Multiple species of La@C_{82} and Y@C_{82}.
Mass spectroscopic and solution EPR studies

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Two dominant electron paramagnetic resonance (EPR) hyperfine patterns for both La and Y fullerenes have been identified and linked to the mass spectroscopic (MS) peaks of La@C_{82} and Y@C_{82}, respectively, as also observed by Suzuki et al. Additionally, lower intensity La@C_n EPR multiplets are identified which have not, as yet, been correlated with specific MS peaks. The intensity ratios of the two dominant EPR multiplets depend on various parameters such as solvent and temperature, suggesting the species possess different chemical properties.

Evidence that metal atoms can combine with arc-vaporized carbon atoms to form metallofullerene molecules [1] was reported shortly after the discovery of fullerene molecules [2]. More recently, correlative mass spectroscopic (MS) and electron paramagnetic resonance (EPR) studies have identified the meallofullerenes La@C_{82} [3], Y@C_{82} [4,5] and Sc@C_{82} and Sc_3@C_{82} [6,7]. Thus, mass spectroscopy has identified novel fullerene compounds while EPR has provided the first detailed information about their electronic ground states.

In the original reports identifying La@C_{82} [3] and Y@C_{82} [4], only one La ($I=7/2$) eight-line (octet) hyperfine pattern or one Y ($I=1/2$) two-line (doublet) hyperfine pattern were observed. In more recent sample preparations of La and Y containing fullerenes, we have observed additional La octet and Y doublet hyperfine patterns. In this report, we identify two dominant La metallofullerene EPR signals and two dominant Y metallofullerene EPR signals, and correlate them with single La@C_{82} and Y@C_{82} MS peaks, respectively. Based on these results, we suggest that there are two dominant species of

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La@C_{82} and Y@C_{82}. Similar results have been reported by Suzuki et al. [8]. Furthermore, we identify additional, lower intensity La@C_n EPR multiplets which are presently not correlated with specific mass peaks.

La and Y metallofullerene samples were prepared by arc-vaporization (in 200 Torr He) of cored rods packed with a mixture of powdered La or Y and powdered graphite. The overall metal/carbon ratio was 1%–2% (atomic). For EPR measurements, the toluene extract of the collected soot was placed in a quartz tube, degassed by the freeze–pump–thaw method, and vacuum sealed while the toluene solvent was frozen. For MS measurements, toluene extract was placed on a gold plated probe surface and the solvent was allowed to evaporate. The residue was analyzed by laser desorption/laser ionization time-of-flight mass spectrometry, using 532 nm light for desorption and 193 nm light for ionization. A commercial Bruker ER300 spectrometer was used to record first derivative EPR spectra at either X-band (9.7 GHz) or S band (4.0 GHz).

The experimental room-temperature 9.7 GHz EPR spectrum of the lanthanum sample is shown in fig. 1a, while fig. 1b displays a spectral simulation. The simulated spectrum of fig. 1b is constructed by superposing the octet of fig. 1c with the octet of fig. 1d.
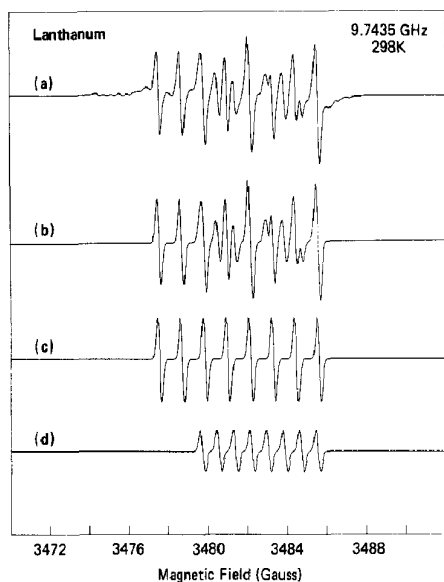
Fig. 1. (a) 9.74 GHz EPR spectrum of a room-temperature toluene solution containing lanthanum metallofullerenes; (b) superposition of two simulated spectra arising from octet (c) plus octet (d).

Fig. 2. Mass spectrum of the La-fullerene residue obtained upon drying the toluene solution of fig. 1.

Spin parameters used to generate fig. 1c are $g = 2.0009$, La hyperfine coupling with $A = 3.22$ MHz (1.15 G), and $\Delta H_{pp} = 0.125$ G (this octet has been reported previously [3]). Those of fig. 1d are $g = 1.9989$, $A = 2.32$ MHz (0.83 G), and $\Delta H_{pp} = 0.13$ G. These parameters are in agreement with those obtained in ref. [8]. The mass spectrum of the La fullerene sample is shown in fig. 2.

If two La@C_n molecules with different n were responsible for the two dominant octets simulated in figs. 1c and 1d, then two La@C_n peaks in about a 3:1 ratio should be observed in the mass spectrum. Since the La@C_{82} peak seen in fig. 2 is more than 10 times as intense as the next strongest metallofullerene peaks (LaC$_{76}$ and LaC$_{80}$), the two superposed octet EPR patterns apparently correspond to different species of La@C_{82}. It is possible in principle that a second metallofullerene is responsible for the octet in fig. 1d, but is suppressed in the mass spectrum due to a significantly lower ionization efficiency. However, in the raw soot (prior to extraction) all metallofullerenes, LaC$_n$ ($n \geqslant 60$ and even), are detected with comparable intensities. By varying the ionization laser power over an order of magnitude, we find
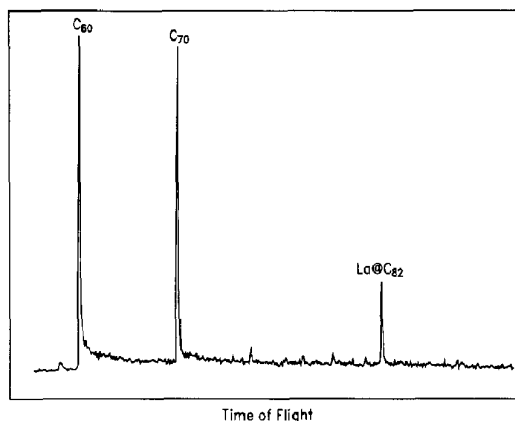
that the signal of all La fullerenes is linear with laser fluence, while that of the bare fullerenes depends on the square of the laser fluence. This result, previously reported by Cox et al. [9], suggests that bare fullerenes have ionization potentials above 6.3 eV (requiring two-photon ionization) while the lanthanum fullerenes have ionization potentials lower than 6.3 eV, allowing them to be ionized by a single photon. Since this behavior is the same for all lanthanum fullerenes, it is likely that the relative abundances of lanthanum species with different numbers of carbons are faithfully reflected by the mass spectrum peak heights. Thus, we propose that the two dominant octet EPR hyperfine patterns arise from two different species of La@C_{82}.

Analogous results are obtained with an Y fullerene sample. Fig. 3a displays a 9.76 GHz EPR spectrum of the Y extract while Fig. 3b displays a lineshape simulation of the two highest intensity doublets. Spin parameters used to construct the simulation are: $g = 2.003$, Y hyperfine coupling with $A = 1.35$ MHz (0.48 G), and $\Delta H_{pp} = 0.10$ G (this doublet has been reported previously [4,5]); and $g = 1.9998$, $A = 1.02$ MHz (0.36 G), and $\Delta H_{pp} = 0.11$ G. The ratio of the doublet intensities is approximately 3:1. Fig. 4a displays a 4.06 GHz EPR measurement of the same sample while fig. 4b displays a lineshape simulation using the *identical* spin parameters as in fig. 3b.

The multiple frequency (9.7 and 4.0 GHz) EPR spectra of the yttrium sample clearly indicate that two Y-related EPR doublets with different g values
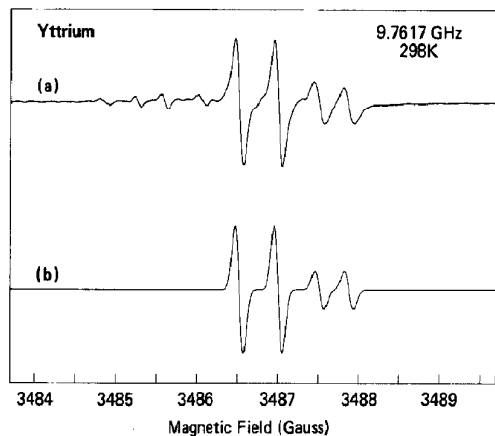
Fig. 3. (a) 9.76 GHz EPR spectrum of a room-temperature toluene solution containing yttrium metallofullerenes; (b) a simulated EPR spectrum consisting of two doublets whose intensities are approximately 3:1.

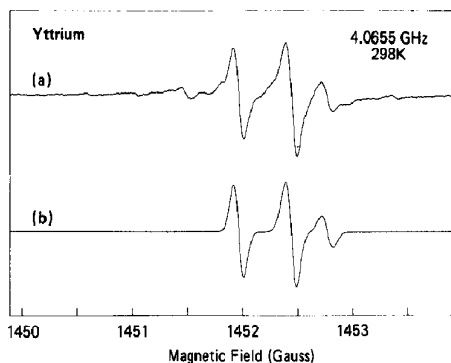Fig. 5. Mass spectrum of the Y-fullerene residue obtained upon drying the toluene solution of fig. 3.

Fig. 4. (a) Room-temperature 4.06 GHz EPR spectrum of the toluene solution fig. 3 containing yttrium metallofullerenes; (b) a simulated EPR spectrum using the *identical* spin parameters and intensities of those used in the simulation of fig. 3b.

are present and that the higher field EPR doublet is not due to ^{13}C hyperfine interaction as was suggested by Shinohara et al. [5]. As in the $La@C_{82}$ case, if the two dominant EPR doublets corresponded to $Y@C_n$ molecules with different values of n, then two $Y@C_n$ peaks should be observed with relative intensities of approximately 3:1 (i.e. the same relative intensities as the two EPR doublets of fig. 3a). Examination of this sample's residue with MS yielded the spectrum shown in fig. 5. Interspersed between the normal fullerenes are two series of peaks corresponding to metallofullerenes with one or two Y atoms associated
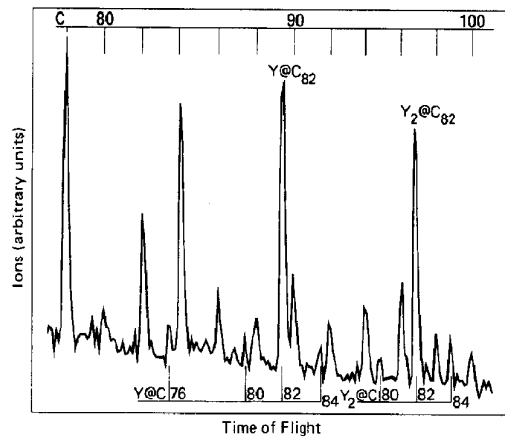
with C_{2n} cages with $2n$ between about 72 and 90. Since the $Y@C_{82}$ MS peak is at least an order of magnitude higher in intensity than any other $Y@C_n$ $(n \neq 82)$ peak, this strongly suggests that the two dominant EPR doublets arise from two different species of $Y@C_{82}$ – each having slightly different spin parameters. Note that Y_2C_{82}, which is very prominent in the MS, is apparently EPR silent.

Several explanations are possible for the observation of two EPR signals associated with species of one mass. One explanation is that only one C_{82} cage structure exists in which the metal atom occupies either of two positions relative to the cage. If a relatively small activation energy barrier separates the metal atom positions, transformation from one form to the other could occur at relatively low temperatures. Another explanation is that the spectra correspond to two different C_{82} cage structures, as suggested by Suzuki et al. [8]. For C_{82}, Manolopoulos and Fowler [10] have shown that there are nine different isolated pentagon cage structures, while Kikuchi et al. [11] have experimentally demonstrated the existence of several C_{82} cage structures with ^{13}C NMR. Transformation between C_{82} cage structures under ambient conditions is probably insignificant since a high activation energy barrier is expected (a barrier of 5.4 eV has been calculated for C_{60} cage rearrangement [12]). A third explanation is that adducts are formed involving metallofullerenes, solvent molecules, or hollow fullerenes [13].

We have observed that the absolute signal intensities of the two dominant La@C_{82} EPR multiplets decrease upon concentrating the toluene solution. This result implies that La@C_{82} species can form aggregates in solution, and in some cases their spins must pair. The observed aggregation of La@C_{82} and Y@C_{82} species could depend on many parameters including their concentration, solvent polarity, temperature and the concentration of hollow fullerenes such as C_{60} and C_{70}. A striking observation is that when a toluene solution showing two paramagnetic La or Y species is dried and the residue is dissolved in TCE, the solution shows only a single species (corresponding to fig. 1c or the left hand doublet in fig. 3, respectively). This observation explains how only a single octet was obtained in a previous La@C_{82} EPR study [3]. The second La octet or Y doublet can be restored by redissolving in toluene and heating slightly. We note that after times on the order of weeks, TCE solutions also being to show the second La octet. This observation argues against the hypothesis that the two spectra arise from a single La@C_{82} species associated in two different ways with solvent molecules. These preliminary results, however, cannot distinguish between the possibilities that the multiple EPR spectra arise from identical cage structures with different metal/cage relationships, metallofullerenes with different C_{82} cages, or adducts of metallofullerenes with hollow fullerenes.

In the low field region of the lanthanum EPR spectrum (fig. 1a), several additional multiples are also present which are not observed on the high field side. Expanded, higher resolution spectra of the La sample are shown in figs. 6 and 7. We interpret fig. 6 in terms of an octet La-hyperfine pattern in which the linewidths (ΔH_{pp}) are approximately the same as the hyperfine coupling separation. In fig. 7, three peaks of equal intensity – separated from one another by equal magnetic field increments – are observed. Since La is the only nucleus in this solution with $I > 1/2$, we interpret these three peaks as resolvable components of an octet La-hyperfine pattern. Thus, lower intensity multiplets of figs. 6 and 7 are clear evidence of additional La@C_n species. Signal-to-noise limitations preclude unambiguous correlations between EPR and MS for these species, due to the fact that several metallofullerene peaks present in MS have intensities at least an order of magnitude below
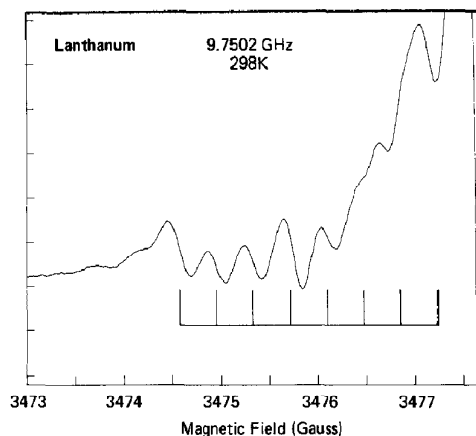

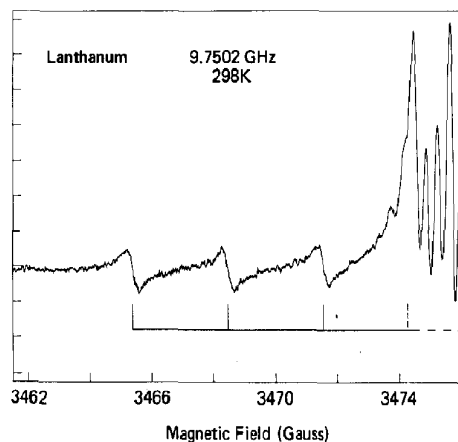Fig. 6. An expanded, higher resolution EPR spectrum of the low-field components of fig. 1a.

Fig. 7. An expanded, higher resolution EPR spectrum of the low-field portion of fig. 1a.

that of La@C_{82}. However, the intensities are such that these multiplets are possibly associated with LaC_{76} or LaC_{80}, which are barely detectable in the MS.

The low field region of the yttrium extract EPR spectrum (fig. 3a) shows peaks which are approximately an order of magnitude lower in intensity than the dominant doublets simulated in fig. 3b. Due to the inability to clearly distinguish peaks arising from ^{13}C hyperfine coupling from those arising from either other Y@C_n (with n not equal to 82) species or additional Y@C_{82} species, assignment of spin parameters to these lower intensity peaks is ambiguous. In

Table 1

La@C_n and Y@C_n spin parameters

Metallofullerene	g	A_{exp}		ΔH_{pp} (G)
		(MHz)	(G)	
La@C_{82} (fig. 1c)	2.0009	3.22	1.15	0.12
La@C_{82} (fig. 1d)	1.9989	2.32	0.83	0.13
La@C_n (fig. 6)	2.0042	1.04	0.37	0.28
La@C_n (fig. 7)	2.0044	8.6	3.07	0.41
Y@C_{82} (higher int.)	2.0003	1.35	0.48	0.10
Y@C_{82} (lower int.)	1.9998	1.02	0.36	0.11

table 1, spin parameters of the La and Y fullerene multiplets used to fit the data are summarized.

In conclusion, we have correlated two La-related EPR octets with a single La@C_{82} MS peak and two Y-related EPR doublets with a single Y@C_{82} MS peak, in agreement with Suzuki et al. [8]. From these results we propose that La@C_{82} do not exist as a single species in solution, but possess either different cage structures or different metal positions, or form adducts with hollow fullerene molecules. Additionally, lower intensity La@C_n EPR multiplets are identified which have not, as yet, been correlated with specific MS peaks.

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