Measurement of Pair Interactions and 1.5 μm Emission from Er^{3+} Ions in a C_{82} Fullerene Cage

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Erbium ions encapsulated in the metallofullerene $Er_2@C_{82}$ emit near infrared fluorescence about 1.5 μm, typical for $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+}. The similarity of spectra measured in glassy and polycrystalline media at 1.6 K, and the very narrow inhomogeneous linewidth (<1 cm^{-1}), show that the fullerene cage provides a locally ordered environment for the two erbium ions, well isolated from the host medium. Spectral fine-structure is observed with line splittings of $\sim$10 cm^{-1}. It is proposed that these splittings are dominated by exchange interaction between the two Er^{3+} ions involving a novel superexchange pathway through the C_{82} cage. [S0031-9007(97)03775-7]

Erbium, like other lanthanides, readily forms metallofullerenes when it is co-vaporized with carbon in an inert gas atmosphere [1,2]. Direct evidence for several metallofullerene species [3,4], and the similar chemical properties of others that can be solvent extracted and purified by high-performance liquid chromatography (HPLC), strongly supports the conclusion that the metal atoms in such species are trapped inside the closed carbon fullerene cages. In contrast to La, Y, and Sc in their preferred trivalent state, the open shell lanthanides have the potential to emit light from their low lying metastable $4f^n$ states, which in some cases may lie below the strong absorption of the negatively charged fullerene cage. In general, the onset of strong absorption in the fullerene cages shifts to a longer wavelength with increasing cage size. For example, it is near 400 nm in C_{60} [5] and 500 nm in C_{82}. The Er^{3+} ion is well known for its emission about 1.5 μm from the $^4I_{13/2}$ level, which has led to numerous applications of this ion in erbium lasers and amplifiers [6,7]. The low energy of this emission makes it likely that strong quenching due to cage states can be avoided, and several reports of such emission have been made [8–10]. Here we provide what we believe to be the first spectroscopic evidence for the interaction between isolated pairs of Er^{3+} ions in the form of small splittings of the erbium emission lines. These splittings are attributed to exchange coupling. We also show that the fullerene cage provides a very homogeneous environment for such pairs of metal ions by measuring the 1.5 μm Er emission linewidths and the spectra of $Er_2@C_{82}$ in different solvent environments.

Erbium metallofullerenes for emission spectroscopy were produced by arc vaporizing 6 mm carbon rods that had been drilled out to 4 mm and packed with a mixture of erbium oxide and graphite powder to give an erbium concentration of about 0.66 at. % with respect to total carbon. A current of $\sim$100 A and a He pressure between 150–200 Torr were used. Fullerenes were extracted from the soot using CS_2 and 1-2-dichlorobenzene. As is typical for lanthanide metallofullerene extracts, species with 82 carbon cages were favored, and both $Er@C_{82}$ and $Er_2@C_{82}$ were prominent in the extracts. The metallofullerenes were purified by repeated HPLC passes on pentabromylbenzyl [11] and Buckyclutcher [12] columns. The retention times for $Er_2@C_{82}$ isomers I, II, and III with two Buckyclutcher columns (10 mm $\times$ 25 cm) connected in a series were 29.44, 31.82, and 32.72 min, respectively. HPLC conditions were 1.2 mL/min of 80:20 toluene/decalin (v/v) mobile phase with 354 nm UV detection. The retention times for $Er_2@C_{82}$ isomers I, II, and III using a 10 mm $\times$ 25 cm pentabromobenzyl (PBB) column were 13.25, 13.51, and 13.54 min, respectively. HPLC conditions in this case were 2.0 mL/min of carbon disulfide mobile phase with 390 nm UV detection. Less than milligram quantities of isomer III of $Er_2@C_{82}$ with >96% purity were obtained, with $\lesssim$3% $Er_2@C_{84}$ and <1% of other species as determined by mass spectrometry. Separated $Er@C_{82}$ was also obtained, mixed with smaller amounts of $Er@C_{76}$, $Er@C_{72}$, and traces of dierbium metallofullerenes. For spectroscopic study, samples of a few tens of μg were dissolved in a mixture of cis and trans decalins (decahydro-naphthalene, $C_{10}H_{18}$) which forms a glass when frozen, or in CS_2, and were then placed in 3 mm glass tubes, degassed by freeze-thaw cycles and sealed under vacuum.

Figure 1 shows the overall absorption spectrum of C_{82} and $Er_2@C_{82}$ at room temperature. The structure in the latter is attributed to modification of the C_{82} cage states by the transfer of electrons from Er to the cage, similar to the spectral changes seen for other negatively charged metallofullerene cages [13]. No absorption between the f^n levels of the Er^{3+} ions was detected at the expected wavelengths at about 530 nm, 650 nm, 970 nm, or 1.5 μm which, by comparison with the spectra of Er:YAG and
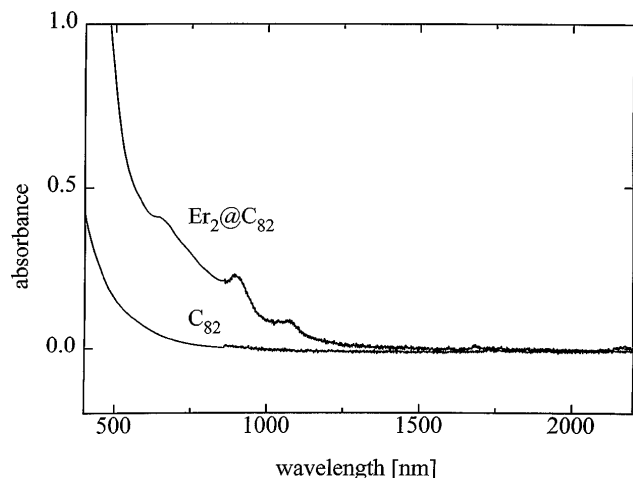
FIG. 1. Absorption spectra of C_{82} and $Er_2@C_{82}$ in CS_2 at room temperature. In the latter, all of the observed structure is assigned to transitions in the cage, modified by the transfer of electrons from the Er.

Er:ZBLAN glass of known doping, suggests that the concentration of $Er_2@C_{82}$ was less than 10^{-4} M.

Fluorescence was excited by ~200 mW of all-lines emission from an Ar^+ laser, which excited directly into the $^2H_{11/2}$ and higher levels of Er^{3+} and also into the C_{82} first singlet absorption. Subsequent nonradiative relaxation among the Er^{3+} levels or to the C_{82} triplet followed by transfer to erbium, populates the $^4I_{13/2}$ level of the Er^{3+} ion. The emission from this level was focused onto the slits of a 0.3 m PTI monochromator equipped with a 600 lines/mm grating blazed at 1.25 μm or a 0.32 m J-Y monochromator with a 600 lines/mm grating blazed at 2.5 μm, and the dispersed light was detected by a North Coast liquid-nitrogen-cooled Ge detector. The Ar^+ laser was chopped at 35 Hz, and fluorescence was recorded using a lock-in detector. The fluorescence spectrum observed at room temperature from the $Er_2@C_{82}$ sample corresponds well with that expected for the $^4I_{13/2}(m) \rightarrow$ $^4I_{15/2}(n)$ transitions of the Er^{3+} ion, where (m) and (n) label the $J + 1/2$ "crystal field" components of the $^4I_{13/2}$ and $^4I_{15/2}$ manifolds. At this temperature, emission is observed from thermally occupied components of the upper state, and phonon scattering and absorption between the different Er levels results in strong broadening and overlap of spectral lines, which makes the spectrum of limited use as a diagnostic of the interaction between the erbium ions and their surroundings.

To make low temperature fluorescence measurements, the sealed samples were immersed in liquid helium pumped to 1.6 K. The spectrum of the sample in decalin glass taken at a moderately low resolution of 5 nm is shown in Fig. 2(a). It consists of eight lines, as expected for transitions from the $m = 1$ component of the upper level to the eight Kramers' doublets of the ground $^4I_{15/2}$ multiplet. The overall position, centered at 1.57 μm, corresponds to that seen for Er^{3+} in a wide variety of ma-
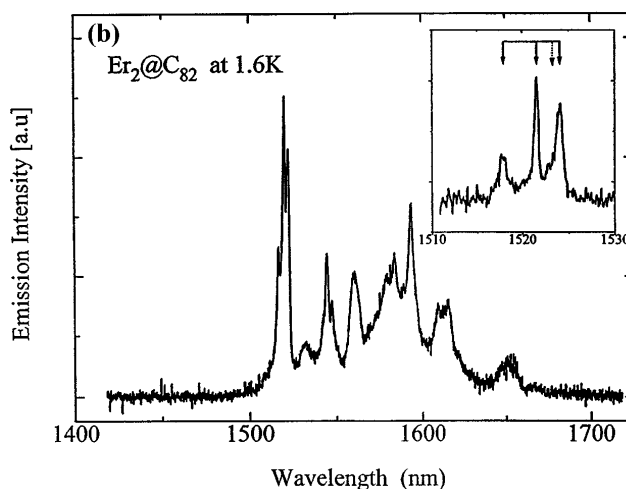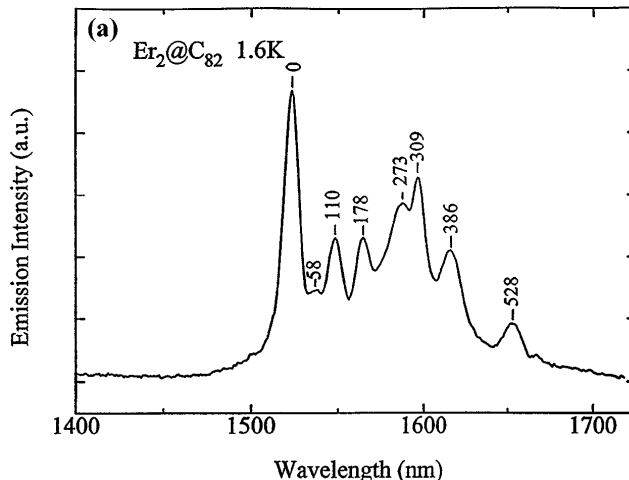

FIG. 2. Emission spectra of $Er_2@C_{82}$ in liquid helium at 1.6 K (a) in a decalin glass at a spectral resolution of 10 nm. The instrument-limited eight-line pattern is characteristic of $^4I_{13/2}(1) \rightarrow {}^4I_{15/2}(n)$ transitions of Er^{3+}. The peak labeled 0, corresponding to 1521 nm, is emission to the $n = 1$ component of $^4I_{15/2}$, and the other peaks are labeled by the energy of the final state in cm^{-1}. (b) A spectrum of $Er_2@C_{82}$ in frozen CS_2 showing fine-structure. The inset shows a higher resolution trace of the line at 1521 nm at a spectral resolution of 0.5 nm. The arrows indicate fine-structure attributed to exchange coupling between the two Er^{3+} ions in the cage.

terials [7]. This establishes the first important result that the Er ions are in the trivalent state. Transitions to all of the $^4I_{15/2}$ ground manifold components are allowed as forced electric dipole transitions between $4f^{11}$ levels of Er^{3+}. The width of the spectral lines has a large contribution from the spectrometer slit width. Figure 2(b) shows a spectrum of $Er_2@C_{82}$ in frozen $CS_{2'}$ taken at an improved resolution of 1.8 nm but with a reduced signal-to-noise ratio. The polycrystalline frozen CS_2 provides a very different local environment for the fullerene cages than the glass formed from the relatively large aromatic decalin molecules. Nevertheless, the crystal field splittings of the

ground state multiplet of Er^{3+} and the relative intensities in the two samples are almost identical, as Table I and Fig. 2 show. This similarity provides good evidence that the two Er ions in the fullerene cage are well shielded from the solvent environment and that it is the interaction with the cage that predominantly determines the intensities and crystal field splittings. An experimental determination of the symmetry of the $Er_2@C_{82}$ molecule has not yet been made; however, calculations of the structure of empty and filled cages suggest a C_2 symmetry [14].

Another remarkable feature of the spectra in Fig. 2(b) is that the line at 1521 nm corresponding to the $^4I_{13/2}(1) \rightarrow {}^4I_{15/2}(1)$ transition consists of at least three components, as shown in the inset taken with a resolution of 0.5 nm (2.2 cm^{-1}), where the lines are still substantially slit broadened. The inhomogeneous linewidth is less than 1 cm^{-1}. This is additional evidence for the picture in which the Er ions sit in a very homogeneous environment determined by the fullerene cage. A similar structure is observed on most of the other lines, but their greater width results in a less well-resolved structure. We attribute the structure seen in the inset of Fig. 2(b) to transitions from the lowest component of the upper states of an Er^{3+} pair to the ground state components split by dipolar and exchange interactions between the two erbium ions. The separation between the ions is assumed to be about 3.6 Å as found theoretically for La^{3+} ions in $La_2@C_{80}$ [15]. Each Er ion has a Kramers' doublet ground state, and coupling these effective spin = $1/2$ levels will result in levels with total spins $S = 0$ and $S = 1$. In axial symmetry, the four components of these spin states will be grouped into three levels with total spin and spin projection $(S, M_S) = \{(1, 1) (1, -1)\}$, $\{1, 0\}$, and $\{0, 0\}$. Reduction in symmetry below axial will split the doubly degenerate component. Three principal components are observed in the emission spectrum [inset to Fig. 2(b)] at 0, 16, and 27 cm^{-1}. This follows qualitatively the level structure outlined above. The splittings are relatively large, but we note that splittings of ~ 5 cm^{-1} have been seen for exchange-coupled Er pairs in $Cs_3Er_2Br_9$ [16]. In this case, the Er ions are bridged by bonded Br^- ions which provide a superexchange path. The great novelty of the Er-Er coupling in the fullerene is that

the erbium ions lack the normal inorganic ligands and instead are surrounded by the carbon cage. The nature of exchange coupling in this configuration has not yet been considered. Since the magnetic dipolar contribution to the interaction is estimated to be only about 1 cm^{-1}, the main part of the interaction is attributed to exchange. A consequence of the picture proposed here is that the dierbium fullerene would be diamagnetic, having a singlet ground state, while the monoerbium compound would be paramagnetic. For two rare earth ions with the f electrons shielded from the environment and separated by over 3 Å, direct exchange is expected to be small and a novel superexchange coupling involving the fullerene cage is the likely mechanism. This is the first study presenting evidence for coupling between ions in a fullerene cage, and it also provides a rare example of exchange coupling between truly isolated pairs of ions situated in a homogeneous environment.

The monometal species $Er@C_{82}$ should not exhibit these splittings, providing additional incentive to find its emission, but so far we have not observed it. Optical measurements of absorption spectra involving transitions between the cage states have been reported for numerous metallofullerene species [13,17–24]. A significant feature of these spectra is that the dominant $M@C_{82}$ isomers typically have strikingly similar broad absorption features extending from 1000–2000 nm, peaking at about 1400 nm. This long wavelength absorption is not seen for the dimetal and trimetal species, whose absorptions cut off near 1100 nm. The 1400 nm absorption has been attributed to the open shell nature of the monometal species [21]. Thus a likely explanation for the apparently weak emission from $Er@C_{82}$ is that in the monometal complex there are cage states that lie lower than in the dimetal compounds, as evidenced by the absorption at about 1.4 μm, and energy transfer to these states quenches the Er emission.

A limit on the lifetime of the $^4I_{13/2}$ level in $Er_2@C_{82}$ was obtained by chopping the exciting light with a small pinhole in a chopper blade such that the excitation pulse was ~ 5 μs. Fluorescence detected following this excitation pulse had a lifetime less than the 50 μs time constant of the detector. A lifetime of this order of magnitude predicts a quantum yield of emission of less than 1%, consistent with the strength of emission relative to that from Er-doped ZBLAN glass or YAG samples, in which the efficiency is close to unity and the lifetimes are ~ 10 ms. This short lifetime most likely results from energy transfer to the cage. Contributions from nonradiative decay by coupling to vibrational modes of the fullerene cage or of the CS_2 matrix may also occur.

In conclusion, we have presented spectroscopic evidence that Er, and by implication other metal atoms in metallofullerenes, experience a very homogeneous environment, isolated from outside perturbations by the surrounding closed carbon cage. For species with accessible

TABLE I. $^4I_{15/2}$ components for $Er_2@C_{82}$.

In decalin glass (cm^{-1})	In frozen CS_2 (cm^{-1})
0	0
58	55
110	108
178	171
273	260
309	307
386	384
528	529

metal atom optical spectra, measurements of these spectra can provide a superior diagnostic of the ion's electronic configuration, since they can be made in zero magnetic field. This avoids the complications introduced by the range of Zeeman splittings of the randomly oriented molecules resulting from the anisotropic g values that would be encountered in an epr experiment, for example. Dimetal species such as $Er_2@C_{82}$ provide rare examples of truly isolated ion pairs. We find that the erbium emission spectrum of $Er_2@C_{82}$ consists of a well-resolved eight-line pattern near 1.55 μm at 1.6 K, showing that the two erbiums are in their 3^+ valence state. The fluorescence lifetime is <50 μs, corresponding to a quantum efficiency for emission of $<1\%$. It is proposed that this low efficiency is due to energy transfer to the cage and that the emission efficiency may be significantly higher in a different fullerene cage. At a resolution of 0.5 nm, the spectrum shows additional splittings, which we attribute to exchange interaction between the two Er ions. We believe this to be the first evidence of coupling between ions in a fullerene cage.

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