HYPERFINE STRUCTURE OF $Sc@C_{82}$: ESR AND DFT STUDIES

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Introduction

$Sc@C_{82}$ is a fullerene cage containing a single atom of Sc [1]. The ^{45}Sc hyperfine (HF) structure of $Sc@C_{82}$ was studied using electron spin resonance (ESR) and modeled using density functional theory (DFT).

Experimental and Computational Techniques

$Sc@C_{82}$ was produced by the DC arc discharge method described in the literature [2]. This sample was dissolved in toluene and purified with high performance liquid chromatography before being deoxygenated and sealed in an ESR tube. Continuous-wave measurements were made on a Bruker ESR spectrometer at X-band (9.5 GHz).

Optimized molecular structures from all electron DFT calculations were used for single point DFT calculations within the Amsterdam Density Functional code (ADF). HF coupling constants were calculated in ADF after van Lenthe [3].

Results and Discussion

In liquid solution the ESR spectrum of $Sc@C_{82}$ has eight sharp hyperfine (HF) resonances, due to the $I = {}^7/_2$ ^{45}Sc nucleus. The isotropic HF constant is 0.381 mT which is 5 % of that for a Sc^{2+} ion [4]. This is consistent with the finding, from DFT, that the spin density in the Sc 3d level is 5 %, with 0.05 % in the 4s level.

Freezing the solution leads to anisotropic line-broadening as shown in Fig. 1. The fit was obtained with a diagonal g-tensor, $g_{xx} = 1.9968$, $g_{yy} = 2.0033$, $g_{zz} = 1.9998$, and a diagonal HF tensor $A_{xx} = 0.55$ mT, $A_{yy} = 0.28$ mT, $A_{zz} = 0.26$ mT. Comparing these data with the HF tensor calculated from DFT shows that the major symmetry axis of the C_{2v} molecule corresponds to the z-axis.

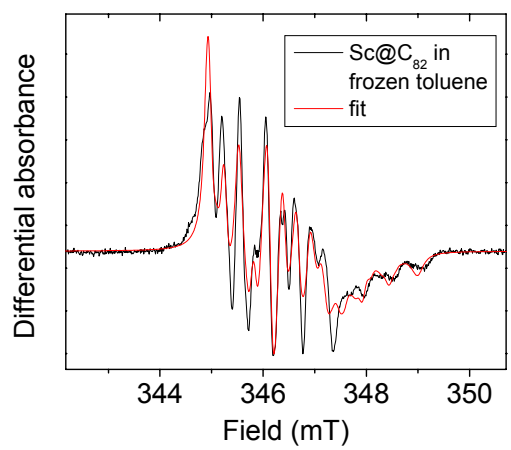

Figure 1. ESR spectrum of $Sc@C_{82}$ at 80 K.

Conclusions

The g-tensor of $Sc@C_{82}$ is non-axial and the HF tensor is almost axial. Comparing these results with DFT simulations allows the tensors to be written in the coordinate system of the molecule. The spin density on the Sc atom is 5 %.

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