Phosphorescence of C_{60} at 1.2 K

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Abstract

Phosphorescence has been observed at 1.2 K both for C_{60} dissolved in a decaline/cyclohexane glass and for single crystals of C_{60}. The phosphorescence spectrum of C_{60} in the glass reveals a weak origin at 798.1 ± 0.5 nm, while most of the intensity shows up in vibronic transitions. The phosphorescence of crystalline C_{60} consists of two parts. One of these, with the origin of its phosphorescence spectrum at 826 nm, derives probably from a shallow C_{60} X-trap although an excitonic origin cannot be excluded. The other, with the origin of its phosphorescence spectrum at 862 nm, originates from triplet states previously recognized by magnetic resonance experiments. These concern excitations delocalized over pairs of C_{60} molecules, so-called mini-excitons that are deep X-traps in the C_{60} crystal.

1. Introduction

One of the remarkable photophysical properties of C_{60} concerns its high quantum yield of triplet formation. From a $^1O_2$ luminescence study Arbogast et al. [1] concluded a lower limit of the quantum yield for C_{60} in benzene upon excitation at 532 nm of 0.96 ± 0.04, while subsequent laser-flash-photolysis [2,3] and photothermal [4] experiments also revealed a value near unity. In spite of the fact that upon optical excitation virtually all molecules seem to decay through the lowest metastable triplet state, as yet phosphorescence has neither been reported from C_{60} in a hydrocarbon glass nor from solid C_{60}.

In an earlier experiment, Zeng et al. [5] made use of the external heavy-atom effect to detect the phosphorescence. The interaction of C_{60} with ethyl-iodide in a methylcyclohexane/2-methyltetrahydrofuran/ethyl-iodide glass was found to effectively quench the fluorescence of C_{60} and to promote radiative triplet decay. From this experiment it was concluded that the lowest triplet state of C_{60} lies 12690 ± 30 cm^{-1} above the ground state. From triplet–triplet energy-transfer experiments in benzene the energy of the lowest triplet state was estimated to be 37.5 ± 4.5 kcal/mol (13116 ± 1574 cm^{-1}) [1], while photoacoustic experiments resulted in values of 12600 ± 200 [6] and 13100 ± 300 cm^{-1} [4]. Oxygen-enhanced absorption spectra pointed to a lowest triplet state of C_{60} at least as low as 14390 cm^{-1} above the ground state [7]. High-resolution electron energy-loss spectra of a film of C_{60} on Si revealed a lowest electronic excitation at 1.55 eV (12500 cm^{-1}) [8] that may well concern the transition to the lowest triplet state.

Triplet–triplet absorption and electron paramagnetic resonance experiments at various temperatures

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have resulted in values of the triplet lifetime between some tens and hundreds of microseconds (see e.g. Refs. [1,9]). Such rather short lifetimes point to an intrinsically efficient radiationless de-excitation. It is unlikely that only the relatively small energy gap between the triplet state and the ground state is responsible for the fast radiationless decay because this gap is about the same for C_{70}, whose phosphorescence is easy to measure and shows a triplet lifetime more than two orders of magnitude longer than that of C_{60} [9]. This observation suggests that a distortion of C_{60} upon excitation plays a role. Both Jahn–Teller and pseudo Jahn–Teller interactions may be expected to contribute, given the orbital degeneracy of the lowest triplet state and the density of triplet states at energies just above the lowest one.

Quantum chemical calculations indicate that the lowest triplet state of C_{60} transforms as T_{2g} under the symmetry operations of the icosahedral point group [10,11]. For the free molecule one would therefore expect a distortion along a vibrational coordinate of h_g symmetry. In a crystal (solvent) field the actual distortion of the C_{60} molecule will be determined by the optimum balance between Jahn–Teller and crystal-field stabilization. Indications for a distortion of C_{60} upon excitation have been obtained from triplet electron paramagnetic resonance (EPR) experiments. Wasielewski et al. [9] were the first to report triplet EPR data at 5 K for C_{60} dissolved in toluene. They observed a complete lifting of the spin degeneracy which is compatible with a symmetry lowering to at least D_{2h}. Electron-spin-echo detected EPR spectra of a single crystal of C_{60} at 1.2 K have revealed several triplet states corresponding to excitations delocalized over more than one C_{60} molecule [12]. Subsequently the existence of such triplet excitations was verified by the observation of the corresponding zero-field transitions between the triplet sublevels as microwave-induced changes of the fluorescence [13]. The interpretation of the fine-structure tensors for these delocalized triplet states of the crystal was found to point to a distortion of the individual molecules to D_{2h} as well [12].

Meanwhile, in spite of all the investigations of the triplet state that are made possible by efficient inter-system crossing, the direct observation of the phosphorescence of C_{60} remained a challenge. In this Letter, we will show that the phosphorescence, although weak and only a minor component of the emitted radiation, can be detected both for C_{60} dissolved in a hydrocarbon glass and for single crystals of C_{60}. Furthermore, the phosphorescence spectra shed considerable light on the photophysics of this interesting fullerene system.

2. Experimental

Crystals of C_{60} have been grown under vacuum by multiple vapour phase sublimation [14] starting from 99.9% pure material and are not exposed to open air. After preparation we added 0.9 bar of helium gas (5N quality) in order to get a good heat contact between the crystals and the glass tube. Each of the samples that we studied optically consisted of some tens of small crystals (diameter ≈ 0.1 mm). For the samples of C_{60} in solution some crystals were dissolved in decaline/cyclohexane (3:1 v/v), a mixture that converts into a nice glass upon cooling. Degassing of the solution by repeated freeze–thaw cycles did not affect the phosphorescence spectrum. It is noteworthy that the air-free solutions turned out to be unstable under exposure to light at room temperature. To measure the iodide induced phosphorescence spectrum of C_{60} a crystal was dissolved in methylcyclohexane/tetrahydrofuran/ethyl-iodide (2:1:1 v/v/v).

The experimental challenge of detecting the phosphorescence of C_{60} rests in the fact that the phosphorescence spectrally overlaps with the fluorescence which is at least a hundred times more intense even at the phosphorescence maximum. To achieve separation, C_{60} samples are irradiated by light pulses with a duration of about 300 µs from an Ar^+ laser or a cw dye laser chopped by an acousto-optic modulator. The light emitted by the sample is focused through a long-pass filter (Schott RG 715 for glassy samples and Schott RG 780 for crystals) onto the entrance slit of a 1 m monochromator (resolution 2.5 nm) and detected by a red-sensitive photomultiplier (RCA c31034A). In order to discriminate the phosphorescence from the fluorescence, emitted photons are counted during a time interval A from 25 up to 525 µs after the excitation pulse. To get rid of the background, photons are counted as well during a time interval B from 1000 to 1500 µs after the light pulse and their number is subtracted from the number

counted during period A. This sequence is repeated at a frequency of 500 Hz. After accumulation of the difference for 20 s, the result is transferred to a computer. Repeating this for different detection wavelengths yields the phosphorescence spectrum. Phosphorescence-excitation spectra are measured by scanning the dye laser, while detecting the phosphorescence at a fixed wavelength.

To detect microwave-induced changes in the phosphorescence the number of emitted photons is counted during a period of 500 μs following a light pulse during which the sample is irradiated by a resonant microwave field. During the next light pulse no microwaves are applied to the sample and the number of emitted photons is counted during a similar time interval and subtracted from the result of the first period. This difference is accumulated for 40 s and then treated in the same way as for the phosphorescence spectrum.

All spectra have been measured at 1.2 K. The laser powers used in this study were always so low that the emission intensity varied linearly with the excitation intensity. The phosphorescence spectra have been corrected for the variation in the quantum efficiency of the photomultiplier, the phosphorescence-excitation spectra for the variation in the output intensity of the dye-laser with wavelength.

3. Results and discussion

Upon pulsed laser excitation of samples of either C_{60} in a glass or crystalline C_{60} a weak phosphorescence shows up which can be detected via a monochromator and a red-sensitive photomultiplier, as illustrated in Fig. 1. During the excitation pulse, fluorescence is observed and a transient is clearly seen related to the building up of triplet state population [15]. After the laser pulse only emission from the long-lived triplet state is left. This weak phosphorescence can be made visible by extensive averaging. For C_{60} in a decaline/cyclohexane glass the phosphorescence decays at 1.2 K exponentially with a time constant of 410 ± 20 μs. The phosphorescence of the C_{60} crystals at 1.2 K is found to consist of two components (vide infra). The phosphorescence at 826 nm decays exponentially with a time constant of 40 ± 5 μs, that at 862 nm with a time constant of 400 ± 20
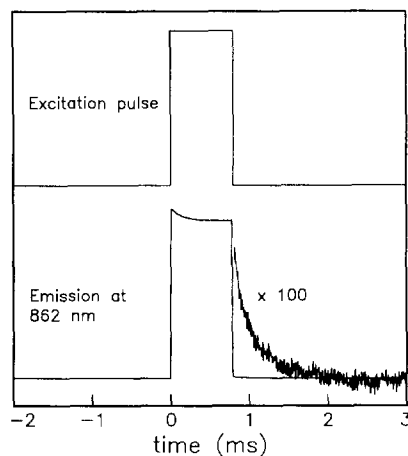

Fig. 1. Upper trace: the timing of the exciting laser pulse. Lower trace: the averaged (50000 times) emission intensity of a crystalline C_{60} sample at 862 nm (excitation wavelength 702 nm). During the excitation pulse fluorescence is observed and a transient is visible. This is due to a building up of population in the triplet state corresponding to about 8% in steady state. After the light pulse the phosphorescence can clearly be distinguished. It has a decay time of about 400 μs.

μs. For one sample the phosphorescence at 862 nm showed a faster decay (220 ± 20 μs). Apparently an extra decay channel was present in the latter case, an observation that deserves further attention.

Even at the wavelength for which the phosphorescence is maximum, the fluorescence is more than a hundred times as intense as the phosphorescence. Therefore, in order to monitor the phosphorescence spectra we made use of gated photon counting as described in Section 2.

3.1. Phosphorescence spectra of C_{60} in a glassy matrix

The phosphorescence spectrum at 1.2 K of C_{60} dissolved in decaline/cyclohexane upon excitation at 514 nm and the phosphorescence-excitation spectrum are shown in Figs. 2a and 2b. The excitation spectrum covers the wavelength region corresponding to the red edge of the singlet absorption. Although the weakness of the phosphorescence limits the quality of this spectrum, bands may be recognized at 652, 638, 630, 623 and 614 nm (with an accuracy of 1 nm). These positions nicely agree with those of the five lowest-energy transitions observed in the fluorescence-excitation spectrum of C_{60} in the same glass
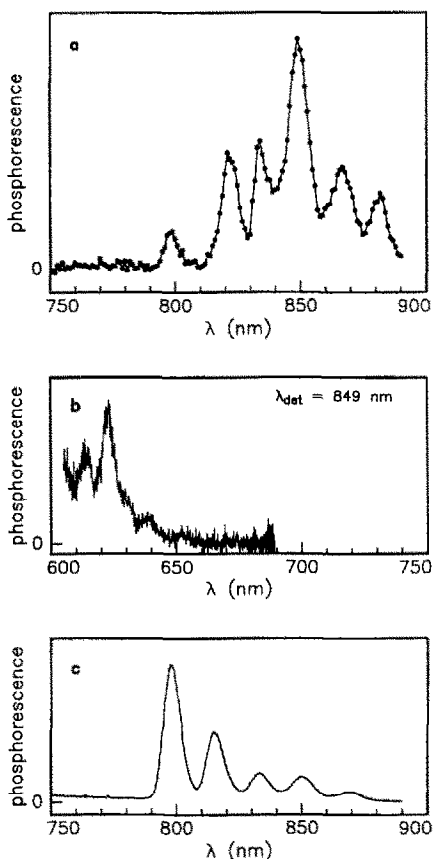
Fig. 2. (a) Phosphorescence spectrum of C_{60} dissolved in decaline/cyclohexane (3:1 v/v) in a concentration of 5×10^{-4} M (excitation wavelength 514 nm). The same spectrum, although noisier, has been observed for a sample with a concentration of 1×10^{-4} M. (b) The corresponding phosphorescence-excitation spectrum detected at 849 nm. (c) Phosphorescence spectrum of C_{60} dissolved in methylcyclohexane/tetrahydrofuran/ethyl-iodide (2:1:1 v/v/v) in a concentration of 5×10^{-4} M (excitation wavelength 514 nm).

[16], which corroborates the interpretation of the long-lived emission as the phosphorescence of C_{60}.

Six bands are clearly recognizable in the phosphorescence spectrum between 795 and 890 nm (Fig. 2a), whose positions are summarized in Table 1. The lack of sensitivity of the photomultiplier beyond 890 nm does not allow us to study the spectrum at longer wavelengths. We consider the band at 798.1 ± 0.5 nm to be the electronic origin of the phosphorescence, while the other bands are assigned to transitions involving vibrational levels of the ground state. The vibrational quanta agree with infrared and Raman data

for C_{60} and comparison with calculated [11,17] and experimental [18] vibrational frequencies suggests an assignment as given in the last column of Table 1. Quantum chemical calculations predict that the triplet state of lowest energy is of T_{2g} character [10,11]. Under icosahedral symmetry the $^3T_{2g} \rightarrow ^1A_g$ transition is both spin and orbitally forbidden, which would explain the weak origin in the phosphorescence spectrum. In addition the spin⊗orbit representation $(G_g + H_g)$ of this triplet state would point to Herzberg–Teller active vibrations of t_{1u}, t_{2u}, g_u, or h_u symmetry. The vibronic components that we observe in the phosphorescence spectrum can be assigned to these symmetry species (cf. Table 1) and most of the phosphorescence intensity seems therefore to be vibronically induced.

The position of the first band in the phosphorescence spectrum at 798.1 nm is close to that reported by Zeng et al. [5] who made use of the external heavy-atom effect to provoke phosphorescence from C_{60} dissolved in a glass. They detected only fluorescence from C_{60} in methylcyclohexane, but showed that this emission is replaced by phosphorescence upon adding ethyl-iodide. Their spectrum consists of a band at 796 nm accompanied by a weaker band at 812 nm, around 250 cm^{-1} from the origin. We have performed a similar experiment. The phosphorescence spectrum of C_{60} dissolved in a methylcyclohexane/tetrahydrofuran/ethyl-iodide glass (2:1:1 by volume) is shown in Fig. 2c. The origin at 798.0 ± 0.5 nm is the strongest transition and vibronic transitions show up at 815.2, 833.0, 850.6, 869.5 nm. The latter correspond to transitions involving one to four quanta of the Jahn–Teller active lowest-frequency h_g mode which is not pronounced in the phosphorescence spectrum of C_{60} in the pure hydrocarbon glass. Whereas the position of the origins in Figs. 2a and 2c is similar, the vibronic intensity distributions are much different. It is noteworthy that the h_g mode at ≈ 260 cm^{-1} is active for all three C_{60} triplets investigated in this study and perturbed by their environment: by iodide for the glass and by the crystal field for the X-traps in the single crystals (to be described in the next section). The orbitally degenerate triplet state is inherently sensitive to matrix variations and the interactions of C_{60} with its surroundings apparently changes the vibronic wavefunction significantly.

Table 1
The vibronic bands observed in the phosphorescence spectrum of C_{60} in decaline/cyclohexane (Fig. 2a). The accuracy of the tabulated wavelengths is ± 0.5 nm (≈ 7 cm^{-1}). The assignment is based on comparison with experimental (Ref. [18]) and calculated (Refs. [11,17]) vibrational frequencies

λ (nm)	ν (cm^{-1})	ν_R (cm^{-1})	Assignment
798.1	12530	0	0–0
820.7	12185	345	350 (t_{2u}) [b] or 358 (g_u) [b] or 361 (h_u) [c]
833.7	11995	535	527 (t_{1u}) [a] or 531 (h_u) [b]
848.7	11783	747	724 (h_u) [b]
866.4	11522	988	1007 (g_u) [b] or 999 (t_{2u}) [b]
881.8	11340	1190	1183 (t_{1u}) [a]

[a] Ref. [18].   [b] Ref. [11].   [c] Ref. [17].

3.2. Phosphorescence spectra of C_{60} crystals

The phosphorescence spectra of two crystalline samples of C_{60} at 1.2 K are shown in Figs. 3a and 3b. These spectra were obtained upon excitation at 702 nm. The spectrum of sample I shows a band at 862 and one at 882 nm and minor intensity at shorter wavelengths (the peak positions of these spectra are measured with an accuracy of ± 0.5 nm). In the spectrum of sample II at least three additional bands are clearly visible, at 826, 845 and around 855 nm. The ratio of the intensities of the part of the spectrum above and the part below 855 nm is found to vary from sample to sample. A sample that originally did

not phosphoresce below 855 nm, developed ample intensity in this region after heating at 160°C for about one week on a vacuum line (10^{-6} mbar). We conclude that (at least) two species can contribute to the phosphorescence of C_{60} crystals at 1.2 K, one with its 0–0 at 826 nm and the other with its 0–0 at 862 nm. The band at 845 nm, shifted by 272 ± 10 cm^{-1} with respect to 826 nm, and the band at 882 nm, shifted by 263 ± 10 cm^{-1} with respect to 862 nm, can be assigned to transitions from the two respective triplet states to the lowest excited vibrational level of the ground state, because this quantum corresponds to the C_{60} vibration of lowest frequency.

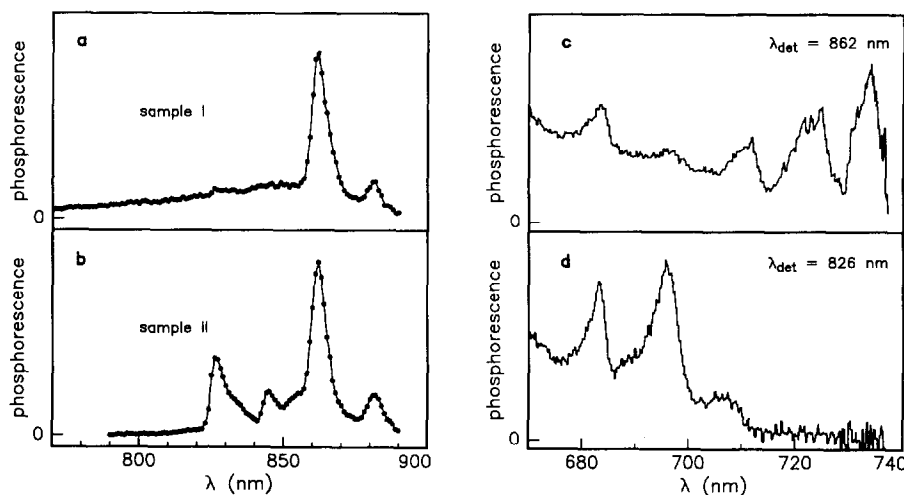As mentioned before, the phosphorescence at 826

Fig. 3. (a), (b) Phosphorescence spectra for two samples of C_{60} crystals (excitation wavelength 702 nm). A weak background is visible, particularly for sample I, which was also present for an empty sample tube. (c), (d) Phosphorescence-excitation spectra for sample II detected at 862 and 826 nm.

nm decays about an order of magnitude faster than that at 862 nm. The difference between the two phosphorescent species also shows up in the excitation spectra, as shown in Figs. 3c and 3d. The phosphorescence-excitation spectrum detected at 826 nm, reveals bands at 707, 696 and 683 nm, the phosphorescence-excitation spectrum detected at 862 nm reveals bands at 734, 725, 722, 711, 696 and 684 nm (the experimental error in these peak position amounts to ± 1 nm). The fact that both spectra have the 696 and 684 nm bands in common may be significant. As interpreted below, these phosphorescences are ascribed to traps of quite different depth. Our observation here suggests a trap-to-trap energy transfer, as is known for molecular crystals. Such an energy transfer may account for the order-of-magnitude shorter triplet lifetime of the 826 nm species and generally corroborates our interpretation.

We interpret the phosphorescence spectrum with its 0–0 at 862 nm, which we will call the 862-spectrum, as the phosphorescence of a trap that consists of two neighbouring C_{60} molecules in the C_{60} crystal. The excitation is delocalized over this pair, i.e. concerns a so-called mini-exciton. This conclusion is based on the observation of microwave-induced changes of this phosphorescence at microwave frequencies that according to previous experiments belong to triplet excitons and on a comparison of the phosphorescence-excitation spectrum in Fig. 3c with fluorescence-excitation spectra of crystalline C_{60}.

Electron-spin-echo experiments at 95 GHz on a single crystal of C_{60} at 1.2 K have revealed triplet states, called α, β and γ, corresponding to delocalized excitations [12]. Both the zero-field splittings and the directions of the principal axes of the fine-structure tensors have been described as projections of tensors of individual molecules on average common axes systems. A consistent interpretation for triplet α was found for a delocalization over C_{60} molecules characterized by a five-ring/double-bond nearest-neighbour contact, for triplets β/γ for a delocalization over C_{60} molecules characterized by a six-ring/double bond nearest-neighbour contact. The excitons β and γ are only distinguishable in magnetic field owing to their different orientations in the crystal. Subsequently the zero-field transitions corresponding to these triplet excitons have been detected as changes in the fluorescence: at 122 and 270 MHz for triplet α,

at 202 and 301 MHz for triplets β and γ [13].

To see whether the observed phosphorescence originates from the triplets α, β and/or γ, we looked for microwave-induced changes of the phosphorescence in zero field. For a microwave frequency of 301 MHz, the double resonance spectrum is given by the upper curve of Fig. 4. Here we used a sample that gives both types of phosphorescence, as can be seen in the lower curve of Fig. 4 (which looks like the spectrum of sample II in Fig. 3b). Only the part of the phosphorescence with its 0–0 at 862 nm is influenced by the microwaves. Similar double-resonance spectra, although weaker in intensity, were found upon irradiation of microwaves of frequencies 202 MHz (belonging to triplet β and γ) and 270 MHz (triplet α). We conclude that the phosphorescence with the 0–0 at 862 nm originates from the triplets α, β and γ. Apparently their phosphorescence spectra are so alike that these cannot be distinguished within the resolution of our experiment.

In a study on the fluorescence of crystalline C_{60} at 1.2 K we concluded that part of this fluorescence, the so-called 734-spectrum with its 0–0 at 734 nm, originates from a singlet state that is the precursor of the observed triplet states α, β and γ [19]. The phosphorescence-excitation spectrum of Fig. 3c looks identical to the fluorescence-excitation spectrum of the 734-
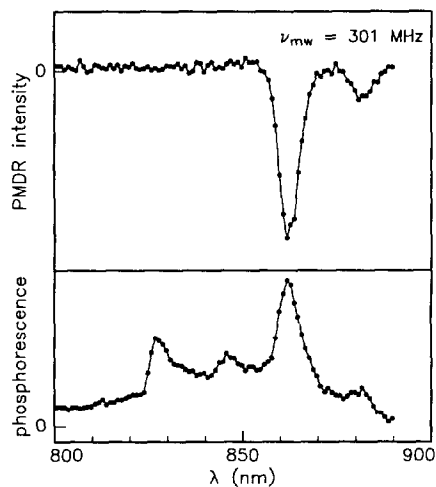

Fig. 4. Upper curve: Phosphorescence-microwave double-resonance (PMDR) spectrum of crystalline C_{60}, excitation wavelength 696 nm, microwave frequency 301 MHz. The lower curve represents the phosphorescence spectrum for the same sample at the same excitation wavelength.

spectrum [19]. They have a 0–0 transition around 734 nm and vibronic bands at shorter wavelengths in common. This confirms the assignment of the 862-spectrum to the triplets α, β and γ. Moreover we concluded in the study on the fluorescence that the singlet state with its 0–0 at 734 nm forms a deep X-trap [1] in the crystal, about 1000 cm^{-1} below the singlet band-edge. The phosphorescent triplet state at 862 nm may be estimated to be at least 500 cm^{-1} below the triplet band-edge, since also a phosphorescing species is observed with its 0–0 at 826 nm. It is unlikely that this 0–0 band originates from a triplet state above the band-edge. Therefore the triplets α, β and γ form deep X-traps in the C_{60} crystal. This suggests, as we concluded from our fluorescence study of crystalline C_{60} [19], that these triplets are not delocalized over many molecules in a chain, but over a pair of C_{60} molecules.

What about the second phosphorescence observed for most crystals, the spectrum with its origin at 826 nm, to which we will refer as the 826-spectrum? The vibronic band in this spectrum at 845 nm is shifted by 270 ± 10 cm^{-1} with respect to the 0–0. Because this is a characteristic vibrational quantum of C_{60}, we can safely exclude that this phosphorescence derives from an impurity. For the time being we lack additional information that allows a specific assignment. We did not observe any fluorescence from a C_{60} crystal with an origin at 707 nm (see the excitation spectrum of Fig. 3d). We did not detect any microwave-induced changes in the 826-spectrum although we looked for it in the microwave region of 50–500 MHz. We paid special attention to the frequencies corresponding to the zero-field transitions of the C_{60} molecule in a glass (357 and 330 MHz [20]), but without success. For the moment we attribute the 826-spectrum to another C_{60} X-trap. The occurrence of more traps in a molecular crystal is not unusual because of the presence of various crystal imperfections such as vacancies, dislocations or chemical impurities. Nevertheless, even the assignment to band-edge phosphorescence cannot be excluded. More experiments are needed and in particular the fact that the

826-phosphorescence may be induced by heating the crystals for some time deserves further attention.

4. Conclusion

Separation of phosphorescence from fluorescence in the time domain has enabled the detection of phosphorescence spectra at 1.2 K for C_{60} in a hydrocarbon glass and for crystalline C_{60}. The phosphorescence in all cases is only a minor component of the emission and spectrally hidden under the long-wavelength tail of the much more intense fluorescence. For C_{60} in a decaline/cyclohexane glass the phosphorescence reveals a weak origin and most of the intensity is found to be vibronically induced. For single crystals of C_{60} the phosphorescence is the sum of two contributions. The longest wavelength phosphorescence originates from previously recognized X-traps consisting of pairs of C_{60} molecules. The shorter wavelength phosphorescence is attributed to a shallow trap although an excitonic origin cannot be excluded.

The energy of the various triplet states of the crystal being known, a more detailed study may well be possible. Experiments in which we try and excite the C_{60} crystal selectively in either of its phosphorescent states are presently underway in our laboratory.

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[1] The term X-trap refers to the fact that we deal with C_{60} molecules in the proximity of physical imperfections or chemical impurities in the crystal. Their fluorescence and phosphorescence spectra are characterized by C_{60} vibrational frequencies.

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