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LUMINESCENCE AND ABSORPTION SPECTRA OF C_{60} FILMS

by

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Luminescence and Absorption Spectra of C_{60} Films

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Abstract

Solid films of C_{60} deposited on CaF_2 under ultra high vacuum show luminescence in the 700-1100 nm spectral range at 20K. A 1400 cm^{-1} progression in the a_g soccerball inflation mode is observed. The low temperature absorption spectrum exhibits similar fine structure. The characterization of vibronic splittings in the ground and emitting state and the transition intensity mechanism are discussed.

The recent report that the spherical all-carbon molecule C_{60} can be made in high yield in a carbon arc[1-4] has stimulated new interest in its molecular and spectroscopic properties.[1-8] This new allotrope of carbon has a graphitic closed cage structure consisting of twelve five-membered rings separated by twenty benzenoid six-membered rings. The molecule, which contains 60 atoms lying at the vertices of a truncated icosahedron, is known as Buckminsterfullerene because the geodesic structures of Buckminster Fuller led to the initial proposal of its structure.[9] Solutions of C_{60} are magenta; the long wavelength absorption edge lies at about 620 nm.[3] It has been reported that no luminescence can be detected at room temperature in solution.[6] The triplet-triplet absorption spectrum has been reported.[6] We report here that films of C_{60} are luminescent in the 700-1100 nm region at low temperature.

Films of material were grown in an ultra-high vacuum chamber.[7] The starting material was made by the method of Krätschmer and Huffman and purified by passing it through an alumina column.[1] The C_{60} was placed in a 2cc quartz crucible which in turn was inserted into a pyrolytic boron nitride crucible. The entire chamber was baked so that the temperature of the crucible would not exceed 240°C in order to eliminate any high vapor pressure contaminants from the starting material. The base pressure of the system after bakeout was 5×10^{-9} torr. To initiate the growth, the crucible was heated to about 300°C and the ambient temperature CaF_2 substrate was positioned within the flux of the material 1.5 cm from the face of the crucible. During the initial stages of growth, the thin films were a deep blue; thicker films appeared more brown. The films were stored in vacuo and were only exposed to the atmosphere for minutes during transfer to the spectroscopic instruments.

Electronic absorption spectra of the films were obtained by using an instrument described previously.[10] The sample was mounted on an OFHC copper block in the vacuum shroud of an Air Products displex closed cycle helium refrigerator and cooled to about 20K. The spectrometer resolution was about 5 Å. The emission spectra were obtained from samples mounted in the same displex using an emission spectrometer described previously.[11] The films were excited at wavelengths ranging from 351 nm to 633 nm. The emitted light was collected by using an RCA C31034 photomultiplier or a cooled germanium detector. The spectrometer resolution varied with the slit width used from sample to sample but was always better than 10 Å and 50 Å for the spectra detected with the photomultiplier tube and the germanium detector, respectively. All emission spectra were corrected for the system response.

The absorption spectrum of a film about 1μm thick on CaF_2 at 20K is shown in Figure 1. The spectral region shown covers the absorption transition to the lowest energy excited state responsible for the luminescence (vide infra). The onset of absorption occurs at about 14,500 cm^{-1}; a weak feature at 14,420 cm^{-1} is somewhat tentatively assigned as the electronic origin (E_{00} in Figure 1). The first well resolved vibronic peak is observed at 14,870 cm^{-1}. The positions of the vibronic bands are listed in Table 1. The spectrum is dominated by pairs of bands (a peak and a higher energy shoulder). The separation between the peak and the shoulder is 230 cm^{-1}. Spectra measured at room temperature are in good agreement with a previously reported spectrum of C_{60} on quartz.[1] It is interesting to note that the low temperature absorption spectrum of the film reported here is very similar to that of C_{60} in a frozen glass at 77 K except that the first band in the glass spectrum is found at 16,200 cm^{-1}.[8] The 1300 cm^{-1} blue shift of the glass spectrum may be a result of the different dielectric constants of the media. In the glass spectrum, the average separation between the peaks comprising the pairs is 235 cm^{-1}. An interpretation of the fine structure in the absorption spectra of solid C_{60} is indicated in Figure 1. Two vibronic origins a and b, at 450 cm^{-1} and 680 cm^{-1} higher energy, are built on the electronic origin E_{00} respectively. Their energy difference gives rise to the 230 cm^{-1} separation of pairs of transitions. Both a and b show side bands at 740 cm^{-1}, 1420 cm^{-1} and 2200 cm^{-1} higher energy. The corresponding side bands are connected by dotted lines in Figure 1. The energy spacings correspond to excited state vibronic splittings that can be roughly compared to ground state Raman frequencies.[5] The 740 cm^{-1} and 1420 cm^{-1} intervals correspond to the 773 cm^{-1} and 1469 cm^{-1} Raman frequencies, respectively. The frequencies are reduced by about 5% in the excited state. The 1469 cm^{-1} mode is the totally symmetric soccer ball inflation mode (denoted by the $\hbar\omega_{ag}$ in Figure 1), whereas the 740 cm^{-1} mode ($\hbar\omega_g$ in Figure 1) has gerade parity but is not totally symmetric. The pair of bands observed 2200 cm^{-1} higher in energy than their vibronic origins each correspond to one quantum of both $\hbar\omega_{ag}$ and $\hbar\omega_g$. Progressions in non totally symmetric modes are often observed in highly symmetric molecules and can be interpreted as a manifestation of the Jahn-Teller effect.

The complete emission spectrum of a film of C_{60} at about 20K is shown in Figure 2. The onset of the first detectable emission occurs at about 14,500 cm^{-1} and overlaps the onset of the absorption band discussed above. The emission spectrum is not as well resolved as the absorption spectrum, i.e., the peaks are much broader. The breadth is evidence for significant inhomogeneity. The excitation energy migrates among the C_{60} chromophores in the solid and emission occurs from a wide variety of different sites, not necessarily from the most abundant ones. The highest energy peak in the emission spectrum occurs at 14,150 cm^{-1} (Figure 3, top trace). A second resolved peak occurs at 12,700 cm^{-1}. A shoulder at about 11,400 cm^{-1} is also observed. The same emission spectra are obtained when the sample is excited at 633 nm (directly into the lowest energy absorption band), 514 nm and 488 nm (into the absorption band with a peak maximum at 450 nm)[3] and 351 nm (into the absorption band with a peak at 330 nm)[3]. The spectral origin of the emission spectra varies slightly from sample to sample. The spectra described above are those with the highest energy origin. Excitation of other samples or regions of the film about 1mm^2 in size gives rise to spectra which are red shifted by a maximum of about 500 cm^{-1}. An example is shown in Figure 3. All of the spectra which have been recorded have the same separations between the peaks and shoulders as those described above and shown in Figure 2, and all of the spectra have about the same relative intensities between the peaks and shoulders. This observation excludes the possibility that impurity C_{70} emission accounts for one of the two distinct spectra; solid C_{70} luminesces at low temperatures in a similar spectral region as C_{60} but shows distinctly different fine structure.[12] Analysis of many spectra indicates that most commonly the first peak either occurs at 14,100 cm^{-1} as discussed above or at 13,700 cm^{-1}. These spectra are superimposable when the latter is offset by 400 cm^{-1}. Frequently a superposition of these two spectra were recorded, as shown in the top trace of Figure 3).

The three main vibronic features in the emission spectrum are separated by about 1400 cm^{-1} as indicated in Figure 2. Because of the width of the resolved bands, the uncertainty is greater than ±100 cm^{-1}. This progression is assigned to the totally symmetric soccerball expansion mode which has been observed in the Raman spectrum at 1469 cm^{-1}.[5] There is some evidence for a second progression in the emission spectrum with a separation of about 800 cm^{-1} which may correspond to the 740 cm^{-1} progression in the absorption spectrum. However the overlap between the broad bands in the emission spectrum prevents any definitive assignments from being made.

The emitting state has a geometry very similar to that of the ground state, since the progressions observed in absorption and emission have their main intensity in the first two members.[13]

Emission spectra of C_{60} in frozen organic glasses at 20 K were studied in order to explore further the medium dependence on the transition energies and the possibility that lattice sites are contributing to the emission spectra of the films. The emission spectra obtained from frozen solutions of 2:2:1 methylcyclohexane : iso-octane : toluene were the same as those obtained from the films. The expected 1300 cm^{-1} medium-dependent shift was not observed. These results may indicate that the observed emission originated from microcrystals suspended in the frozen solvent.

The overlap between the onset of the emission and the absorption bands indicates that the same electronic excited state is responsible for both. Molecular orbital calculations suggest that the irreducible representations of the HOMO and LUMO are h_u and t_{1u} respectively.[14] The excited states arising from a one-electron transition are T_{1g}, T_{2g}, G_g and H_g. Transitions from the A_g electronic ground state are electric dipole forbidden but become vibronically allowed with one quantum of an ungerade vibrational normal mode. An interpretation of the emission and absorption spectra consistent with the above selection rules is that the electronic origin (the energy of the transition between the ground vibrational levels of the electronic ground and excited states) occurs between the first observed peaks in the emission and absorption spectra at about 14,500 cm^{-1}. The first observed peaks are thus assigned to one quantum of an ungerade promoting mode. Because the first observed peaks are separated by 720 cm^{-1}, the promoting modes involved must be on the order of several hundred wavenumbers. Low frequency modes in this wavenumber range are known, but detailed IR spectra which are required to measure the ungerade modes have not yet been carried out.

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Table 1

Transition energies and assignments for the low temperature absorption spectrum of C_{60} in Figure 1.

transition energy [cm^{-1}]	difference [cm^{-1}]	assignment
14,420		electronic origin E_{00}
14,870	230	vibronic origin a
15,100		vibronic origin b
15,640	240	$a + \hbar\omega_g$
15,880		$b + \hbar\omega_g$
16,260	240	$a + \hbar\omega_{ag}$, $a + 2\hbar\omega_g$
16,500		$b + \hbar\omega_{1g}$, $b + 2\hbar\omega_g$
17,100	220	$a + \hbar\omega_g + \hbar\omega_{ag}$
17,320		$b + \hbar\omega_g + \hbar\omega_{ag}$

Figure Captions

Figure 1

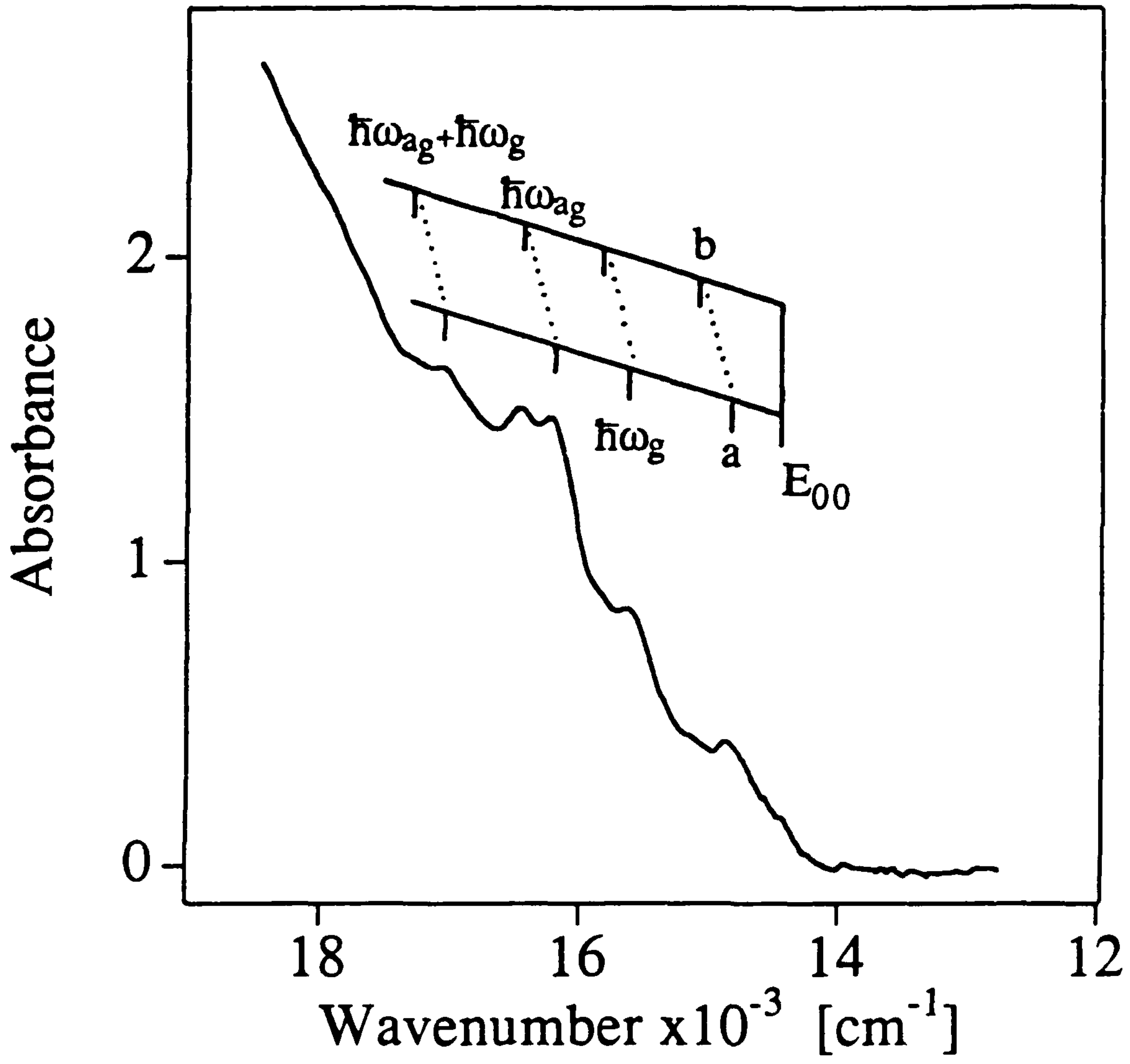
The 20 K absorption spectrum of solid C_{60} deposited on CaF_2. For the assignment of the fine structure see text and Table 1.

Figure 2

20 K luminescence spectrum of solid C_{60} deposited on CaF_2 taken with a Ge detector, $\lambda_{exc} = 514$ nm. The main progression in the totally symmetric a_g mode at an interval of 1400 cm^{-1} is indicated.

Figure 3

20 K luminescence spectrum of solid C_{60} deposited on CaF_2 taken with a photomultiplier. The two spectra were obtained from two different regions of the sample. Top trace: $\lambda_{exc} = 351$ nm; bottom trace: $\lambda_{exc} = 488$ nm.



Absorbance
0
1
2
18
16
14
12
Wavenumber x10^-3 [cm^-1]
ħω_ag+ħω_g
ħω_ag
b
ħω_g
a
E_00

Figure 1

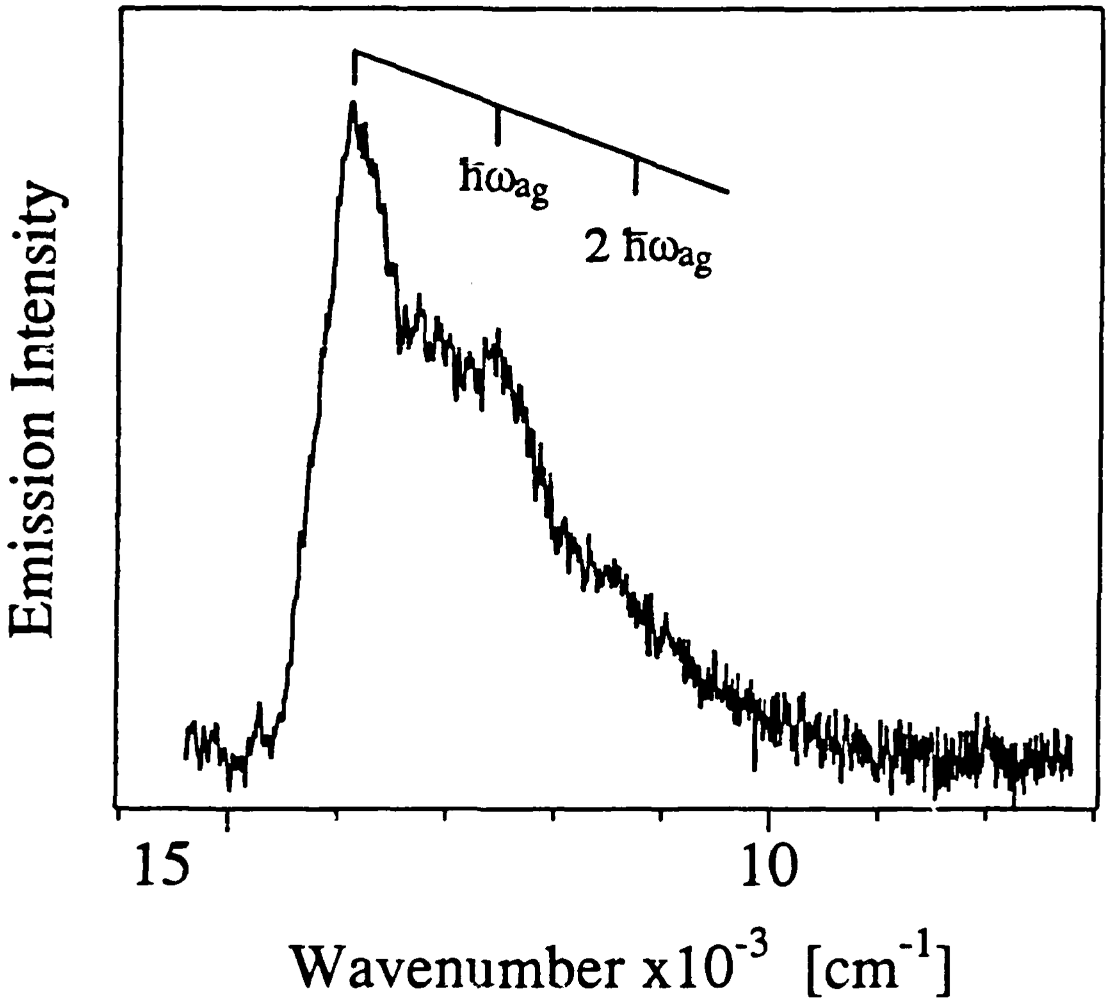


Figure 2

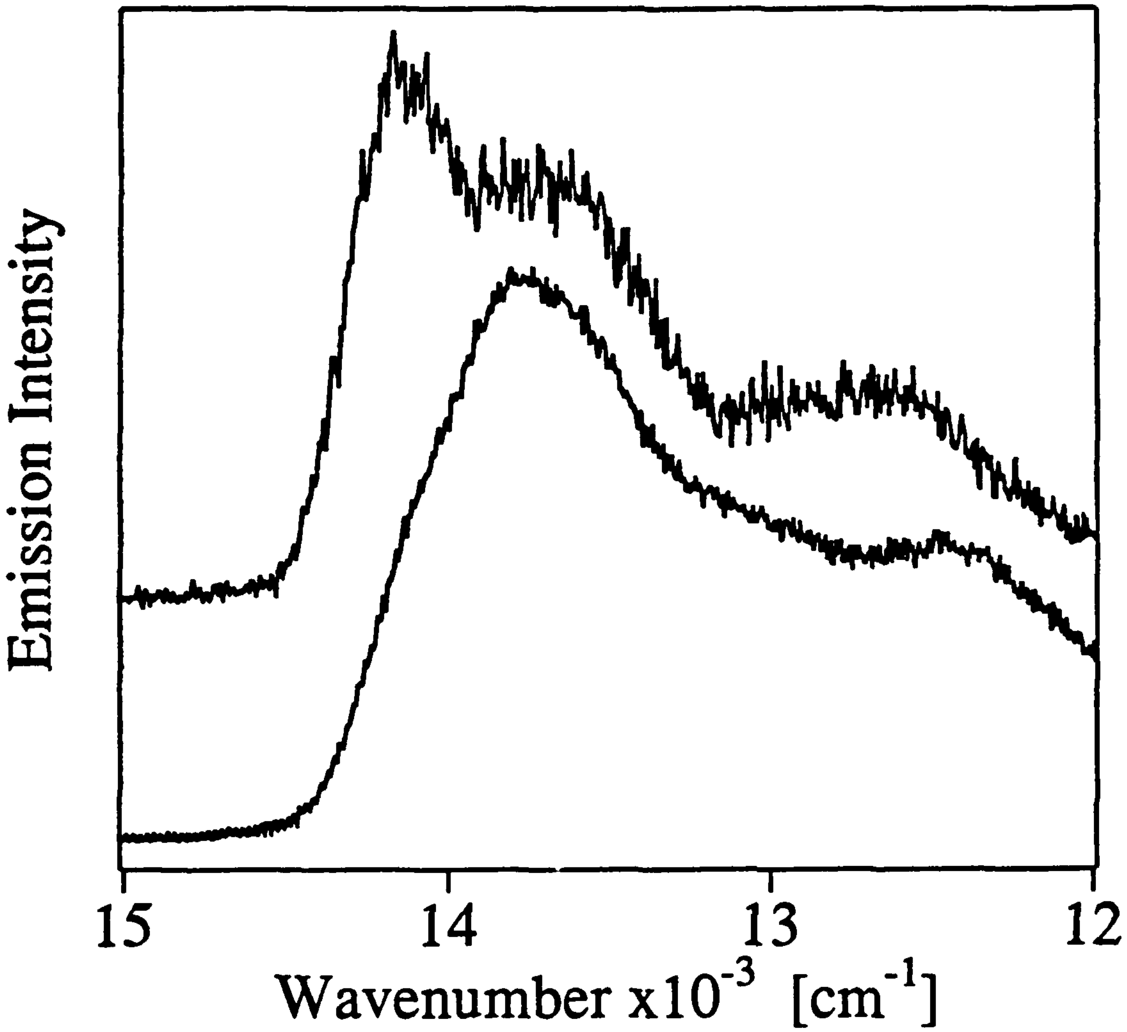


Figure 3