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Triplet excitations of crystalline C₆₀. An optically detected magnetic-resonance study in zero field

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Upon excitation of a single crystal of C₆₀ in the visible, microwave transitions have been detected optically in zero field. The transitions derive from triplet states and their frequencies verify that these states are delocalized over more than one C₆₀ molecule, as previously inferred from EPR experiments. Different triplet states seem to correspond to excitations that are trapped in different domains of the crystal which indicates that structural or impurity-induced defects may be involved.

1. Introduction

Knowledge of the electronically excited states of fullerenes is still rather elementary notwithstanding the overwhelming interest of scientists in these new carbon compounds. For C₆₀, the central species of this family of cage compounds, the lowest triplet state might be located at about 12690 cm⁻¹ above the ground state [1]. Quantum chemical calculations for icosahedral C₆₀ predict this state to be of T_{1g} or T_{2g} symmetry [2], which points to a structural instability of C₆₀ upon excitation. Microwave [3] and optically [4] detected triplet EPR spectra of C₆₀ in glasses and films have indeed revealed a structural distortion of the molecule in the triplet state but the way the molecule distorts remains unclear.

Recently we have reported on a study of triplet excitations of a single crystal of C₆₀ by 95 GHz electron-spin-echo (ESE) experiments in a magnetic field at 1.2 K [5]. It was established that the individual C₆₀ molecule distorts upon excitation thereby lowering its symmetry from I_h to D_{2h}. For the single crystal two distinct triplet species, indicated by α and β , were recognized and it was demonstrated that they

correspond to excitations that are delocalized over either pairs or linear chains of C₆₀ molecules. Triplet states α and β differ as regards the orientation of the neighbouring C₆₀ molecules with respect to each other. The extent of the delocalization remained undetermined because the ESE-detected EPR lines were too broad to reveal the details of the band structure of these Frenkel excitons.

Meanwhile additional ESE experiments, to be described elsewhere [6], have revealed the presence of at least one more triplet, henceforth called γ . The zero-field splitting of the triplet sublevels of γ is found to be the same as for β but these two triplet excitations are distinguishable in the magnetic field owing to the different directions of the principal axes of their fine-structure tensors with respect to the crystal axes. It is found that γ is present in all crystals studied up to now but the ratio of γ on the one hand and α and β on the other varies strongly from one crystal to the other.

Since the ESE-detected EPR spectra are very complicated, as they derive from three triplets each in six different orientations in accordance with the crystal symmetry, we have performed an independent investigation through experiments in zero field. Here we present the first results of this study which show that the microwave transitions between the sublevels of triplets α , β and γ in the single crystal of C₆₀ can

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be detected optically in zero field. They occur at frequencies that are consistent with the energy differences between the sublevels as derived from ESE-detected EPR experiments. This corroborates the earlier interpretation of the spectra in the magnetic field and thereby verifies the delocalized character of the triplet excitations of the C_{60} crystal.

2. Experimental

Single crystals of pure C_{60} (>99.9%), grown as described previously [7], were irradiated at 514 nm with an argon ion laser. The emission was detected with a silicon diode (HUV 4000). To eliminate excitation light from the detection channel, a fluorescein solution filter was used in combination with a high-pass filter (Schott RG715). Microwaves were applied to the sample using an LC resonant circuit ($Q \approx 500$) with a variable capacitor that allowed tuning of the resonator over one octave. The microwaves were provided by a sweep oscillator (HP 8350B) and amplitude modulated by a p-i-n diode at 423 Hz. The synchronous change of the total emission was detected by a lock-in amplifier. Scanning of the microwave frequency was achieved by changing the capacitance of the circuit while locking the frequency of the microwave source to the resonator.

3. Results and discussion

The optically detected magnetic-resonance (ODMR) spectrum of C_{60} crystals in zero field at 1.2 K upon laser irradiation at 514 nm is represented in fig. 1. Monitoring the C_{60} luminescence while scanning the microwave frequency reveals four transitions at 122, 202, 270 and 301 MHz with a width of about 8 MHz. The ratio of the intensities of the 202 and 270 MHz transitions varies from sample to sample and depends on the position of the laser spot on the crystal. Intensity ratios between 1 to 2 and 5 to 1 have been observed. On the other hand, the ratio of the intensities of the 202 and 301 MHz transitions does not vary with sample or laser spot position. The intensity of the 122 MHz transition cannot be compared with that of the other transi-

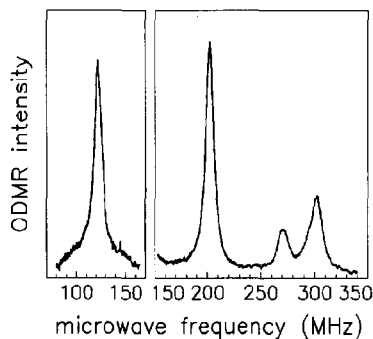


Fig. 1. The ODMR spectrum in zero field of a single crystal of C_{60} at 1.2 K.

Table 1

Frequencies ν of the ODMR transitions and sublevel energies E for triplet states of crystalline C_{60} as derived from experiments in zero field and in a magnetic field (ref. [5])

	Zero field		Magnetic field
	ν (MHz)	E (MHz)	E (MHz)
triplet α	122	± 9	± 8
	270	± 131	± 132
		∓ 140	∓ 140
triplets β, γ	202	± 34	± 39
	301	± 133	± 132
		∓ 168	∓ 171

tions because to measure this transition a different coil had to be used in the LC circuit.

Assuming that the 202 and 301 MHz transitions derive from one triplet state, compatible with their parallel intensity behaviour, and the 122 and 270 MHz transitions from another, the zero-field energies of the triplet sublevels have been calculated. These are given in table 1 and compared to the sublevel energies for the triplets α , β and γ of the C_{60} crystal as determined from the ESE experiments in magnetic field [5]. The two transitions at 122 and 270 MHz are found to correspond to triplet α . The third transition for triplet α , expected around 148 MHz, does not show up in the ODMR spectrum which points to about equal (radiative) decay rates or equal steady-state populations for two of the sublevels of triplet α . Similarly, the transitions at 202 and 301 MHz correspond to triplets β and γ which are indistinguishable in zero field.

Given this assignment of the observed zero-field transitions and the one to one ratio found for triplets α and β in the ESE experiments at 95 GHz, the variation in the intensity of the 202 and 301 MHz transitions as compared to that of the 270 MHz transition with sample and laser spot position most probably derives from a variation in the contribution of triplet γ to the 202 and 301 MHz transitions. This would imply that the ratio of α and β triplets to γ triplets varies from crystal to crystal, which is consistent with our observations in magnetic field [6]. The fact that this ratio even varies within one crystal suggests that the triplets α and β on the one hand and γ on the other hand correspond to electronic excitations that are trapped in different domains of the crystal. Such a trapping process will depend on the presence of structural or impurity-induced defects. It may well be that the surface of the crystal plays a particular role. Upon changing the excitation wavelength to the red, from 514 to 685 nm, we observe a gradual increase of the intensity of the 202 and 301 MHz transitions relative to that of the 270 MHz transition. At 514 nm the excitation light only penetrates a few μm into the crystal. At 685 nm the extinction is about 20 times smaller, which means that the excitation light penetrates much further. A larger part of the emission may then be generated at positions deeper in the crystals. If so, the relative increase of the intensity of the 202 and 301 MHz transitions upon excitation at longer wavelength could imply that triplets α and β specifically occur at the surface. This suggestion will be further investigated through double-resonance experiments.

From the orientation of the fine-structure axes with respect to the crystal axes and the magnitude of the zero-field splitting we have previously interpreted the triplet excitations of the C_{60} crystal as being delocalized over pairs or linear chains of C_{60} molecules that have well-defined orientations with respect to each other [5]. The observation of the corresponding zero-field transitions supports this interpretation of the magnetic field data and thereby the assignment of the triplets α , β and γ as Frenkel excitons. No ODMR transitions have been observed at about 321 or 363 MHz where zero-field transitions for a triplet excitation localized on one C_{60} molecule should occur [3]. A comment is in order here because the use of the concept of an "exciton" in the

literature on C_{60} seems confusing [4]. The C_{60} crystal is a molecular crystal. The interaction between the molecular C_{60} units is weak compared to the intramolecular forces. For such systems, electronic excitations are of a molecular kind but collective in nature. They are called Frenkel excitons and concern transitions between eigenstates, characterized by a wavevector, that are linear combinations of product states. The product state represents a configuration in which one molecular unit is excited while the others are in the ground state. In the limit of two product states, i.e. delocalization of the excitation over only two molecules, one sometimes refers to the excitations as a mini-exciton. Unfortunately, for C_{60} the word exciton has repeatedly been used when an isolated molecular excitation was meant.

The zero-field transitions for the C_{60} crystal are still remarkably broad, although narrower than those observed in a magnetic field (30–50 MHz, ref. [5]). There is no indication of a distribution of zero-field splittings owing to the band structure of the exciton. The zero-field transitions do not show any structure and their shape does not vary as a function of temperature from 0.75 K to several tens of K. The linewidth of about 8 MHz cannot result from hyperfine interaction which is only a second-order effect in zero field. For a crude estimate of the hyperfine contribution to the linewidth, let us assume the spin density to be distributed uniformly over two C_{60} molecules. The relevant atomic orbital on carbon is p-like. For ^{13}C (natural abundance 1.11%), spin density one in a 2p orbital results in an anisotropic hyperfine interaction of about 90 MHz and spin density one in a 2s orbital in an isotropic hyperfine interaction of about 3100 MHz [8]. For spin density $\frac{1}{120}$ and 10% s-character we calculate a hyperfine coupling A of less than 4 MHz which would limit the second-order hyperfine contribution to the linewidth to $A^2/\Delta E = 16/120 \approx 0.1$ MHz. From a recent linewidth analysis for the triplet EPR spectrum of C_{60} in a glass, the hyperfine coupling constant was estimated to be only 0.17 MHz [9] which would reduce the second-order contribution even further by two orders of magnitude. Although 49% of the C_{60} molecules have one or more ^{13}C nuclei, we have to conclude that the hyperfine contribution is negligible compared to the observed linewidth.

A plausible explanation for the linewidth in zero

field comes from the character of the triplet excitations. The zero-field splitting is very sensitive to the mutual orientation of the C_{60} molecules that constitute the exciton. For example, starting from the fine structure of individual triplet C_{60} molecules it is easy to show that variations in this orientation of only 1° lead to shifts up to 10 MHz in the zero-field transitions for the triplet exciton. Only a narrow distribution of orientations therefore already accounts for the linewidth in zero field.

Finally we emphasize that the zero-field microwave transitions monitored upon optical excitation of single crystals of C_{60} confirm the excitonic character of the triplet excitations in this system. Several such delocalized excitations have been observed in varying proportions in different crystals which indicates that defects play a role in the trapping of the excitation energy. Optical detection of triplet transitions in zero field is found to be feasible which opens the way for double-resonance experiments. These will enable a correlation of optical and microwave transitions and thereby a further characterization of the triplet excitons in C_{60} crystals. Such experiments are in progress in our laboratory.

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