C_{70} Fulleryl Radicals

Alexandros Lappas, Konstantinos Vavekis and Kosmas Prassides*

School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton, UK BN1 9QJ

The C_{70} fullerene molecule has five distinct addition sites; all five possible $C_{70}Mu$ isomers (Mu ≡ muonium, the light isotope of hydrogen) are observed for the first time by muon spectroscopy.

Following the isolation of the fullerenes, the predicted molecular structures of C_{60} (truncated-icosahedral, I_h) and C_{70} (ellipsoidal, D_{5h}) were quickly confirmed. While only a single line was observed in the ^{13}C NMR spectrum of C_{60}, five lines with intensities in the ratio 1 : 1 : 2 : 2 : 1 were observed for C_{70} and each was assigned to one of the predicted five sets of inequivalent C atoms ($n_A : n_B : n_C : n_D : n_E$ = 10 : 10 : 20 : 20 : 10, as indicated in Fig. 1).[1] Single atom attachment to each symmetry-inequivalent carbon site should result in the formation of a unique fulleryl radical for C_{60} and five distinct fulleryl radicals for C_{70}. Such radicals of hydrogen (HC_{60} and HC_{70}) are not only interesting for their simplicity, allowing us to test the fundamental theories of fullerene electronic structure and reactivity, but they can also provide important benchmarks for the spectroscopic search for fullerene adducts in the interstellar medium.[2] The HC_{60} fulleryl radical was quickly characterised both by muon (μSR)[3] and by EPR[4] spectroscopy. Of the five possible C_{70} radicals, only three initially,[5] and four subsequently,[6,7] have been identified. In this communication, we report the muon spectra of C_{70}, obtained with the transverse-field muon spin rotation (TF-μSR) technique and identify all five isomers, resulting from Mu addition to the five inequivalent sites.

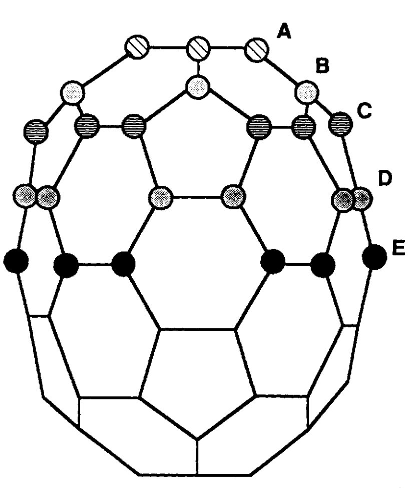

Fig. 1 Schematic diagram of the C_{70} molecule with the five symmetry-inequivalent types of C atoms labelled **A** to **E** consecutively from the pole towards the equator

The TF-μSR experiment was performed at 324 K on a sublimed 300 mg highly pure (>99%) C_{70} sample,[8] using surface muons (μ^+) at the πM3 port of the accelerator at the Paul Scherrer Institute, Villigen, Switzerland. The 100% spin polarised μ^+ were stopped in the sample and placed in a magnetic field of 0.3 T, applied perpendicular to the muon spin direction. Relaxation of the muon polarisation was monitored by detecting the decay positrons emitted preferentially along the muon spin direction of the incoming beam, in counters positioned 'behind' and 'in front' of the sample.

Positive muons (μ^+) may bind an electron to form a muonium atom (Mu ≡ μ^+e^-), which is in a chemical sense a light isotope of hydrogen ($m_{Mu} \approx (1/9)m_H$). Solid fullerenes are very effective media for the formation of such muonium centres. Some Mu can enter the fullerene cage, forming an endohedral fullerene complex.[3,9,10] Other Mu atoms add exohedrally across high π-order C–C bonds to form fulleryl radicals. These adducts are simple two-spin-1/2 systems and can be distinguished by their isotropic muon-electron hyper-

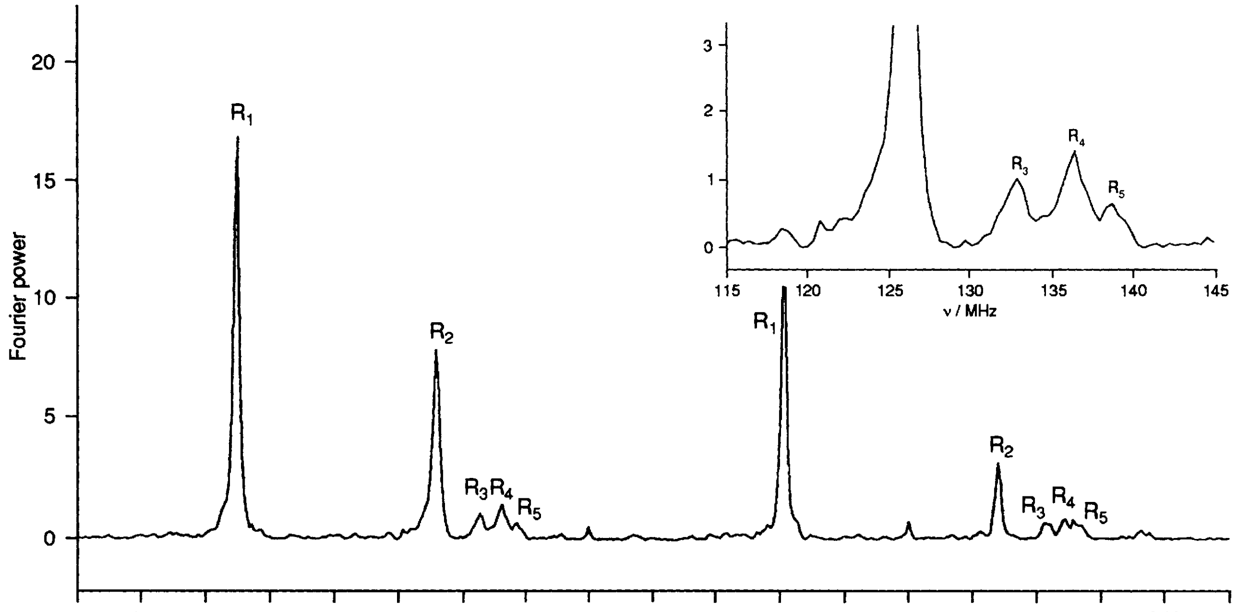

Fig. 2 Transverse field μSR spectrum of C_{70} powder at 324 K and 0.3 T. Data from the two sets of detectors (forward, backward) have been summed. The doublets corresponding to the five radicals are labelled R_1 to R_5 in ascending order with increasing precession frequency. The lines at 150 and 200 MHz are instrumental (clock frequency). The inset shows an expanded view of the 115–145 MHz region.

Table 1 Isotropic muon-electron hyperfine coupling constants, A_{hf}, and linewidths, λ, of the five fulleryl MuC_{70} radicals at 324 K. The predicted values using the spin density distributions calculated by a number of theoretical techniques are also included

Radical	A_{hf}/MHz	$\lambda/\mu s^{-1}$	A_{hf}^{a}/ MHz	A_{hf}^{b}/ MHz	A_{hf}^{c}/ MHz	Tentative assignment
R_1	275.42(4)	1.0(1)	184	182	163	**D**
R_2	339.96(5)	1.6(2)	224	236	214	**C**
R_3	354.4 (3)	4(1)	270	290	283	**A**(?)
R_4	361.5 (5)	9.3(5)	328	324	320	**B**(?)
R_5	365.7 (8)	11(1)	455	426	511	**E**(?)

[a] Predicted, ref. 6. [b] Predicted, ref. 12. [c] Predicted, ref. 7.

fine coupling (A_{hf}) constants: endohedral Mu shows values close to the one of a Mu atom in vacuum (4463 MHz), while exohedral fulleryl radicals have values reduced by approximately one order of magnitude and comparable with what is known for other alkyl radicals.[11] Fig. 2 shows Fourier power spectrum of the time evolution of the μ^+ polarisation at 324 K at the applied field of 0.3 T. Five pairs of lines can be identified, each assigned to a different C_{70} fulleryl radical, labelled R_1 to R_5. The extracted hyperfine couplings, A_{hf} are listed in Table 1 together with the corresponding linewidths, λ.

Attempts at assigning the observed radicals to specific isomers have been based on comparisons between the observed A_{hf} constants and those computed by a number of theoretical approaches, including AM1/RHF,[12] MNDO/UHF[6] and QCFF/PI[7] calculations. At present, there is poor agreement between calculated and observed values for A_{hf}, strongly necessitating the performance of more sophisticated calculations in order to understand the reasons for such discrepancies.

The availability now of data on all five isomers places severe constraints on future attempts to understand the electronic structure of these simple derivatives of C_{70} together with their reactivity. At present, we can use the results of the existing calculations of the distribution of electron spin in the vicinity of the addition sites as a qualitative guide towards tentative assignments. In addition, the measured hyperfine anisotropies in avoided-level-crossing muon spin resonance (ALC-μSR) experiments[8,13] may also be used to check the consistency of such assignments. For instance, addition to a carbon site **D** (Fig. 1) leads to a delocalised radical which is expected to have the smallest A_{hf} among the C_{70} fulleryl radicals. This is then identified with radical R_1 (275.4 MHz) of Fig. 2. Such an assignment is also supported by the experimentally observed positive axial hyperfine anisotropy of this adduct measured in ALC-μSR experiments.[8,13] On the basis of computed hyperfine interactions, radical R_2 (340.0 MHz) may also be assigned to the isomer resulting from addition at site **C**.[6,7,12] However, the existence of three radicals with very similar hyperfine couplings (354, 361 and 366 MHz) makes identification of the remaining isomers highly demanding. Of particular interest for understanding the differing chemical reactivity of non-spherical fullerenes like C_{70} at different sites[14] on their surface (*e.g.* polar versus equatorial attack[15]) will be the rationalisation of the low value of A_{hf} found experimentally for radical **E**, contrary to the results of the various computations. We note that the relative reactivity of each site on the C_{70} surface in the present experiments is controlled by the kinetics of radical formation.[6,12] Chemical reactions like hydrogenation[16,17] display a different selectivity pattern with the most reactive bond being the **A**–**B** bond, followed by the **C**–**C** bond.

We thank the EPSRC for financial support, the Paul Scherrer Institute for provision of muon beam time and the staff at PSI for experimental help.

Received, 5th September 1994; Com. 4/05387G

References

1 R. Taylor, J. P. Hare, A. K. Abdul-Sada and H. W. Kroto, *J. Chem. Soc., Chem. Commun.*, 1990, 1423.

2 J. P. Hare and H. W. Kroto, *Acc. Chem. Res.*, 1992, **25**, 106.

3 E. J. Ansaldo, C. Niedermayer and C. E. Stronach, *Nature*, 1991, **353**, 121.

4 J. R. Morton, K. F. Preston, P. J. Krusic and L. B. Knight, *Chem. Phys. Lett.*, 1993, **204**, 481.

5 C. Niedermayer, I. D. Reid, E. Roduner, E. J. Ansaldo, C. Bernhard, U. Binninger, H. Glückler, E. Recknagel, J. I. Budnick and A. Weidinger, *Phys. Rev. B*, 1993, **47**, 10923.

6 B. Addison-Jones, P. W. Percival, J.-C. Brodovitch, F. Ji, S. Wlodek, J. P. Selegue, M. S. Meier and J. B. Wakefield, *Hyperfine Interact.*, 1994, **86**, 817.

7 J. R. Morton, F. Negri and K. F. Preston, *Chem. Phys. Lett.*, 1994, **218**, 467.

8 T. J. S. Dennis, K. Prassides, E. Roduner, L. Cristofolini and R. DeRenzi, *J. Phys. Chem.*, 1993, **97**, 8553.

9 R. F. Kiefl, J. W. Schneider, A. Macfarlane, K. Chow, T. L. Duty, T. L. Estle, B. Hitti, R. L. Lichti, E. J. Ansaldo, C. Schwab, P. W. Percival, G. Wei, S. Wlodek, K. Kojima, W. J. Romanow, J. P. McCauley, N. Coustel, J. E. Fischer and A. B. Smith, *Phys. Rev. Lett.*, 1992, **68**, 1347.

10 K. Prassides, T. J. S. Dennis, C. Christides, E. Roduner, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Phys. Chem.*, 1992, **96**, 10600.

11 E. Roduner, *Chem. Soc. Rev.*, 1993, **22**, 337.

12 I. D. Reid and E. Roduner, *Hyperfine Interact.*, 1994, **86**, 809.

13 R. M. Macrae, K. Prassides, I. M. Thomas, E. Roduner, C. Niedermayer, U. Binninger, C. Bernhard, A. Hofer and I. D. Reid, *J. Phys. Chem.*, in the press.

14 A. V. Nikolaev, T. J. S. Dennis, K. Prassides and A. K. Soper, *Chem. Phys. Lett.*, 1994, **223**, 143.

15 A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead and S. R. Parkin, *J. Am. Chem. Soc.*, 1991, **113**, 8953.

16 C. C. Henderson, C. M. Rohlfing, K. T. Gillen and P. A. Cahill, *Science*, 1994, **264**, 397.

17 A. G. Avent, A. D. Darwish, D. K. Heimbach, H. W. Kroto, M. F. Meidine, J. P. Parsons, C. Remars, R. Roers, O. Ohashi, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1994, 15.