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Cathodoluminescence of fullerene C₆₀

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Abstract. Fullerenes are not automatic candidates for luminescence analyses due to their highly absorptive nature. Consequently, very few luminescence experiments have been performed on fullerenes. This paper focuses on the luminescence properties of commercially available C₆₀ when bombarded by electrons (cathodoluminescence) and, to a lesser extent, x-rays (radiothermoluminescence) between 20 and 270 K. Wavelength resolved luminescence signals have been recorded as a function of temperature. CL experiments reveal pronounced anomalies that truncate the emission spectrum between 155 and 170 K. Other less pronounced anomalous features are detected at 70 and 245 K. These dramatic changes in the luminescence spectra are cautiously interpreted to be manifestations of phase transitions and support the view that cathodoluminescence (CL) can be used to monitor for phase transitions in fullerenes. The luminescence signals offer information on the mechanisms of the relaxation processes, including changes in charge trapping energies and emission spectra.

1. Introduction

The fullerenes, the third molecular form of carbon, have attracted an increasing amount of attention since their discovery in 1985 [1]. Their exceptional properties make them desirable as future components in numerous applications but in order to exploit fully their potential it is imperative to understand fullerene chemistry and physical properties. Consequently the fullerenes are being analysed with a suite of techniques and various probes at different temperatures. However, apart from photoluminescence [2–4], a literature search reveals no reports from other groups on studies of other luminescence technique applied to fullerenes.

Fullerenes invariably appear as black material and therefore would not immediately be associated with luminescence studies. Nevertheless, detection of light with photomultiplier tubes is extremely efficient and, even for strongly absorbing materials, photons can escape from depths of the order of the wavelength. Hence, as a surface probe of bulk material, or for carbon cages and nanotubes, luminescence is a viable and sensitive method for characterizing fullerenes. For any serious luminescence study, one must not only detect the total light, but must do so as a spectrally resolved signal. Additionally, caution is required for the detection and analysis of weak luminescence from fullerenes, since there are potential problems of

surface contamination that may also provide optical emission. However, surface contaminants may equally act as a sensitive probe.

Several Japanese papers have observed the fullerene photoluminescence signals from isolated particles suspended in toluene [2–4]. Such signals differ slightly depending on the fullerene concentration and changes in low temperature signals are related to solidification of the toluene. There was also some evidence for particle aggregation in the liquid. The influence of solvents should be recognized even in attempts to measure the solid-state properties of fullerenes as many of the methods of preparation can include solvent contamination, albeit at a very low concentration. Trace solvents may in fact be beneficial if they act as efficient luminescence probe sites.

It has previously been shown that no emission is detected from sublimed C₆₀ and that one can confidently assume that the emissions detected from unsublimed samples originate from impurities within the material, the prime candidates being solvents used in synthesis and extraction, in this particular case toluene [5]. A wider range of fullerene luminescence signals has included techniques such as radioluminescence (RL), thermoluminescence (TL), radio-thermoluminescence (RTL); where a sample is simultaneously irradiated, heated and monitored for luminescence emission and cathodoluminescence (CL). Some preliminary TL and RTL data from these sensitive routes to further characterize fullerene samples have been published [5, 6] and more details of the CL work are presented here.

In normal situations all techniques offer very sensitive means of detecting impurities and imperfections to concentrations well below parts per million. For bulk solids of transparent insulators RL is non-destructive. Whilst CL is a sensitive probe it is also a potential source of surface damage, since the electron beam can both redistribute electrons between existing trapping and luminescence sites, and generate both permanent and transient defects. For 'black' samples such as fullerenes or high-*T_c* superconductors light can escape from the surface and so CL is a valuable probe; however, any investigation involving CL excitation requires an appreciation of the alternative effects. It must also be recognized that for fullerenes all the sample is effectively 'surface' material. By electron irradiation, it has been possible to successfully detect the CL from highly absorbing materials such as the high-temperature superconductor material YBa₂Cu₃O₇ [7]. The performance of high-*T_c* superconductors is strongly influenced by impurities, therefore by RTL and CL it is theoretically possible to detect such defects by their influence on the luminescence properties of the material. CL is particularly attractive as an optical probe of the surface layers, since it is this region that will be most sensitive to oxygen loss or atmospheric chemical reactions.

Luminescence techniques are additionally attractive for studying fullerenes as they can potentially reveal discontinuous changes in material structures i.e. phase changes. One can use anomalous luminescence signals as a rapid exploratory probe for studying phase transitions [8]. During a first-order phase transition, whether exo- or endo-thermic, the lattice structure alters resulting in changes in the normal phonon spectrum and, more importantly, the relaxations and expansions of the lattice during the phase change will significantly modify both the band structure, the trap depths and the luminescence decay routes. As a result of a structural phase transition, the intensity of luminescence signals will alter, and as a result of changes in the energy levels the emission spectrum will change, most probably by broadening to lower energies. A classic example of the effects is seen for ammonium bromide [8].

The fullerene C₆₀ is understood to undergo two structural phase transitions at atmospheric pressures at 90 and 261 K. At room temperature, C₆₀ molecules rotate rapidly with three degrees of rotational freedom, i.e. orientationally disordered [9]. The structure of crystalline C₆₀ in phase I above 260 K is close packed face centred cubic, in which the rotations and orientations of individual C₆₀ molecules are unrelated to adjacent molecules [9].

The structure of phase II (between 260 and 90 K) is ordered simple cubic, in which the C₆₀ molecules shuffle [10]. Explanation of the structure of phase II has been given in terms of electrostatic repulsion and van der Waals bonding resulting in the facing of opposed faces of electron-poor and electron-rich regions [10]. Diffraction data also indicate the existence of a subtle anomaly at *circa* 155 K, which could represent another phase change dividing phases involving uniaxial rotations about a number of distinct directions and uniaxial rotation about a single (111) direction below 155 K [11].

At about 90 K C₆₀ undergoes a second major phase transition, below which the reorientational motion freezes with the persistence of some static disorder to 5 K [11]. Supporting evidence for the 90 K change also arises from PL experiments involving excitation by an Ar ion laser at 488 nm. Habuchi *et al* [12] report that the PL intensity from C₆₀ films decreases rapidly above 90 K and attributes it to the reorientational motion. These phase transitions represent major discontinuous changes in the lattice constant.

In contrast the 'rugby-ball-shaped' C₇₀ is not known to undergo any phase changes below room temperature [13]. At temperatures below ~ 276 K C₇₀ adopts a monoclinic structure and free rotation about the *c*-axis ceases. Documented experimental values for the temperature of this transition vary, which can be explained by a large supercooling effect at this transition (15–50 K), the possibility of minor C₇₀ phases and the presence of C₆₀ and solvent impurities, which can alter the stability, alternative phases and transition temperatures.

2. Experimental details

These experiments form part of a larger study on the luminescence characteristics of the fullerenes. This paper will concentrate on CL experiments on C₆₀. Nominally 'pure gold grade' C₆₀ in powdered form, supplied by Hoechst, was analysed, which is 99.78% pure. The solvent residues in this batch, determined by the manufacturer are toluene 0.21%, acetone 0.021% and diethylether at 0.032%.

Samples, in powdered form, were retained on thin aluminium discs by silicone spray and attached by vacuum grease to the cryostat heater stage. The luminescence emissions of samples were measured by the high sensitivity wavelength multiplexed spectrometer system at Sussex [14]. Spectral information is achieved by a wavelength multiplexed system with *f*/2.2 optics, capable of detection between 200 and 800 nm with a resolution of ~ 4 nm. In order to achieve this wavelength coverage with a high sensitivity and resolution, two sets of spectrometers and imaging photon detectors are employed; one set designed for the 'blue' spectral region (200–440 nm) and a second for the 'red' (380–800 nm) with an overlapping region. One advantage of wavelength multiplexing during dynamic heating experiments such as TL, RTL or CL, is that it is possible to confidently quote differences in the wavelengths of the peak temperatures to within ~ 1 K. Absolute values are less certain.

An electron beam is targeted vertically onto a sample with emission being recorded by the spectrometers positioned at 45° to the sample. Beam conditions vary depending upon the velocity and beam current. Electron beam conditions can vary significantly between experiments, for this research every effort has been made to keep conditions consistent from sample to sample. To avoid beam heating and electron beam damage experiments used a defocused beam with small currents (< 100 nA cm⁻²). Electron energy was typically 15 keV. Note that the spectral component from the reflection of the electron gun filament incandescence is not subtracted. Additional RTL experiments were conducted using a Philips MG 102 x-ray tube positioned at 45° to the sample giving an irradiation of 20 Gy min⁻¹.

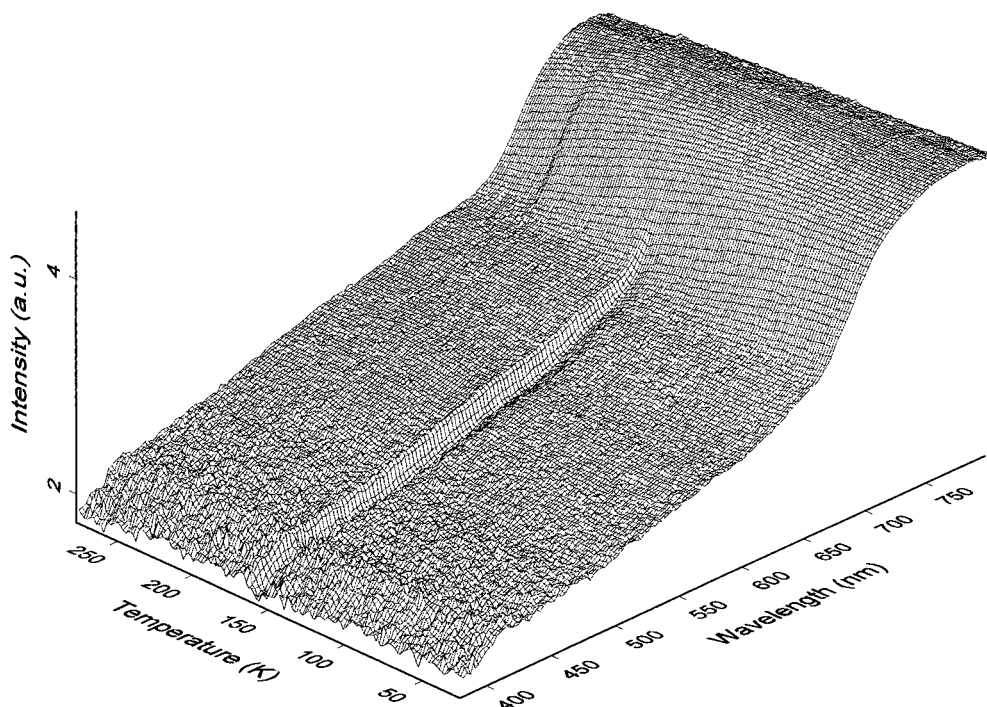


Figure 1. CL of C_{60} (supplied by Hoechst) on heating plotted in isometric form. Note that luminescence intensities are plotted on a logarithmic scale. The anomalous feature truncating the spectrum at ~ 155 K is clearly visible.

3. Results

3.1. CL of C_{60}

The signal is dominated by emissions at long wavelengths that decrease with temperature, with several orders of magnitude less intense emission at shorter wavelengths. Figure 1 presents an isometric view of the data and figure 2 a contour map of a limited temperature range. The emissions are dominated by anomalous features which cross the spectrum, the most pronounced of which is detected between ~ 155 and 170 K. It should be noted that no such anomalous features have been detected in the CL of C_{70} .

The anomaly takes the form of a marked intensity drop accompanied by a wavelength shift to longer wavelengths, and then it sharply reverts back to its original spectral form. The entire feature occurs over a ~ 15 K range. Notably, this pronounced feature is not detected at wavelengths longer than ~ 700 nm. Two other anomalous features appear less prominently at ~ 70 K and ~ 245 K. In contrast to the ~ 155 K anomaly, both these features are more noticeable at longer wavelengths, above 700 nm. On careful inspection of the isometric plot, further subtle anomalies are observed, but their presence is subjective and will not be considered further. Whilst the exact process(es) responsible for the anomalies is uncertain, one can confidently claim that the emissions are emanating from the sample, since repeat experiments with a blank aluminium disc and silicone spray revealed no such features.

The extent of the ~ 155 K feature is best appreciated on the contour plot shown in figure 2, where the intensity scale has been plotted logarithmically in order to adequately represent

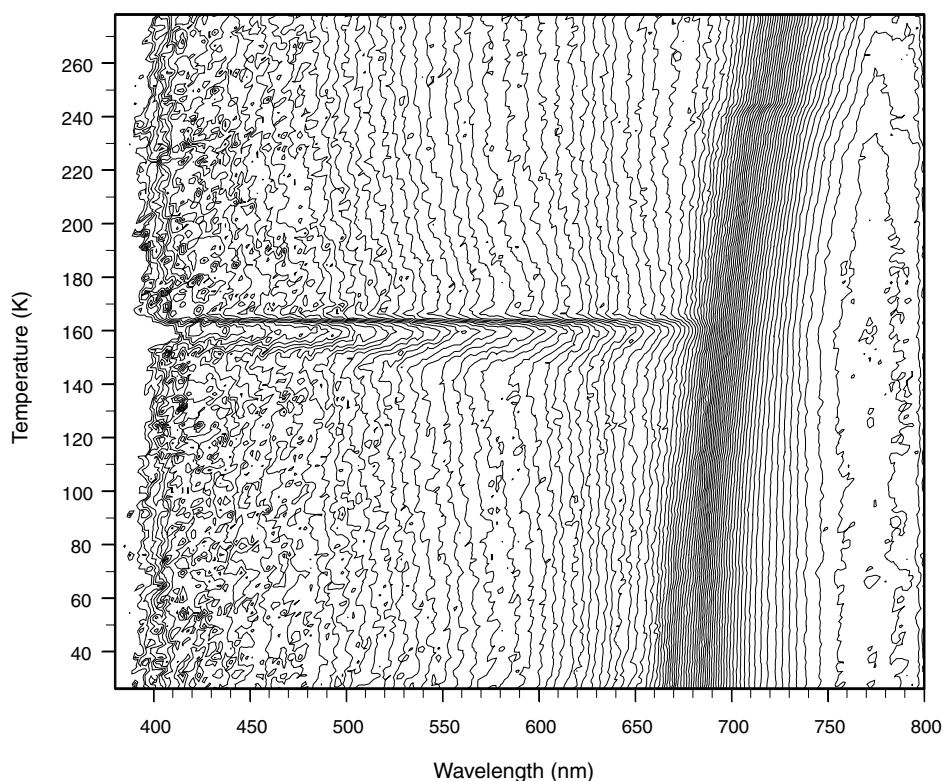


Figure 2. Contour plot of figure 1. This figure shows the anomaly at ~ 245 K. Note that it is only detected at longer wavelengths, which contrasts significantly to the ~ 155 K feature.

the dynamic intensity range. These results have been reproduced on a second sample from a different batch, and different electron beam conditions. The emission is similar to that described previously, with the exception that the anomalous features are not as pronounced, which could be a product of different beam conditions. The scale of the anomalies varies with wavelength and certain features are prominent over particular emission ranges. Slices taken at appropriate wavelengths provide compelling evidence of the existence of anomalous features in the emission spectrum and confirms that the anomalies do not affect the emission spectrum uniformly (figure 3). For example, the ~ 155 K feature is most evident in the emission at 500 nm, less so at 680 nm and not detected above 700 nm. The emission at 650 nm has anomalous features at ~ 70 K, ~ 115 K, ~ 155 K and at higher temperatures. From the longer wavelength slices, one can only confidently state that an anomaly is observed near 245 K.

3.2. RTL of C_{60}

The RTL emission of the same material does not exhibit any of the anomalous features observed in CL and is dominated by the feature previously noted in the near infra-red region which decreases gradually as temperature is increased (figure 4). Overall the intensity of this emission is several orders of magnitude less intense than the analogous feature detected in the CL. At shorter wavelengths, very weak emission is detected in the 400 to 500 nm region. This emission pattern differs significantly from that described previously for unsublimed C_{60} from a Sussex labora-

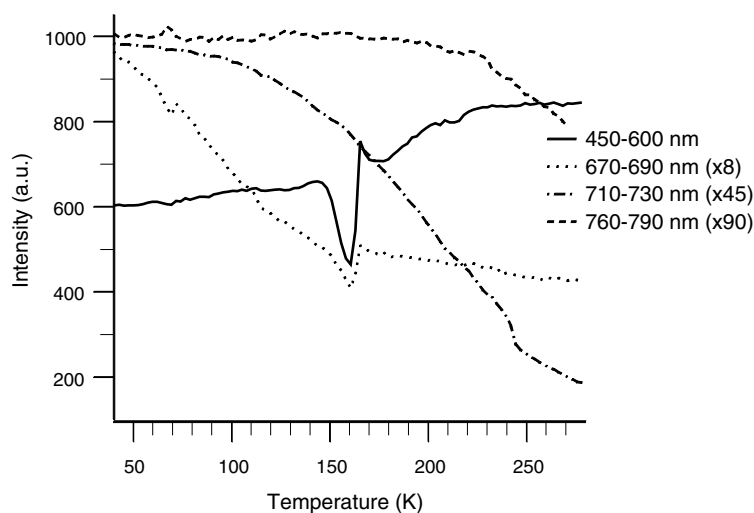


Figure 3. Wavelength slices taken at 450–600, 670–690, 710–730 and 760–790 nm from the CL of C_{60} supplied by Hoechst. In addition to the pronounced 155 K feature, this figure also reveals an anomaly at 70 K. At this particular temperature, the emission at 680 nm decreases whereas longer wavelength emission at 770 nm increases.

tory [5]. The additional weak emission feature detected at 780 nm, which decreases gradually as temperature is increased from 20 K, is probably that of iron since similar emission is seen in iron doped insulators in this wavelength range from a variety of minerals and glasses [15, 16].

4. Discussion

The sharply defined property changes at specific temperatures observed in the CL luminescence data are likely to be associated with phase transitions. The interesting questions are how to relate them to fullerene chemistry and structure. The first, and overriding issue is to discover the origin of the emission and its temperature dependence. As with all surface sensitive studies, it is essential to differentiate between the effects resulting from the host fullerenes and surface contaminants that have become attached to them during preparation (or even during cooling within the cryostat). Since the fullerenes are not in the form of bulk single crystals the importance of the very high surface to bulk ratio is particularly crucial. The data so far suggest that no problems occur within the cryostat (e.g. from condensation of background gases) but the luminescence suggests there are traces of iron and solvents bonded onto (or within) the surface of the fullerenes. These can provide luminescence signals, even when present at levels below parts per million.

The means by which impurities and C_{60} molecules interact is unknown; however one could speculate that the solvent impurities could intercalate to sites between the C_{60} molecules such that changes in structure of the fullerene will influence the emission of the impurity. A similar explanation has been given for the presence of pairs of fluorescence lines from C_{60} in PL experiments [17]. Pairs of fluorescence lines are said to originate from C_{60} in a 'perfect environment' with other pairs of peaks assigned to C_{60} molecules adjacent to chemical impurities, crystal defects or to crystal surfaces. Such defect related luminescence from host molecules are called X traps, and could originate from a suite of chemical impurities including residual solvent molecules, residual C_{70} and oxygen molecules intercalated and/or bonding

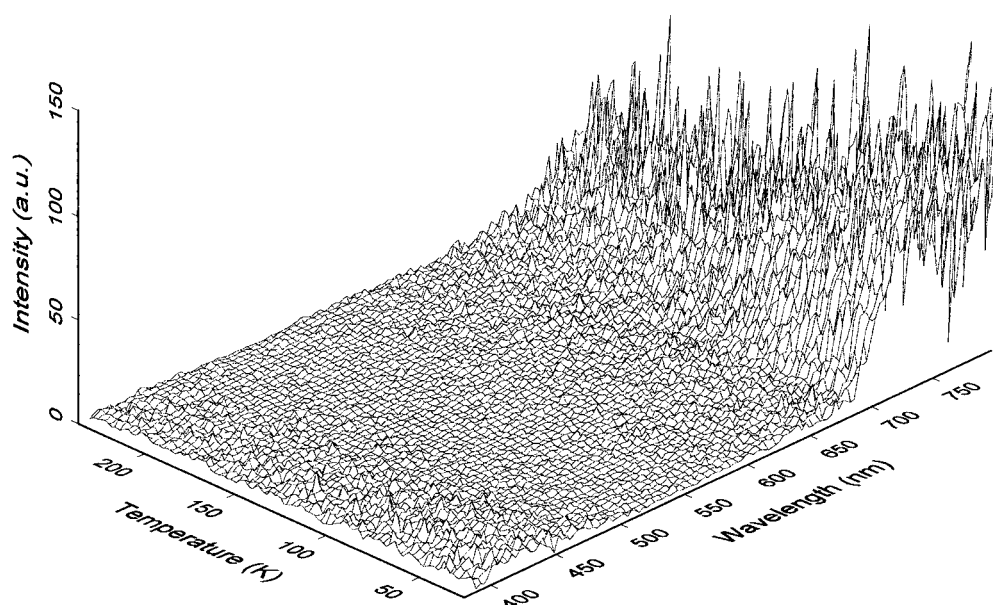


Figure 4. Isometric plot of the RTL emission of C_{60} (supplied by Hoechst). This figure is dominated by long wavelength emission and no anomalous features have been detected.

chemically to the C_{60} molecule. Alternative explanations have been provided in terms of self-localized excitons [18].

The simple fact that anomalous features are observed in the emission spectra suggests that there are other contributing components determining the emission pattern. It is therefore our view that these emissions are the product of the combined effect of the solvent and some other component(s), namely the fullerene molecules. Changes in the emission pattern are then inferred to be the result of structural modifications of the C_{60} molecules with some form of interaction between the impurity and C_{60} molecules.

These preliminary results of the CL experiments are intriguing, particularly since the anomalies tend to occur at temperatures where phase changes were noted by other methods. It might therefore be expected that the same features are apparent from other luminescence techniques but, as shown from figures 5 and 6, the RTL experiments of C_{60} produced at a Sussex laboratory generate an unusual pattern of spectral data that contain a mixture of wavelength dependent TL type data and discontinuities in intensity reminiscent of phase changes (either of the fullerene or attached solvents).

A temporary problem in the interpretation of the long wavelength data is that part of the signal arises from reflected light from the electron gun; however this is a constant background so at least the changes can be treated as meaningful signals. Nevertheless the detected emission could be the sum of two excitation mechanisms from the electron gun, namely electron and photo-excitation, i.e. photoluminescence from the filament. This is quite conceivable since photoluminescence in fullerenes following pumping by a visible light source is well documented.

All fullerene samples investigated show intense luminescence at longer wavelengths, which are detected above the background filament emission. This emission corresponds, in wavelength and temperature dependence, to that detected in RTL, which has been attributed to the presence of iron.

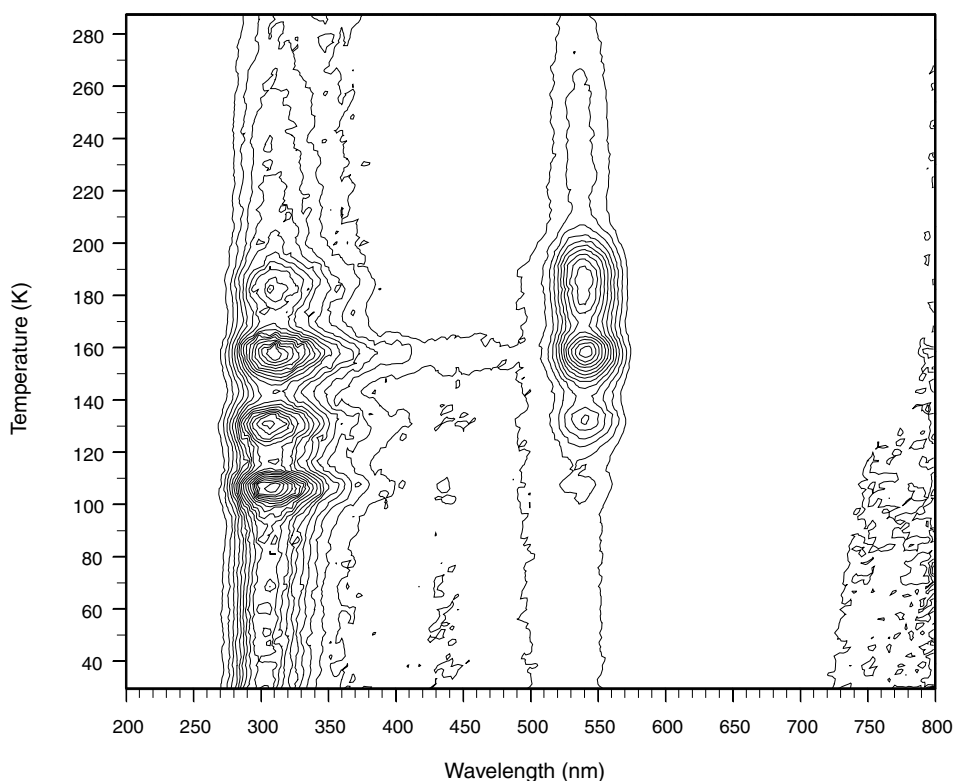


Figure 5. Contour representation of the RTL spectrum of unsublimed C_{60} supplied from a Sussex laboratory on heating. The sample was irradiated by x-rays at 10 Gy min^{-1} and simultaneously heated at 6 K min^{-1} .

Overall the anomalies that occur in the CL spectra are obvious and unequivocal features whose presence must be related to some process operating within the sample. The nature of the anomalies is similar to what one would expect if the material were undergoing a series of phase changes. CL provides powerful supporting evidence to prove that the 155 K transition from uniaxial rotations about a number of distinct directions to uniaxial rotation about a single direction is detectable by these techniques. The fact that this anomaly has been detected for C_{60} powder from two different batches and experimented under different electron beam conditions confirms that the features are conclusively originating from the samples. No comparable anomalies are detected in the CL of C_{70} , which is as one would expect, given that it has no known phase transitions in this temperature range. There are however RTL type features from C_{60} , C_{70} and nanotubes that differ in detail, but broadly follow the pattern shown in figures 5 and 6. The temptation is thus to ascribe these to the presence of attached solvents that respond to changes in the host material. This separation of direct and indirect fullerene responses may therefore explain why certain anomalies in the CL emission spectra are more pronounced than others (e.g. near 155 K).

Assignment of RTL signals to indirect responses from attached solvents, such as toluene, could explain the less obvious responses expected at phase changes and also the fact that sublimed samples are devoid of any emission at short wavelengths, consistent with a negligible solvent content.

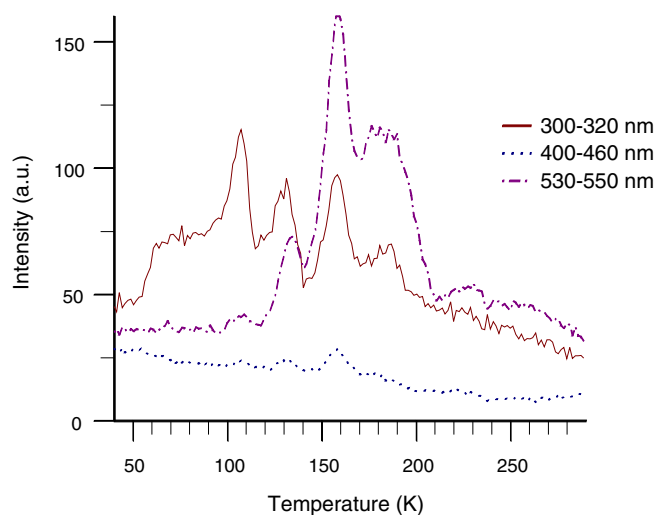


Figure 6. Wavelength slices taken from figure 5. Slices taken along the main emissions to emphasize the scale of the features and to note that peaks do not align.

5. Conclusions

This research constitutes the first attempt to use CL and RTL to actively probe for phase transitions in the fullerenes. Although not immediately obvious candidates for luminescence research, fullerenes have proved to be interesting subjects and offer sufficient spectrally resolved data to aid in the detection of phase transitions, detection of trace impurities (particularly iron) and the presence of attached solvents. CL and RTL therefore offer a means of improving our understanding of these materials through further characterization, particularly by exploiting luminescence, which is sensitive to impurities within the fullerenes, or attached to the surfaces of the samples. Sensitivity can be to concentrations well below parts per million of impurity. Since the signal intensities and emission wavelengths respond quite dramatically during heating the first tentative analyses relate these variations to relaxations in the host fullerene structures and perhaps to the presence of phase changes during heating. Further, the spectral discontinuities are consistent with phase, or structural relaxations and they appear to differ between the various forms of fullerene.

Although the level of confidence in the data set is high, the interpretations given remain cautious at this time. Pronounced anomalies in the 90 K region are interpreted as being due to the structural change from phase II to III, i.e. from shuffling simple cubic to the freezing of reorientational motion. The major anomaly detected in CL near 155 K probably represents the change from uniaxial rotation about a number of distinct directions to rotation about a single direction at lower temperature. An anomaly in the CL data of C_{60} at ~ 250 K agrees with, and may represent, the high temperature phase transition at 261 K.

Overall the use of luminescence analyses of fullerenes, ranging from high purity material to samples with impurities incorporated during preparation, or with intentionally added dopants, opens a powerful route to give temperature and wavelength dispersive analyses of these materials. This could have particular importance in studies of material perfection, doped fullerenes and identification of phase changes in normal fullerenes as well as superconducting fullerenes.

Acknowledgments

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