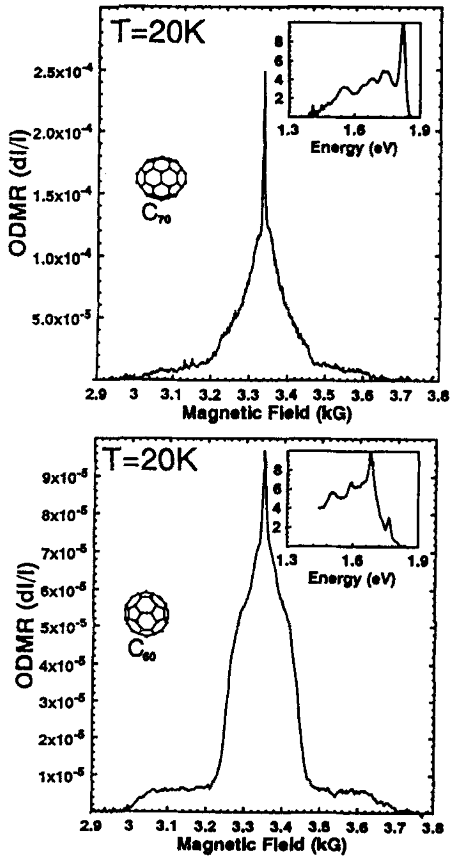

Figure 2. *The full-field X-band total PL-ODMR of (a) C_{60} and (b) C_{70} films at 20 K. Insets: The respective PL spectra.*

C_{70} *Films*

Figure 2 and its insets display the full-field ($\Delta m = 1$) total PL-detected ODMR of C_{60} and C_{70} films and their PL spectra, resp. The quantum yields were $\eta \approx 0.07\%$ and 0.13%, resp. Here again several features of the spectrum of C_{70} should be noted and discussed: (i) As in C_{60}[12] and numerous π-conjugated polymers,[20-23] a sharp narrow resonance is observed, attributable to spin 1/2 polarons. Theoretical models have indeed predicted the occurrence of polaron states in C_{60}.[25,26] Their absence from the ODMR of the glasses is discussed below.

Two other features of Figure 2 are noteworthy: (i) The narrow (delocalized) triplet pattern is narrower in C_{70} than in C_{60}, again clearly due to the larger molecule and consequent greater delocalization of that triplet. However, while the values of D in the films are similar to those in the glasses, the patterns are strikingly different, probably reflecting a distribution of values of the ZFS parameter $E \leq D/3$ due to the coupling with neighboring molecules. (ii) Whereas the ODMR of C_{60} films is unobservable above 100 K, it is still detectable in C_{70} films at room temperature, probably due to the slower rotational dynamics (see below). (iii) In C_{60} films, the integrated intensity of the broad (650 G wide) localized triplet pattern is comparable to that of the narrow delocalized exciton. In C_{70} films, however, the broad pattern is very weak. Not surprisingly, Figure 3 shows that the half-field resonance of this broad localized triplet is also much weaker than that of the delocalized narrow exciton. Yet the intensity of the delocalized exciton decays more rapidly with increasing temperature than that of the localized exciton. These observations are also discussed below.

IV. DISCUSSION AND CONCLUDING REMARKS

The asymmetric pattern of $^3C_{70}$:T/PS

We first turn to the asymmetric triplet-like pattern of C_{70}:T/PS (Figure 1). As mentioned above, its width is clearly consistent with triplet excitons delocalized over the C_{70} molecule. However, the asymmetries of the pattern are striking and not clearly understood. One may speculate that they not only reflect a distribution of crystal fields, but possibly qualitatively distinct sites. Yet, even within such a scenario, it is still difficult to envision a sum of symmetric triplet powder patterns yielding an overall asymmetric envelope.

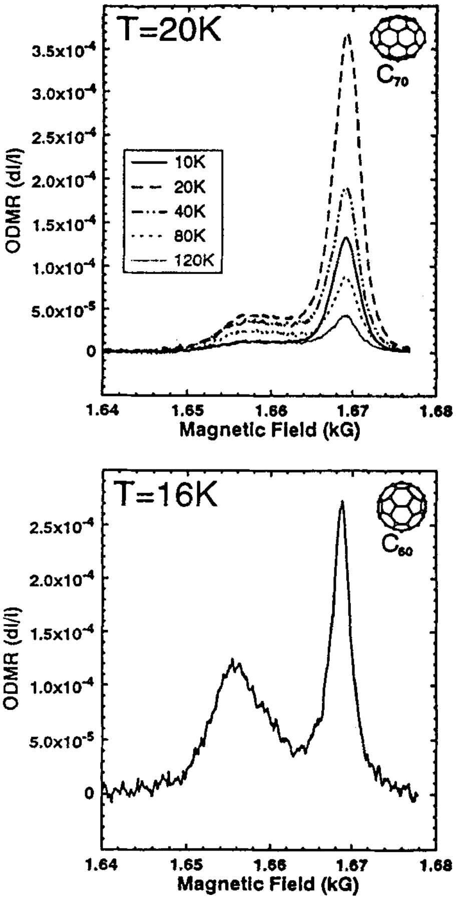

Figure 3. *The half-field X-band total PL ODMR of (a) C_{60} at 16 K and (b) C_{70} films at various temperatures.*

The half-field resonances and the nature of the triplet exciton ODMR

A second interesting issue is the clear observation of half-field resonances in both C_{60} and C_{70} films, but their absence from the glasses. This behavior may be due to the different symmetry of the triplets; whereas they are nearly axially symmetric and E is small in the glasses, their symmetry is distinctly lower in the films, probably due to coupling with neighboring molecules, and the patterns then reflect a distribution of values of E. While we have previously attributed the triplet exciton ODMR to the generation of singlet excitons by triplet-triplet fusion, migration of triplets enabling their fusion is ruled out when they are isolated in glass matrices. We therefore wonder if the triplet resonances in the Fullerene and π-conjugated polymer films result from triplet exciton migration and triplet-triplet coupling, whereas in isolated C_{60} and C_{70} they result from direct transitions from the m = 0 triplet level to the singlet exciton state.[27]

The polaron resonance of the Fullerene films

Figure 2 shows that both C_{60} and C_{70} films exhibit a narrow spin 1/2 polaron resonance similar to that of π-conjugated polymers.[20-23] This resonance has previously been attributed to magnetic resonance enhancement of fusion of positive (p^+) and negative (p^-) polarons into singlet excitons. However, this scenario should be reexamined in light of recent UV-excited ODMR measurements of various π-conjugated polymers, which in many cases yield a narrow PL-quenching resonance in addition to, or in place of, the PL-enhancing polaron resonance.[28] This PL-quenching resonance is discussed in relation to the role of p^+ and p^- as singlet exciton quenching centers, in addition to their fusion into singlet excitons. Hence, the polarons in the Fullerenes should also be considered as nonradiative singlet excition quenching centers.[29]

The dynamics of the triplet resonances of C_{70} films

Figure 2 also shows that the ODMR of C_{70} films is still observable at room temperature, whereas that of C_{60} is undetectable above 100 K. This is probably due to the slower rotational dynamics of C_{70}, which probably results in a longer spin-lattice relaxation time of both the polarons and triplet exciton, and hence a greater contribution of the microwave to the spin-dependent decay channels of both. Figure 3 then shows that with increasing temperature the intensity of the delocalized (narrow) triplet decreases much more rapidly than the intensity of the localized (broad) triplet. We have previously suggested that the localized triplet, observed in the films but not the glasses, is due to an exciton localized on a face adjacent to a neighboring molecule. Very recent results on photopolymerized Fullerenes[30] are indeed consistent with this assignment. The different temperature dependence of the half-field resonances can then be expected, if the (hindered) rotation about the axis perpendicular to the face adjacent to a neighboring molecule is much more rapid than about the axes in the plane of that face.

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