

Luminescence excitation spectra of C60 films

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The luminescence excitation and emission spectra of C60 films are presented as functions of temperature and sample thickness. Especially for thicker films, but even for thin films, the excitation spectra deviate from the absorption spectra. The excitation spectra are compared with photoconductivity spectra of C60 films. The changes in excitation and photoconductivity spectra bear a certain resemblance.

1. INTRODUCTION

This paper deals with the luminescence excitation and emission spectra of C60 films as functions of temperature and sample thickness. The excitation spectra also add information on effects which occur with photoconductivity experiments.

2. EXPERIMENTS

2.1. Materials

The material used in the experiments involved commercially obtained C60 with a purity exceeding 99.9% as established with HPLC. Films on quartz substrate were obtained by vacuum deposition. The thickness of C60 films for luminescence experiments ranged from about 20 nm to 150 nm. In case of samples for photoconductivity experiments, first a pair of interdigitated gold electrodes was deposited.

2.2. Luminescence measurements

Both emission and excitation spectra of C60 films were recorded at various temperatures in the range of 77 K to 300 K. The excitation wavelengths used for the emission spectra were: 330, 360, 510, 550, 610 and 640 nm; the monitoring (or emission) wavelengths for the excitation spectra were chosen: 735, 745, 805 and 820 nm. The luminescence measurements were carried out on a JASCO FP-777 Spectrofluorometer in its most sensitive mode. An Oxford DN1704 cryostat (adapted for a temperature range of 77 - 500 K) with ITC-4 temperature controller was used for all here reported spectra. The artefacts arising in this spectrometer mode and with the cryostat were investigated and corrected for.

All samples for luminescence have been exposed subsequently to argon on releasing vacuum of the deposition chamber; to air during transport to the

spectrometer and during storage in small perspex boxes; and to helium after evacuation of the cryostat. The helium improves the heating and cooling of the sample. To investigate the effect of the oxygen content of the samples, the luminescence of several samples was measured again after baking in the cryostat for at least 16 hours at 500 K and in vacuum (about 10^{-4} Torr). After baking and cooling down to room temperature, helium was introduced.

In addition the emission intensity of one C60 sample was measured as a function of temperature. The sample had been baked prior to these luminescence measurements. In this experiment the excitation occurred at 330 nm and the emission was monitored at 745 nm. The temperature scan ran stepwise from 77 K to 450 K. The stepsize was chosen smaller near expected phase transitions. The emission was recorded every time the temperature of the sample appeared stabilized at the set temperature as judged from the temperature of the sample cell and the luminescence intensity.

2.3. Photoconductivity measurements

The photoconductivity spectra were measured using the same vacuum chamber as for vacuum deposition of the C60 films. This enabled to measure films also without exposing them to air (and oxygen in particular). Such measurements are referred to as 'in-situ'. The presence of oxygen, in contrast to that of nitrogen, has a large impact on the photoconductivity of C60 thin film [1]. The exciting light was obtained from a xenon lamp with an attached monochromator. The C60 was irradiated through the substrate, i.e. directly at the electrodes. The photon flux was kept constant at $2 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ for all wavelengths by means of a computer controlled neutral density filter. Both oxygen exposed and in-situ samples were measured.

3. RESULTS AND DISCUSSION

3.1. Emission spectra

Emission spectra measured at 77 K and with various excitation wavelengths are shown in figure 1. The spectra show the characteristic maximum at about 735 nm. The second order derivative of the spectra revealed the position of at least two other peaks, namely at about 772 and 820 nm, though indications for the presence of weaker features are also found. Except for the intensity, the emission spectra did not seem to vary with the excitation wavelength. Baking samples for about 16 hours at 500 K and in vacuum (about 10^{-4} Torr) increased the emission with not more than 50% and the general shape of the spectrum remained unaltered. Preliminary in-situ luminescence measurements followed by oxygen exposure indicated that the resulting quenching reduces the luminescence intensity not more than about 50%.

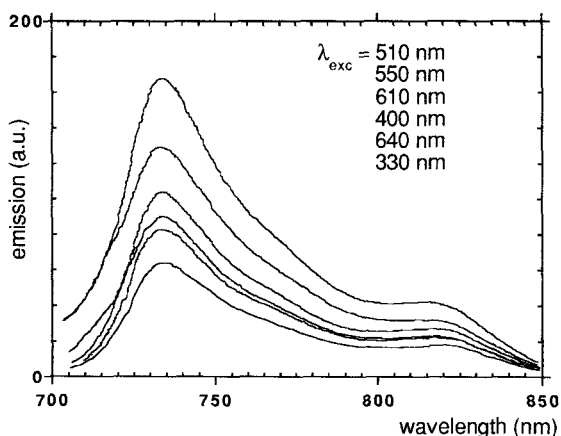


Figure 1. Emission spectra of C60 film obtained at various excitation wavelengths

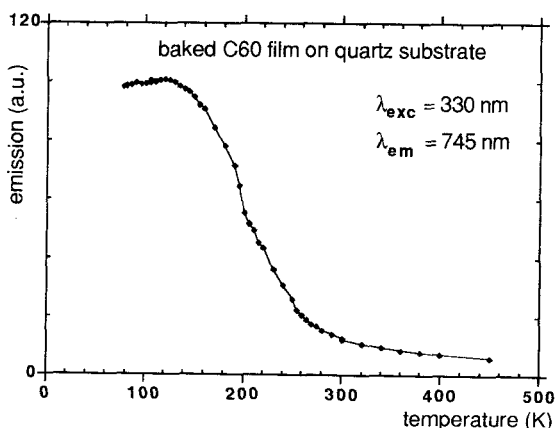


Figure 2. Temperature dependence of luminescence intensity

The emission increases with decreasing temperature down to roughly 100 K, which is in agreement with reports of various authors (e.g. [2,3]). A more detailed study is shown in figure 2. With increasing temperature the luminescence slightly increases until about 120 K after which the intensity drops dramatically. From about 260 K the intensity starts to fall off less rapidly. A phase transition of C60 occurs at about 260 K (primitive cubic to face centered cubic) [4]. Furthermore C60 is known to reorientate between 260 K and about 100 K [5,6,7], which apparently is accompanied with a drastic change in luminescence properties. On the slope other changes in gradient can be seen. These may be associated with structural reorientation of the C60 solid.

3.2. Excitation spectra

The shape of the luminescence excitation spectra appeared to be similar at all monitoring wavelengths. The thickness of the sample appeared to have a significant effect on the excitation spectra (see fig.3), particularly at short wavelengths. All spectra have a maximum at about 510 nm and the characteristic fine structure (phonon replicas) in the 510-700 nm range. The fine structure has been assigned to the $1T_{2g}$, $1T_{1g}$ and $1G_g$ states [8,9]. The intensity of this part of the excitation spectrum (about 510-700 nm) increases with the film thickness.

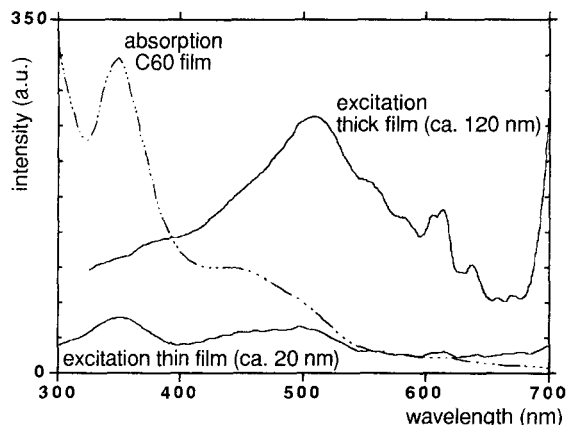


Figure 3. Excitation and absorption spectra of C60 films

The region of roughly 510-400 nm is also associated with forbidden transitions, which become more allowed in a solid as a result of a reduction in symmetry due to intermolecular interactions. This is in agreement with the fact that the absorption in this part of the spectrum is very weak for C60 solutions compared to C60 films. Especially for thick films, the excitation intensity at 510 nm appears much larger

than at about 435 nm, which is reverse to the case of absorption spectra. The reason for this is not yet understood. One possible explanation can be that the respective transitions at 435 and 510 nm both become more allowed in a solid, but contribute to the luminescence emission to a different degree. Other explanations involve the shape of the 350 nm peak or the penetration depth (see below).

In the range of about 350 nm, a second peak occurs for very thin films (order of 20 nm), which is in good agreement with the absorption spectrum of C60 film. This peak is due to an allowed transition, i.e. a T_{1u} state [8], but it becomes weak compared to the intensity at about 510 nm with increasing film thickness. It is almost absent in films with thicknesses of about 100 nm and up. For thick films relatively weak peaks are visible at about 330 and at 400 nm. These peaks may be due to the 350 nm peak appearing negative on a broader positive peak at the same position. A negative appearance of the peak would reflect an optical filtering effect, e.g. a layer of the sample might absorb light followed by non-radiative relaxation. If e.g. another layer might contribute to luminescence in such a way that a broader peak appears in the excitation spectrum, then this might yield two apparent peaks at 330 and 400 nm. In addition, such a negative peak in the 350 nm range might support the reverse order in intensity of the 510 and the 435 nm peak mentioned above. One way in which such a filtering effect could be brought about, is when the substrate plays an important role in the occurrence of luminescence and the C60 material would hardly luminesce by itself. This seems not to be the case however as with increasing film thickness also the absolute luminescence intensity increases over the complete spectral range. This was found for film thicknesses in the range 20 - 150 nm.

The relative increase of the 510 nm excitation peak compared to the 350 nm peak can be, at least partly, understood if the penetration depth of irradiating light is taken into account. The penetration depth of light with wavelengths 350 nm, resp. 510 nm, is about 26 nm, resp. 1400 nm. With increasing film thickness the maximum number of excited electrons is sooner approached for 350 nm than for 510 nm. This may explain the on-going increase of luminescence excitation at 510 nm with increasing film thickness. This would predict that for very thick films (order of .5 mm) the ratio of these two excitations would become stable.

The sample thickness dependence of the excitation spectrum may also be related to energy transfer. If luminescence only occurs at specific centers,

which may be in competition with quenching centers. If energy transfer takes place, then the quenching of excitation energy corresponding to the 350 nm peak, may be more likely as this transition is supposed to be allowed, in contrast to the 510 nm peak. If the distribution and/or spectral efficiency of these centers is related to the sample thickness, then energy transfer may add to the thickness effect. More measurements are however necessary to better assess the changes in this part of the spectrum and to resolve the effect of film thickness.

The overall intensity did depend on the temperature, which is in agreement with the case of the emission spectra. Albeit that the temperature dependence may be gradually different for several parts of the spectrum.

3.3. Photoconductivity spectra

Photoconductivity spectra are shown in fig.4. An absorption spectrum of C60 film is again included for comparison. The samples, of which the spectra are shown, have been exposed to oxygen to obtain a similar situation as in the case of the luminescence data. The photoconductivity spectra resemble the excitation spectra in broad outline. The characteristic fine structure, though less resolved due to the limited number of data points, is detectable in the spectra. For very thin films the photocurrent as a function of wavelength follows the absorption spectrum well. The 400-650 nm region of the photoconductivity spectra appears to be more pronounced however.

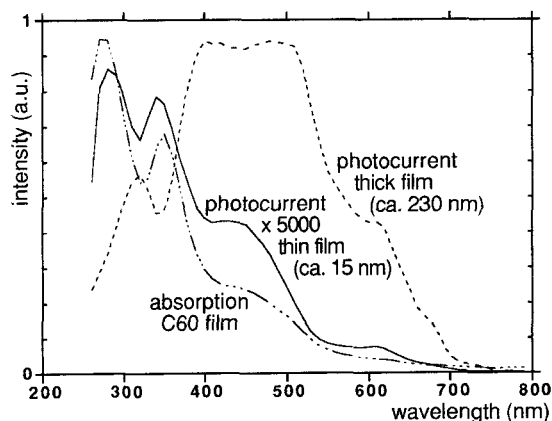


Figure 4. Photoconductivity and absorption spectra of C60 film

For thick films the photocurrent spectrum is dominated by two peaks at about 510 and 400 nm. A third peak appears at about 320 nm. The spectra of thick films show changes in the 300-450 nm range which are similar to the changes in the luminescence excita-

tion spectra. The absorption peak at 350 nm seems to coincide with an excitation dip. More experiments probing gradual changes are however necessary.

Exposure to oxygen decreases the photoconductivity with more than one to three orders of magnitude depending on the thickness of the sample. This effect happens within a few minutes [1]. The dark conductivity is even more affected, namely about one to four orders of magnitude. The least reduction is found for very thin (about 20 nm) samples. Baking of thin samples ($T=390\text{K}$, $p=10^{-6}\text{Torr}$, $t=4\text{hr}$) restores the photoconductivity to about 55% and the dark current to about 70% of the levels that are found for samples which have not been exposed to oxygen ('in situ' measurements).

3.4. Comparison of the spectra

The fact that the shape of the emission spectrum is practically independent of the excitation wavelength, indicates that internal conversion takes place to lower state(s) which are responsible for the luminescence emission. Alternatively or additionally, also radiative transitions might take place to the luminescent state(s). The emission of such transitions would be at wavelengths of 850 nm and longer, which is out of our detector range. For films the main responsible state for luminescence seems to be the $1T_{1g}$ state [8], but for solutions possibly both the $1T_{1g}$ and the $1G_g$ states are responsible [9]. These states together with the $1T_{2g}$ state are almost degenerate [8].

The similarity between the excitation spectra and the photoconductivity spectra is noteworthy. It is even more remarkable considering that the irradiation for photoconductivity is through the substrate. The similarity may suggest that the film thickness effect on the photoconductivity spectra may still largely originate from excitation processes as such. Though effects involving lifetimes and carrier transport on the photoconductivity spectra are likely to occur as well.

Baking of samples to eliminate or at least to reduce the presence of oxygen, has a much stronger effect on the photoconductivity spectra than on the luminescence spectra. The dark current and the photoconductivity could be restored to about 70%, resp. 55%, of the in-situ values. This is an increase of 1 or more orders of magnitude. The luminescence improved with not more than 50%. The quenching effect of oxygen on the photoconductivity seems only partly related to the excitation, and may be largely assigned to interference with the photogeneration and/or transport, like trapping electrons by oxygen with subsequent recombination.

4. CONCLUSIONS

Emission, excitation and photoconductivity spectra were presented in the present paper. A film thickness effect on the shape of both excitation and photoconductivity spectra is apparent. As this effect on these spectra is quite similar, it may have the same cause in both cases.

The emission and excitation spectra show a strong temperature dependence. Starting from 77 K initially the luminescence intensity slightly increases until about 120 K, after which a fast drop is encountered until about 260 K. The temperature dependence of the luminescence is supposed to be related to the reorientation of C60 in the temperature range 120-260 K. Luminescence measurements are thus able to monitor phase transitions in the case of C60.

Oxygen has a much stronger quenching effect on the photoconductivity than on the luminescence of C60 films.

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