

On the fluorescence of crystalline C₆₀ at 1.2 K

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Abstract

Well-resolved fluorescence spectra are reported for single crystals of C₆₀ at 1.2 K. The fluorescence is found to be composed of two contributions. Fluorescence-microwave double-resonance experiments indicate that the dominant component originates from deep X-traps that consist of pairs of C₆₀ molecules. The minor component most likely derives from shallow monomolecular C₆₀ X-traps.

1. Introduction

The icosahedral symmetry of the C₆₀ molecule makes the electronic structure of the lower electronically excited states of this fullerene both interesting and difficult to study [1]. In a one-electron molecular-orbital picture the lowest excited configuration corresponds to a fifteenfold degenerate level. All excited states that result from this configuration are of gerade symmetry. Quantum-chemical calculations indicate that the first excited singlet state S₁ most likely is of T_{1g} or T_{2g} symmetry. The radiative decay from this singlet state to the ground state is electric dipole forbidden and the electronic origin will not be

visible in the fluorescence of the isolated molecule. Vibronic bands are expected to show up that involve Herzberg–Teller active modes (of a_u, t_{1u}, g_u or h_u symmetry) and, in view of the triple orbital degeneracy of S₁, Jahn–Teller active modes (of h_g symmetry). This picture has been found to provide at least a qualitative insight into the fluorescence of molecular C₆₀ in solution. Fluorescence spectra have been reported for C₆₀ in various solvents at room temperature [2–4] and 77 K [5,6]. For a methylcyclohexane glass the origin band becomes weakly visible at about 655 nm as the result of a slight, solvent-induced reduction of the local symmetry while most of the fluorescence intensity goes into bands between 690 and 1700 cm⁻¹ from the origin. The latter bands have been interpreted as to derive from transitions between the vibrationless S₁ state and ground state vibrational levels each involving a Herzberg–Teller active mode [7].

Whereas consensus seems to exist as regards the experimental fluorescence spectrum of C₆₀ in solu-

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tion, the situation is less clear for solid state C_{60} ³. In the solid molecules are being held together by weak van der Waals forces. Apart from emission of chemical impurities, fluorescence is expected from band-edge states and/or X-traps. The latter correspond to sites in the crystal where the translational symmetry is broken due to a defect of chemical or physical (e.g. vacancy or dislocation) origin in the neighbourhood. Fluorescence has been observed for films, polycrystalline powders and single crystals of C_{60} but different spectra have been reported even for nominally similar samples. For films of C_{60} on various supports commonly a broad fluorescence spectrum has been found with a maximum around 735 nm and more or less pronounced shoulders at longer wavelengths [9–13]. In some cases the fluorescence spectrum revealed an additional band around 705 nm [9,14,15]. A spectrum similar to the latter has been reported for a polycrystalline powder sample of C_{60} [16]. Better resolved spectra have been obtained for single crystals of C_{60} . In particular the very recent data by Guss et al. [17] show a large number of well-resolved bands in the fluorescence spectrum at 10 K. These authors interpret a series of bands ranging from 683 to 790 nm as false origins corresponding to Herzberg–Teller induced vibronic transitions originating in the bulk of the crystal and in five different X-traps. The spectrum was found to vary with the position of the exciting laser spot on the surface of the crystal.

In order to unravel the fluorescence of C_{60} single crystals we have made use of fluorescence-microwave double-resonance spectroscopy. Previously, 95 GHz electron-spin-echo detected EPR experiments have revealed that upon optical excitation of single crystals of C_{60} triplet states are formed [18]. These were found to correspond to Frenkel excitons but the EPR data were not conclusive as regards the delocalization of the excitation over pairs or chains of C_{60} molecules. Subsequently we have shown that transitions between sublevels of these triplets can be detected optically as microwave-induced changes of

the fluorescence [19]. This then presents a tool to further characterize the fluorescence.

In this Letter, we report fluorescence and fluorescence-excitation spectra of high-purity single crystals of C_{60} . At 1.2 K two species have been found to contribute to the fluorescence and their fluorescence spectra have been obtained. From the fluorescence-microwave double-resonance experiments we conclude that the dominant part of the fluorescence comes from a singlet state that is the precursor of the previously observed triplet exciton states. The position of the fluorescence origin indicates that we have to do with a trap. The excitation concerns a so-called mini-exciton consisting of two neighbouring C_{60} molecules. The second and minor component of the fluorescence rapidly loses intensity upon raising the temperature and vanishes above ≈ 10 K. It is interpreted as fluorescence from a shallow trap and the spectrum points to a monomolecular C_{60} X-trap.

2. Experimental

Crystals of C_{60} have been grown under vacuum by multiple sublimation starting from 99.9% pure material [20]. Each of the samples that we studied consisted of some tens of small crystals (diameter ≈ 0.2 mm). After crystallization we added 0.9 bar of helium gas (5N) in order to achieve a good heat contact between the crystals and the glass tube. Control experiments in the presence of air resulted in fluorescence spectra comparable to those reported here. The solution of C_{60} has been prepared by dissolving some crystals in decaline/cyclohexane (3:1 v/v).

To measure fluorescence and fluorescence-excitation spectra, C_{60} was excited by an Ar^+ laser or an Ar^+ pumped dye laser. Plasma lines from the Ar^+ laser were suppressed using a 545 nm low pass filter. The laser powers used in this study were always so low that the emission intensity varied linearly with the excitation intensity. The emission of the sample was focused onto the entrance slit of a 1 m monochromator (resolution 0.2 nm) and fluorescence spectra were detected using an optical multichannel analyzer (EG and G OMA-Vision-CCD). We corrected these spectra for the wavelength dependence of the quantum efficiency of the CCD. For fluores-

³ In solid-state spectroscopy emission is often referred to as photoluminescence. We will use the term fluorescence throughout to emphasize that we consider singlet–singlet transitions, i.e. to distinguish this emission from the long-lived phosphorescence [8].

cence-excitation spectra we detected the fluorescence – at a fixed position of the monochromator – with a photomultiplier (RCA c31034A). The fluorescence-excitation spectra have been corrected for the variation in the output intensity of the dye laser with wavelength. Wavelength calibration was performed using a neon lamp, which results in an accuracy of $\pm 3 \text{ cm}^{-1}$ for the fluorescence spectra and $\pm 7 \text{ cm}^{-1}$ for the fluorescence-excitation spectra.

To obtain fluorescence-microwave double-resonance spectra use was made of a resonant LC circuit ($Q \approx 500$). Microwaves were provided by a sweep oscillator (HP 8350B) and amplitude modulated by a p-i-n diode at 250 Hz. The emission was focused onto the entrance slit of a 1 m monochromator and detected with a germanium detector (North Coast EO-817L). The synchronous change of the emission was measured by a lock-in amplifier and recorded while scanning the monochromator. We did not correct the double-resonance spectra for the variation in the quantum efficiency of the germanium detector. It is known that this detector is sensitive above 800 nm and much less at shorter wavelengths.

3. Results and discussion

Fluorescence spectra of different single-crystal samples of C_{60} at 1.2 K are shown in Fig. 1. The spectra have been obtained upon excitation at 514 nm. A spectrum like the one in Fig. 1a we typically observe when crystals are excited at wavelengths shorter than 684 nm albeit that the intensity ratio of some bands, e.g. those at 734 and 757 nm, varies with sample. On the other hand, for excitation wavelengths between 684 and 734 nm we invariably register a spectrum like the one in Fig. 1b. The bands seen in this spectrum also occur in the spectrum of Fig. 1a which suggests that the latter spectrum actually represents a superposition of spectra. This is corroborated by the observation of the spectrum in Fig. 1c that we found for one of our samples. Indeed, the spectrum in Fig. 1a can be reconstructed as a weighted sum of the spectra in Figs. 1b and 1c.

Besides the fluorescence spectra, the corresponding excitation spectra are given in Figs. 1b and 1c as well. The excitation spectrum in Fig. 1b shows some structure, while the one in Fig. 1c is more or less

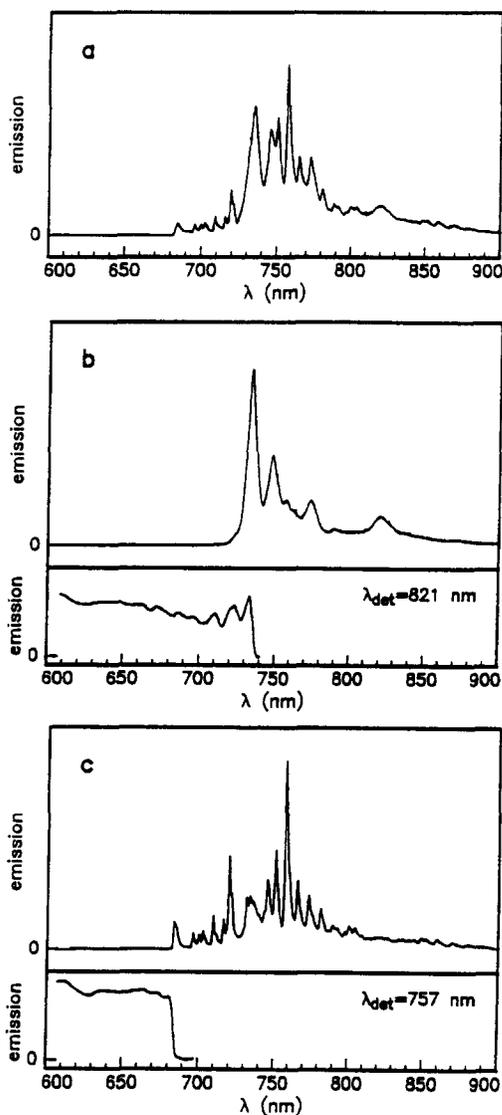


Fig. 1. Fluorescence (excitation wavelength 514 nm) and fluorescence-excitation spectra for different single-crystal samples a, b and c of C_{60} at 1.2 K. From top to bottom: (a) fluorescence spectrum, (b) fluorescence spectrum and fluorescence-excitation spectrum, detection wavelength 821 nm, (c) fluorescence spectrum and fluorescence-excitation spectrum, detection wavelength 757 nm.

flat. Both show saturation behaviour because of complete absorption of the exciting light by the crystals owing to their thickness. The important observation is that the onsets of excitation and emission coincide within the resolution of the present experiments (1

nm). Apparently the bands at highest energy in the fluorescence spectra, at 734 and 684 nm respectively, represent electronic origins and the bands at lower energies vibronic transitions. The bandwidth and the intensity distribution over the various vibronic bands largely differs in the two fluorescence spectra. The 734-spectrum, as we will call the fluorescence spectrum in Fig. 1b from now on, consists of a few relatively broad bands whose intensity decreases with the distance from the 0–0 transition. The 684-spectrum, the fluorescence spectrum in Fig. 1c, is rich in narrow bands and the intensity is maximum for a vibronic band at 1425 cm^{-1} from the 0–0 transition. The energies corresponding to the maxima of the vibronic bands relative to the origins for the 734-spectrum and for some prominent vibronic bands in the 684-spectrum are summarized in Table 1.

Apparently the fluorescence of crystalline C_{60} at 1.2 K originates from (at least) two emitting species unless the excitation energy is insufficient to reach both emitting states, i.e. for wavelengths longer than 684 nm. It is as yet unclear which factor determines the ratio between the two fluorescences. We noticed that heating of the crystal at 160°C for about one week on a vacuum line (10^{-6} mbar) favours the 684-spectrum, an observation that deserves further attention. Above ≈ 10 K only the 734-spectrum is left. The 684-spectrum loses intensity upon raising the temperature above 1.2 K and disappears around 10 K. There is no irreversible change of the crystal,

since the 684-spectrum reappears upon lowering the temperature. This suggests that the emission at higher energy originates from a shallow trap although an interpretation in terms of band-edge fluorescence cannot be excluded.

Fluorescence-microwave double-resonance experiments at 1.2 K allow a further characterization of the fluorescence of crystalline C_{60} . Previously we have shown that transitions between triplet sublevels of crystalline C_{60} can be detected as microwave-induced changes of the fluorescence [19]. The corresponding fluorescence-detected magnetic-resonance spectrum, upon excitation of a single crystal of C_{60} at 514 nm, is reproduced in Fig. 2a. Spectra like this one are being measured by scanning the microwave frequency and detecting on the total fluorescence. If we now keep the microwave frequency fixed at 202 MHz, one of the resonances in Fig. 2a, and disperse the fluorescence, the spectrum in Fig. 2b is found. Identical, although weaker, spectra have been observed when irradiating the crystal with microwaves of 122, 270 or 301 MHz. The fluorescence-microwave double-resonance spectrum in Fig. 2b is identical to the 734-spectrum in Fig. 1b. No trace of the bands in the 684-spectrum of Fig. 1c is present although the fluorescence spectrum of the sample under the same excitation condition looked like the one in Fig. 1a. This means that the triplet states characterized by the zero-field transitions in Fig. 2a get populated through the singlet state that gives rise to the 734-spectrum and not through the singlet state

Table 1

Data corresponding to the fluorescence spectra for single crystals of C_{60} at 1.2 K. Positions for some bands of the 684 spectrum (cf. Fig. 1c) and for the bands of the 734 spectrum (cf. Fig. 1b). Shifts of the vibronic bands with respect to the electronic origins and the possible assignment of these bands based upon calculated infrared and Raman frequencies (Refs. [23–25])

684-spectrum				734-spectrum			
λ (nm)	σ (cm^{-1})	$\Delta\sigma$ (cm^{-1})	assignment	λ (nm)	σ (cm^{-1})	$\Delta\sigma$ (cm^{-1})	assignment
683.6	14629			733.6	13631		
695.9	14370	259	h_g	747.7	13374	257	h_g
719.6	13897	732	h_u	773.5	12928	703	h_g
745.2	13419	1210	a_u/t_{1u}	789.6	12665	966	$703 + 257$
750.6	13323	1306	h_u/g_u	821.1	12179	1452	h_g/a_g
757.3	13204	1425	t_{1u}				
765.3	13067	1562	h_g				
773.0	12937	1692	$1425 + 259$				
781.1	12802	1827	$1562 + 259$				

that gives rise to the 684-spectrum. Most likely the microwave transitions and the 734-fluorescence spectrum belong to the same species, different from the one responsible for the 684-fluorescence spectrum.

Combining the present spectral information with the earlier analysis of the triplet data, we interpret the 734-spectrum as the fluorescence from traps that consist of pairs of C_{60} molecules, i.e. the emitting state corresponds to a Frenkel mini-exciton. Electron-spin-echo experiments at 95 GHz [18] have shown that the microwave transitions seen in Fig. 2a derive from triplet Frenkel excitons which have been called α (at 122 and 270 MHz) and β/γ (at 202 and 301 MHz). The observed principal values and axes directions of the fine-structure tensors have been consistently described as averages of the fine-structure data for pairs of C_{60} molecules. For α the interpentagon bond of one C_{60} molecule faces a

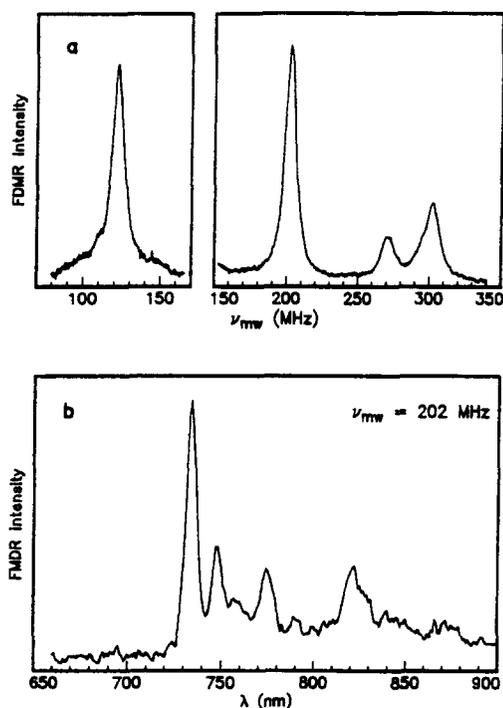


Fig. 2. (a) Fluorescence detected magnetic-resonance (FDMR) spectrum in zero field of a single crystal of C_{60} at 1.2 K, excitation wavelength 514 nm. (b) Fluorescence-microwave double-resonance (FMDR) spectrum in zero field of a single crystal of C_{60} at 1.2 K, excitation wavelength 628 nm, microwave frequency 202 MHz.

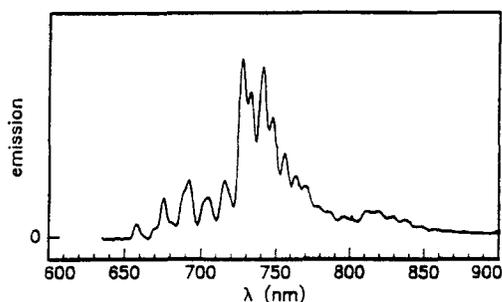


Fig. 3. Fluorescence spectrum of C_{60} in decaline/cyclohexane at 1.2 K; excitation wavelength 514 nm, concentration 5×10^{-4} mol l^{-1} .

pentagon of a C_{60} neighbour while for β and γ the interpentagon bond of one C_{60} molecule faces a hexagon of a C_{60} neighbour. Both orientations occur in a C_{60} crystal at low temperatures [21]. Triplets β and γ are only distinguishable in a magnetic field because they only differ in their orientation with respect to the crystal axes and not in their molecular properties. The detection of the corresponding microwave transitions on the 734-spectrum reveals that the α , β and γ triplet excitons become populated via the singlet state responsible for the 734-fluorescence. Although no proof, this singlet state therefore most probably concerns a Frenkel exciton as well. Because the emitting state lies about 1000 cm^{-1} below the band (vide infra), we conclude that we have to do with an X-trap that consists of a pair of C_{60} molecules over which the excitation is delocalized.

The vibronic intensity distribution of the 734-spectrum presents circumstantial evidence for this inference. This intensity distribution in no way resembles that of the fluorescence spectrum of an individual C_{60} molecule, as is clear from a comparison of the spectrum in Fig. 1b with that in Fig. 3, where we display the fluorescence spectrum of C_{60} dissolved in a decaline/cyclohexane glass. For the 734-spectrum the origin corresponds to the strongest vibronic band whereas the origin of the glass spectrum is weak. A pair that consists of neighbouring C_{60} molecules in the crystal does not possess the inversion symmetry of the individual C_{60} molecule. Consequently the origin is no longer strictly forbidden. An incidental distortion of the C_{60} molecule might well contribute to the exciton fluorescence and it is noteworthy in this respect that all vibronic

intensity in the 734-spectrum may be ascribed to Jahn–Teller active h_g modes (cf. Table 1).

What about the origin of the second fluorescence of the C_{60} single crystal at 1.2 K, the 684-spectrum? Although an impurity can never be fully excluded, we interpret this spectrum in terms of monomolecular C_{60} fluorescence. Possible impurities like $C_{60}O$ [22], C_{70} [5,6] as well as the photoproduct of C_{60} [22] can be excluded because their fluorescence spectra do not correspond to the 684-spectrum. The intensity distribution over the various vibronic bands in the 684-spectrum qualitatively resembles that observed for C_{60} in a glassy solution (cf. Figs. 1c and 3). Also a number of vibrational quanta occur that are characteristic for C_{60} (cf. Table 1). Two prominent bands at 732 and 1425 cm^{-1} from the origin can be assigned to Herzberg–Teller active h_u and t_{1u} modes, respectively [7]. The fact that the intensity is maximum for the 1425 cm^{-1} mode is particularly noteworthy. Negri et al. calculated this mode at 1437 cm^{-1} [23] and according to their CNDO/S calculations [7] this t_{1u} mode induces the largest oscillator strength for the lowest $^1T_{1g}$ to ground state transition. The vibronic bands in the 684-spectrum are all relatively narrow which points to a weak and homogeneous interaction of the emitter and the matrix. We tentatively conclude that this fluorescence derives from a shallow monomolecular C_{60} trap in the C_{60} crystal, although an interpretation in terms of band-edge fluorescence cannot be excluded. This conclusion positions the lowest singlet exciton band slightly more than 14600 cm^{-1} above the ground state which means that the 734-spectrum results from a trap state about 1000 cm^{-1} below this band. A more detailed description and full vibronic analysis of the spectrum in Fig. 1c will be given elsewhere [22].

The observation and assignment of the 734-spectrum for a high quality C_{60} single crystal provides insight into the various fluorescence data reported for solid state C_{60} in the literature. The film spectra in Refs. [9–13] follow the overall shape of the 734-spectrum in Fig. 1b albeit that the vibronic structure becomes obscured due to strong inhomogeneous broadening in the film compared to the crystal. In some of the reported film spectra an additional band shows up around 705 nm which has no pendant in our crystal spectrum [9,14,15]. This extra fluorescence most probably derives from a C_{60} -related

chemical impurity. The single crystal spectra reported by Guss et al., measured at 10 K, were interpreted as a superposition of six spectra assigned to bulk C_{60} and five X-traps [17]. The authors describe each spectrum as composed of h_u and t_{1u} false origins in combination with a weaker a_g band. The fluorescence spectrum of the crystals that we studied corresponds at 10 K to the 734-spectrum in Fig. 1b. We have no reason to assign the 734-spectrum to more than one emitting species because the corresponding excitation spectrum, as given in Fig. 1b, is the same for detection at all the vibronic bands in the 734-spectrum. In addition we need not invoke false origins in order to describe the intensity distribution. The origins of excitation and fluorescence coincide which led us to interpret the 734 nm transition as a true origin and the shift of the vibronic bands in the fluorescence spectrum with respect to this origin as ground-state vibrational quanta. The fluorescence does not result from a molecular state of gerade symmetry but from an excited state delocalized over a pair of C_{60} molecules. The symmetry is no longer I_h and the 0–0 transition becomes allowed.

In summary, the fluorescence spectrum at 1.2 K of the high-purity single crystals of C_{60} that we studied is found to be a superposition of two spectra. The first one, the spectrum in Fig. 1c, was only present when exciting at wavelengths shorter than 684 nm and even then rather weak for most crystals. It is assigned to a shallow monomolecular C_{60} trap although an interpretation as band-edge fluorescence cannot be excluded. The second and dominant one, the spectrum in Fig. 1b, is assigned to a trap consisting of a pair of C_{60} molecules whose excitation corresponds to a Frenkel mini-exciton. The vibronic structure of this spectrum, the relatively strong electronic origin and the prominence of h_g modes points to a Jahn–Teller induced distortion of the C_{60} molecule in the excited state.

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