

Hyperfine structure of Sc@C₈₂ from ESR and DFT

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Abstract

The electron spin g - and hyperfine tensors of the endohedral metallofullerene Sc@C₈₂ are anisotropic. Using electron spin resonance (ESR) and density functional theory (DFT), we can relate their principal axes to the coordinate frame of the molecule, finding that the g -tensor is not axially symmetric. The Sc bond with the cage is partly covalent and partly ionic. Most of the electron spin density is distributed around the carbon cage, but 5% is associated with the scandium d_{yz} orbital, and this drives the observed anisotropy.

(Some figures in this article are in colour only in the electronic version)

The reports of a scandium atom being trapped in fullerenes [1, 2] raised fundamental questions about the electronic and geometric structures of these species [3–9]. Initial characterization of the most stable molecule, Sc@C₈₂(I), with electron spin resonance (ESR) [1, 2], yielded a hyperfine coupling between the Sc nucleus and the unpaired electronic spin of only 0.38 mT, with a g -factor close to the free electron value. These results were interpreted as evidence for the transfer of three electrons away from the metal atom to the cage. This conclusion was later supported by the small value for the nuclear quadrupole interaction measured by temperature-dependant ESR [3]. Other studies have suggested less electron transfer. Hartree–Fock calculations [4, 5] described the electronic state as Sc²⁺C₈₂²⁻, which was consistent with ultraviolet photoelectron spectroscopy [6] and absorption spectroscopy with UV–vis–NIR radiation [7]. Moreover, analysing synchrotron powder diffraction with the maximum entropy method [8] provided a value of 2.2 e⁻

for this charge transfer. Recently, density functional theory (DFT) calculations [9] have provided a compromise: strong hybridization was found between the d valence orbitals of the Sc atom and the π orbitals of the C₈₂ cage. This is similar to the hybridization that gives significant La character to the occupied part of the valence band of La@C₈₂ in resonant photoelectron spectroscopy [10]. The extraordinarily long spin lifetimes exhibited by Sc@C₈₂ and related compounds have led to proposals for their application as components in quantum information processing devices [11, 12]. In order to assess further the potential of this molecule, the nature of the spin state and its coupling to the molecule must be understood.

In this paper, we systematically study the hyperfine structure of the endohedral metallofullerene Sc@C₈₂ using all electron DFT calculations and ESR measurements. From the comparison between the theoretical and experimental data for the isotropic hyperfine splitting (hfs) constants of ⁴⁵Sc and ¹³C, we confirm that the Sc@C₈₂(I) isomer has C_{2v} symmetry. The calculated anisotropy of the hfs tensor is in good agreement with our low temperature experimental measurements and allows the axes of the tensor to be identified with the coordinate

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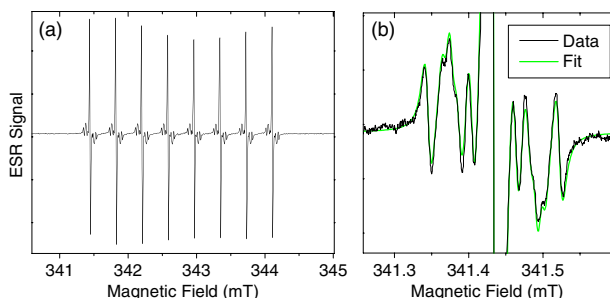


Figure 3. Room temperature CW-ESR spectra of Sc@C₈₂: (a) full spectrum; (b) enlargement of lowest-field line, with the best fit using five Lorentzian curves in grey (green online), using the hfs constants in table 2.

Table 2. The hfs constants for the experimental fit in figure 3(b). Zero coupling corresponds to no ¹³C atoms in the fullerene cage or ¹³C in sites with negligible spin density.

| ¹³ C hfs (mT) | 0 | 0.06 | 0.09 | 0.11 | 0.13 | 0.18 |
|--------------------------|-------|-------|-------|------|------|------|
| % of molecules | 52.42 | 13.38 | 19.65 | 6.14 | 2.55 | 5.86 |

These predicted hfs constants for the C_{2v} isomer may be compared directly with measurements from room-temperature ESR experiments. Sc@C₈₂ was prepared by the literature procedure [1]. A small amount of Sc@C₈₂ was dissolved in toluene and sealed in a quartz ESR tube after degassing. Measurements were made on a commercial X-band (9.5 GHz) Bruker ESR spectrometer. The continuous wave (CW) ESR spectrum is shown in figure 3. Due to the nuclear spin $I = 7/2$ of ⁴⁵Sc it contains eight resonance lines equally spaced by an hfs constant of 0.381 mT [2]. This identifies the sample as Sc@C₈₂(I) rather than the less common Sc@C₈₂(II) isomer which has previously been observed [7]. The sharpness of the lines indicates that the Sc atom is stationary with respect to the cage over the 100 ns timescale of the ESR measurement. Each ⁴⁵Sc hyperfine line has a series of satellite lines arising from the hyperfine coupling with ¹³C atoms on the cage [18]. Since the natural abundance of ¹³C is 1.1%, over half of the Sc@C₈₂ molecules contain one or more ¹³C atoms, and of these 63% contain only one. Hence the ¹³C hyperfine structure is dominated by coupling to a single $I = 1/2$ ¹³C nucleus. These can be in different positions, giving different hyperfine splitting into two lines. In figure 3(b) the grey curve gives the best fit to the hyperfine structure using five pairs of Lorentzian lines equally split about their centre (five were used on pragmatic grounds, since four were inadequate and six gave little improvement over five). Table 2 gives the fitted hfs constants and their weightings.

These ESR measurements may be directly compared with the calculated DFT results in table 1. Our measurement of the ⁴⁵Sc hyperfine constant is comparable with the calculated values for the C₂(III) and the C_{2v} symmetries, though as expected the calculations somewhat underestimate the strength of the coupling. The ambiguity between these two isomers is removed by the ¹³C coupling. The largest experimental value that can be taken from the measurements in table 2 is 0.18 mT. The calculated value for C_{2v} is 17% less than this, but the calculated value for C₂(III) is 67% greater. We conclude that the isomer in our experiments does indeed have C_{2v} symmetry,

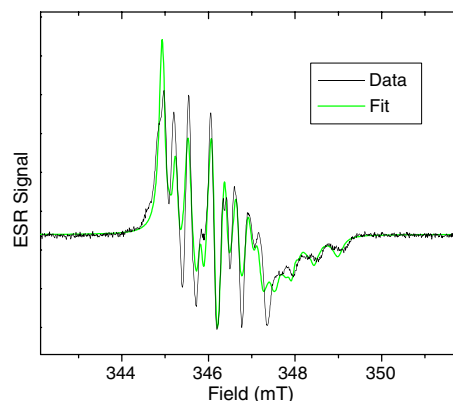


Figure 4. ESR spectrum of Sc@C₈₂ at 80 K in frozen solution. The data were fitted using the g -tensor and hfs tensor given in equations (2) and (3). The slight change in resonant field compared with figure 3(a) arises from retuning the microwave frequency following the change in the cavity temperature.

and that the ADF calculations are giving consistent values for the hfs constant.

Further confirmation of the consistency of the DFT calculations with experiment is provided by the anisotropy of the hfs tensor, which we have measured at 80 K after freezing the solvent. This removes the isotropic averaging which is present in the room temperature ESR spectra. No g -factor reference was used to check the calibration of the spectrometer, as the value of the isotropic g -factor has previously been reported [7, 18]. Figure 4 shows the resultant ESR spectrum at 80 K for the same sample of Sc@C₈₂ as was measured at room temperature in figure 3. We see that without the motional averaging due to molecular tumbling the eight lines that were sharp in figure 3(a) are now broadened by the anisotropy. We have fitted this experimental spectrum to the effective spin Hamiltonian

$$H = \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} \quad (1)$$

with $S = 1/2$ and $I = 7/2$, restricting the g - and A -tensors to be diagonal. The six fitted parameters were optimized using standard numerical iteration techniques, yielding the grey curve in figure 4.

This procedure gave a g -tensor

$$\mathbf{g} = \begin{pmatrix} 1.9968 & 0 & 0 \\ 0 & 2.0033 & 0 \\ 0 & 0 & 1.9998 \end{pmatrix} \quad (2)$$

and an hfs tensor

$$\mathbf{A} = \begin{pmatrix} 0.55 & 0 & 0 \\ 0 & 0.28 & 0 \\ 0 & 0 & 0.26 \end{pmatrix} \text{ mT}. \quad (3)$$

The g -tensor is not axially symmetric, even though the hfs tensor is approximately axial. This is consistent with C_{2v} symmetry. Previously, the g -tensor had been obtained from experiment by assuming that it is axial and using the Kivelson equations to determine the two unknown constants from a series of ESR spectra obtained at a range of temperatures. This yielded differences between the constants of 0.013 [19] and more recently 0.0050 [20], which may be compared with the

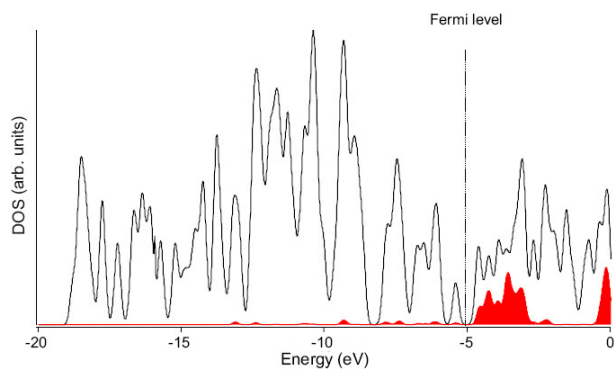


Figure 5. The calculated total DOS (curve) and Sc PDOS (solid area, red) of Sc@C₈₂ by ADF code [15]. Gaussian bands of 0.25 eV half-width were used. The solid area at energies lower than the Fermi level corresponds to the 2.09 electrons in the 3d, 4s, and 4p orbitals of the Sc atom.

rms difference of 0.0033 between the three constants in our non-axial tensor.

The hyperfine tensor of the C_{2v} isomer was calculated using the ADF code [15] for a single molecule with a known geometry and orientation. In the coordinate system shown in figure 2, the hfs tensor is

$$\mathbf{A} = \begin{pmatrix} 0.47 & 0 & 0 \\ 0 & 0.23 & 0 \\ 0 & 0 & 0.19 \end{pmatrix} \text{ mT}, \quad (4)$$

which may be compared with the experimentally determined tensor in equation (3), with an underestimate of the constants by about 20%.¹⁰ The relationship between the calculated and measured hfs tensors enables the principal axes of both of the experimental tensors to be related to the molecular orientation indicated in figure 2. The spin density on the Sc site in figure 2(b) is associated with the d_{yz} orbital, which is found to account for 5% of the semi-occupied molecular orbital (SOMO), corresponding to the spin 1/2 eigenstate of Sc@C₈₂. This controls the anisotropy of the resultant *g*- and hfs tensors: the d_{yz} orbitals define an axis in the *x*-direction.

The orbital structure of the molecule is displayed as a density of states (DOS) in figure 5. The partial density of states (PDOS) attributable to Sc is shown by the filled area. Contributions of Sc to the occupied valence levels are dispersed over the upper part of the valence band and are small at any energy. The orbital structure is similar to that described by Lu *et al* [9] except that their Sc PDOS shows a large peak at the Fermi level. The principal Sc 3d levels are unoccupied and are centred at -3.5 eV. The main Sc 4s level lies within the d level and the Sc 4p levels are found at about 0 eV. Mulliken population analysis of the Sc valence orbitals assigns a charge of +0.8 to Sc (other methods of charge estimation give slightly lower values). The combined electron density in the 4s and 4p orbitals is 0.56, with the d orbitals containing a further 1.53 electrons. Most of the spin density on Sc is contained in the d orbitals, with the major contributor being the d_{yz} orbital as shown in figure 2(b). For comparison, ESR measurements of

¹⁰ The anisotropy factors $\Delta A = A_{zz} - (A_{xx} + A_{yy})/2$ may also be compared: from DFT $\Delta A = 0.26$ mT; from our ESR $\Delta A = 0.26$ mT; from previous ESR $\Delta A = 0.3$ mT [20] and 0.31 mT [19].

Sc²⁺ ions substituted for Ca²⁺ in a CaF₂ crystal yield an hfs constant of 6.92 ± 0.05 mT [21]. Linear interpolation from this experiment predicts that 5.5% of an electron spin is in the d orbital, consistent with DFT calculations¹¹. The lack of occupancy of orbitals with predominant Sc character suggests the optimum assignment of oxidation state [23] as Sc(III).

In summary, we have determined the hyperfine and *g*-tensors of Sc@C₈₂(I) with respect to the coordinate frame of the molecule by combining information from both theory (DFT) and experiment (ESR). Although the hfs tensor is almost axially symmetric, the *g*-tensor is not, in contrast to previous assumptions. Our results confirm that Sc@C₈₂(I) has C_{2v} symmetry with the metal atom lying far off-centre along the symmetry axis, adjacent to a six-membered carbon ring. This results in strong hybridization between the Sc d orbitals and C π orbitals, so that the bond is partially covalent, partially ionic, with a Mulliken charge of +0.8 on the Sc site. The electron spin density is distributed mainly around the carbon cage with 5% of the spin eigenstate associated with the Sc d_{yz} orbital, which determines the anisotropy of the resultant *g*- and hfs tensors.

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¹¹ A spherical Sc ion (both 4s electrons removed) GGA calculation using the Program for Linear-combination of Atomic Type Orbitals (PLATO) [22] gives a good linear dependence of the hfs constant on the d-orbital occupation over the range from zero to one electron. A value of 0.44 mT is found at 5% occupation whereas at the end of this range it is found to be 8.50 mT.

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