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Spin Signature of the C₆₀ Fullerene Anion: A Combined X- and D-band EPR and DFT Study

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Abstract

Fullerenes attract a lot of attention in various scientific fields, but their electronic properties are still not completely understood. Here, we report on a combined EPR and DFT study of the fullerene anion C₆₀[−] in solid glassy environment. DFT calculations were used to characterize its electronic structure through spin density distribution and magnetic resonance parameters. The electron spin density is not uniformly distributed throughout the C₆₀[−] cage but shows a similar pattern as seen in PC₆₁BM[−]. EPR spectroscopy reveals a rhombic g-tensor sensitive to the environment in the frozen glassy solutions which can be rationalized by deformation of the fullerenes along low frequency vibrational modes upon cooling. DFT modeling confirms that these deformations lead to deviations in the C₆₀[−] g-values. The decrease of g-tensor anisotropy with sample annealing is related to the lessening of g-tensor strain upon temperature relaxation of the most distorted sites in the glassy state.

TOC GRAPHICS

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Notes

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ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge on the ACS Publications website at DOI: Effects of functional and basis set on the calculated g-values, effect of distortion along normal modes on the energies and calculated g-values.

Keywords

C₆₀; PC₆₁BM; Fullerene; Radical Anion; g-tensor; Electron Paramagnetic Resonance; Density Functional Theory

TEXT.

Fullerenes were discovered more than 30 years ago and represented a new carbon allotrope.^{1–2} They have attracted a lot of attention in various fields of chemistry, physics, material science and even biological and medical fields.^{3–12} The prototypical, most stable, and most important fullerene is the spherical one with 60 carbon atoms, called carbon 60 or simply C₆₀. This molecule has also colloquially been named Buckminsterfullerene or buckyball, after Buckminster Fuller, whose geodesic domes they resemble. The 60 carbon atoms are arranged in 12 hexagons and 12 pentagons with icosahedral symmetry (I_h), thus essentially having the shape of a soccer ball. The electronic properties of C₆₀ and its derivatives were extensively studied by a variety of experimental and theoretical methods.³ A most remarkable chemical property is its ability to accept one or more electrons.^{3, 13–14} The electron affinity of fullerenes determines their extensive use as an electron acceptor in organic electronics, organic donor-acceptor photovoltaic cells and molecular donor acceptor systems like dyads.^{15–21} In fact, the very first photovoltaic effect in polymer-fullerene blends was demonstrated using C₆₀ as electron acceptor.²² The invention of PC₆₁BM,²³ a better soluble derivative of C₆₀, and other derivatives, lead to a dramatic increase in conversion efficiencies and, as a consequence, enhanced research effort on fullerenes in general. Due to the successful application of the PC₆₁BM in organic photovoltaics,^{16, 21, 24} the electronic properties of PC₆₁BM as well as its anion in condensed phases are in many cases better understood than its parent molecule C₆₀.^{25–30} For example, even central Electron Paramagnetic Resonance (EPR) parameters of the C₆₀ anion are not yet definitely established.¹³ The magnetic resonance parameters are fingerprints of the molecular electronic structure and their knowledge should clarify energetics of C₆₀ and its interactions with environment. The electronic g-tensor provides an excellent, sensitive indicator of the electronic structure of paramagnetic molecules, in particular of the unpaired spin distribution

and energetics of the frontier orbitals. In an organic molecular radical, like a fullerene anion, the three principal values of the g-tensor deviate from the free electron g-value ($g_e \approx 2.002319$) due to several effects.^{31–34} The most important one being the properties of the frontier orbitals and their effect on the spin-orbit coupling. In spite of the large number of publications on this topic, the cause and the extent of the g-anisotropy in the C_{60} anion remain unclear.^{13, 35–40} To clarify and remove inconsistencies in the literature we carried out a comprehensive multifrequency EPR study of the C_{60} anion in the solid glassy state and combined it with an extensive set of DFT calculations.

In multiple previous EPR studies, salts of a C_{60} anion with cation counterions were investigated.^{13, 36, 41} Obviously, the neighboring positive charge will have a strong effect on the electronic structure of the C_{60} anion. In order to avoid the influence of a neighboring cation on the C_{60} anion, in this study the C_{60}^- radicals were created at cryogenic temperature by *in situ* illumination of donor-acceptor solutions in the resonator of the EPR spectrometer. This type of generation of cation and anion radicals has been described previously.^{22, 27–29} The P3HT polymer was used as the electron donor component, since it is well characterized by EPR spectroscopy, and has been employed in many previous studies with various fullerenes.^{28, 42} Upon illumination of the donor-acceptor mixture, excited singlet states are generated, which subsequently decay via charge transfer to radical cations, $P3HT^+$, and radical anions, C_{60}^- .^{16, 21} The C_{60}^- observed by steady-state spectroscopy are long-lived and well separated from the P3HT radical cations ($>25 \text{ \AA}$), since closer pairs recombine rapidly even at cryogenic temperatures.⁴³ At these large distances, the magnetic interactions between radicals are negligible, the C_{60}^- signals can thus be treated like an isolated radical species.²⁸ The C_{60}^- anion radical generated under these conditions has not been studied yet in detail by EPR spectroscopy.

For EPR on organic radicals, there are two important types of magnetic interactions, described by hyperfine coupling tensors and the g-tensor. The only hyperfine couplings in the C_{60}^- anion radical are due to interaction of the unpaired electron spin with the 1.1% abundant ^{13}C isotope. These interactions are not resolved in frozen solution EPR spectra, and thus the g-tensor is the most important magnetic parameter in this case. Conventional X-band EPR (9–10 GHz) spectroscopy allows only the partial separation of the signals of C_{60} anion and P3HT cation radicals, and their g-tensors are not fully resolved.^{25, 42, 44} These problems were overcome by using high frequency D-band (130 GHz), which has 14 times greater g-tensor resolution compared to X-band (Figure 1).

The high-frequency EPR spectrum of C_{60}^- demonstrates rhombic symmetry of the g-tensor with one narrow, ca. 0.4–0.5 mT, low field component and two very broad, ca. 4–5 mT, high field components. Computer simulation does not allow accurate spectra simulation with one set of g-tensor parameters. Reasonable simulation were obtained using substantial broadening of the high field components and three sets of g-tensors (2.0001; 1.9989; 1.9932; relative weight 0.4), (2.0001; 1.9975; 1.9948; relative weight 0.3), and (2.0000; 1.9970; 1.9965; relative weight 0.3) (Figure 1 and Table 1). Note, that the symmetry of the g-tensor is quite different from that of the C_{60} derivative $PC_{61}BM^-$, which has an almost axial g-tensor (2.0006; 2.0005; 1.9985) with two narrow perpendicular components and a broad parallel one (see Figure 1 for comparison).^{25, 27, 29, 44}

We discovered that the line shape and g-tensor of C_{60}^- markedly depends upon sample treatment. Figure 2 shows transformation of the X-band EPR spectra of the C_{60} :P3HT solution recorded at 20 K after annealing at 100 K for 5 minutes. Similar sensitivity of the samples was observed upon different cooling rates of the solution and illuminations at different temperature. While the low field peak of the C_{60} anion (g_3) always stays narrow and does not shift, the two components at higher field (g_1 , g_2) are shifting and broadening depending on sample treatment conditions. The $P3HT^+$ signal in the low field part of the spectrum does not experience any changes upon the sample annealing process (beside decay due to recombination processes). Since the C_{60} molecules didn't undergo chemical transformations, we consider the interactions of the fullerene anion with the environment as a plausible explanation of this effect. At low temperatures, C_{60} is trapped within a "cage" of frozen solvent molecules (in our study toluene). The solvent "cage" (environment) can deform and distort the C_{60} molecule in different ways, thus leading to the shift and broadening of g-tensor components for C_{60}^- . The deeper the trap, the larger distortion of the g-tensor components. Upon annealing the shape of the EPR spectra changes due to the temperature induced matrix relaxation of distorted sites at higher temperatures.

In order to evaluate this hypothesis and to understand in a more quantitative way why some of the EPR lines shift depending on the sample treatment and some are not, we address these questions with DFT modeling. Prior work on the C_{60} derivative, $PC_{61}BM$, radical anion demonstrated good agreement between experimental and DFT calculated g-tensors.²⁹ For the $PC_{61}BM$ anion, the side chain breaks the higher symmetry of C_{60} resulting in the values for g_2 and g_3 being nearly identical, while g_1 is much smaller. As mentioned above, we list the g-values for the C_{60} anion as $g_3 > g_2 > g_1$, where g_1 , g_2 , and g_3 are the principal axis components of the electronic g-tensor. Experimental and computational studies have shown that the lowest energy state of the C_{60} anion $^2T_{1u}$ is about 1.4 V ($>11.000\text{ cm}^{-1}$) lower in energy than other (excited) valence states, which are also doublet states ($S=1/2$).⁴⁶ This large separation in energy ensures that g-tensor calculations on the DFT level with a single Slater determinant are appropriate and that higher level g-tensor calculations, which can take potential multiconfigurational or multideterminantal aspects in account, are not required.

The neutral C_{60} molecule (without the PCBM sidechain) has I_h symmetry. The anion C_{60}^- , due to Jahn-Teller effects, has already reduced symmetry with structures of D_{5d} , D_{3d} , and D_{2h} symmetry possible.⁴⁷ From our calculations and previous computational studies it can be concluded that three symmetries are nearly isoenergetic with the ranking sensitive to the level of theory used and – due to low barriers – can easily interconvert.⁴⁸ In any case, the solvent surrounding the fullerene anion in frozen glassy solution will lower the symmetry as compared to gas phase calculations. The starting structure⁴⁹ was neutral C_{60} with I_h symmetry, and the optimized structure was D_{2h} for the monoanion C_{60}^- . The unpaired electron density and the g-tensor principal axes are shown in Figure 3. In contrast to the neutral C_{60} , the anion is very slightly shortened along the direction of the g_1 principal axis and lengthened along the g_2 and g_3 axes. Measuring from the center of mass, the distance to the edge of the cage is 3.47 Å (vs 3.48 Å in neutral C_{60}) along the g_1 axis, and 3.49 Å (vs 3.48 Å) along g_2 and g_3 . The unpaired electron spin density is not uniformly distributed throughout the system; instead, it forms a kind of belt around the center, around g_3 in the g_1 -

g_2 plane (see Figure 3 right panel). This is very similar to the distribution seen in $\text{PC}_{61}\text{BM}^-$ with the greater electron spin density being present along the g_1 and g_2 axes.²⁹

Importantly, the geometry distortion from the original I_h starting structure (for geometry optimization) is quite small as the introduction of a single additional electron into the molecule is not enough to produce a large Jahn-Teller distortion.⁵⁰ For this reason, the experimental EPR results (Figure 1 and Table 1) showing significant anisotropy of the g-tensor with three different g-values and the large width of the g_1 and g_2 peaks were rather unexpected. DFT calculations of the g-tensor in gas phase C_{60}^- did not reproduce the experimental difference between g_1 and g_2 ; the calculated g-tensor is axial ($g_3 > g_1 = g_2$), while the experimentally observed g-tensor is rhombic ($g_3 > g_2 > g_1$). The match between DFT calculation and experiment is quite good for g_2 and g_3 , but g_1 is higher than observed in the experiment. A systematic study shows that these deviations from experimental data are not a function of the basis set or functional choice (Supporting Information Table S1).

As the calculations did not reproduce the rhombicity of the g-tensor, we hypothesized that a physical deformation in the solid state (“cage” effect, which we discussed above) was causing the discrepancy between theory and experiment. These physical deformations are most likely to occur along those vibrational modes with low frequencies, *i.e.* small force constants (“soft”) in a simplistic model like the harmonic oscillator. To mimic such deformations in gas phase calculations, low frequency vibrational modes were calculated and the system was deformed along these normal modes. Multiple deformations along a normal mode were obtained and the energies and g-values for each deformed structure were calculated. These low frequency deformations are generally full body breathing motions (see Supporting Information). An example of such motions is shown for the 344 cm^{-1} mode in Figure 4. The deformation can be imagined as squeezing the molecule, alternately elongating it along g_3 while compressing it along g_1 and g_2 or compressing along g_3 while elongating along g_1 and g_2 . The results of these deformations on both the molecular energetics and the g-values are shown in Figure 4.

As the molecule is deformed along the normal mode, the value of g_3 remains relatively insensitive to the deformations. This was found for all of the low frequency modes we investigated (see Supporting Information), and is in excellent agreement with our observation that in the EPR spectra the g_3 peak stays relative narrow and is not affected by annealing or sample treatment. The effects on g_1 and g_2 were more varied depending on the normal mode investigated, but the deformations shown in Figure 4 clearly result in separating the g_1 and g_2 values and thus breaking the axial symmetry of the calculated g-tensor. These effects increase as the deformations increase in magnitude, resulting in higher energy structures. This behavior of the g-values is also found for other low frequency modes (Supporting Information). It appears that C_{60} in frozen glassy solution experiences a range of structures with varying deformations resulting in both the increased width of the g_1 and g_2 peaks and increased g-tensor anisotropy. When comparing experimental results obtained in frozen solution with gas phase calculations, the consideration of molecular deformation of the solute due to its environment is essential.

Similar effect of EPR line shape dependence upon sample preparation was observed for the $\text{PC}_{61}\text{BM}^-$ anion radical. The pronounced broadening of the parallel component of the $\text{PC}_{61}\text{BM}^-$ anion g-tensor was tentatively assigned to the mechanical interactions of the flexible fullerene cage with the heterogeneous environment.^{25, 29} We decided to use a similar approach to check if variation of the g-values can be also explained by the deformation of the $\text{PC}_{61}\text{BM}^-$ structure along normal vibrational modes. For this reason we performed analogous DFT modeling on $\text{PC}_{61}\text{BM}^-$ calculating the normal modes. Based on those we calculated the g-tensor values for structures deformed along low energy normal modes, which primarily stretched the fullerene cage rather than the phenyl or ester arm. The calculated g-values for a representative motion are shown in Figure 5. In contrast to the C_{60}^- anion where the deformations primarily removed the degeneracy of the two smaller g values (g_1 and g_2), in $\text{PC}_{61}\text{BM}^-$ the deformations primarily affected the non-degenerate g-value (g_1). Thus, like the C_{60}^- anion, deformations to $\text{PC}_{61}\text{BM}^-$ seem to explain the experimentally observed broadening.

In conclusion, we have carried out a comprehensive EPR and DFT study of the characteristic EPR parameters of the C_{60} monoanion radical. DFT modeling shows that the electron spin density is not uniformly distributed throughout C_{60} cage in its radical monoanion form. Instead, it forms a kind of belt around the center with the greater density being present along the g_1 and g_2 axes. This is very similar to the distribution previously seen in $\text{PC}_{61}\text{BM}^-$. EPR spectroscopy reveals a remarkable sensitivity of the C_{60}^- g-tensor to the sample treatment. We were able to explain this sensitivity by deformation of fullerene molecules in various ways upon solvent cooling to low temperatures. Deformations of the C_{60}^- along low frequency vibrational modes leads to the modulation of the g-values in such a way that yields good qualitative agreement with experimental data. While calculated g-values are slightly higher than experimental ones, the trend of the changes explains the broad features of g_1 and g_2 components, the narrow nature of the g_3 component, and the decrease of the line width with sample annealing. The latter is related to the lessening of the g-tensor strain upon temperature relaxation of the most distorted sites in the glassy state.

These results clarify inconsistencies in the literature concerning the magnetic resonance parameters and electronic structure of the anion radical of C_{60} in the glassy state and explain several differences and similarities in the electronic structure of C_{60}^- and $\text{PC}_{61}\text{BM}^-$, as well. This work clearly demonstrates that advanced EPR spectroscopy in combination with DFT is a powerful approach for investigation of the electronic structure of paramagnetic organic molecules and its interactions with solid state environment.

Experimental and Computational Methods

EPR spectroscopy.

Continuous wave (cw) X-band (9–10 GHz) EPR experiments were carried out with Bruker ELEXSYS E580 and ELEXSYS E500 II EPR spectrometers (Bruker Biospin, Rheinstetten, Germany), equipped with an Bruker ER4102ST resonator, ER4122SHQE resonator, or Flexline dielectric ring resonator (Bruker ER 4118X-MD5-W1). Helium gas-flow cryostats (Oxford Instruments and ICE Oxford, UK) and an ITC (Oxford Instruments, UK) were used

for cryogenic temperatures. Light excitation was done directly in the resonator with 532 nm Laser light (Nd:YAG Laser, INDI, Newport) or with a white light LED (Thorlabs).

High frequency (HF) EPR measurements were performed on a home-built D-band (130 GHz) spectrometer equipped with a single mode TE₀₁₁ cylindrical cavity.^{51–52} D-band EPR spectra were recorded in pulse mode in order to remove the microwave phase distortion due to fast-passage effects at low temperatures. Light excitation was done directly in the cavity of the spectrometer with 532 nm Laser light through an optical fiber (Nd:YAG Laser, INDI, Newport). Data processing was done using Xepr (Bruker BioSpin, Rheinstetten) and MatlabTM 7.11.2 (MathWorks, Natick) environment. Simulations of the EPR spectra were performed using the EasySpin software package.⁵³

Density Functional Theory Calculations.

Initial fullerene structures were constructed from available structures of neutral C₆₀ with I_h symmetry.⁴⁹ The geometry optimizations were carried out using density functional theory (DFT) and the B3LYP functional^{54–57} using, successively, the 3–21G, 6–31G, and the 6–31G+(d) basis set, as implemented in PQSMol.⁵⁸ While inclusion of diffuse functions is generally required for anions, it has been shown that 6–31G* and the 6–31+G* basis give similar results for geometries, charge distributions, and relative energies of anionic C₆₀ structures.⁵⁹ Frequency calculations were performed on all optimized structures to ensure stable minima were obtained. The program package ORCA (v. 3.0.3)⁶⁰ was used to obtain the normal modes. All distorted structures were obtained by applying the MTR subroutine in ORCA which scans the potential energy surface as a function of the normal coordinates (q) producing a trajectory. The increment change in q for each step in the trajectory was selected on the basis of an estimate for the expected change in the total energy E due to the displacement with values of 1.5 mE_h and 1 mE_h. The spectroscopic parameters for each structure along the trajectory were obtained via single point DFT calculations, with the B3LYP functional in combination with the EPRII basis set.^{61–62} The principal electronic g-values were calculated employing the coupled-perturbed Kohn-Sham equations and the spin orbit operator computed using the RI approximation for the Coulombic term and the one-center approximation for the exchange term (RIJCOSX SOMF(1X)).⁶³

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

EPR spectra of illuminated fullerene:P3HT blends in toluene at cryogenic temperatures ($T = 15\text{--}20\text{ K}$). Spectra of blends with C_{60} are shown on the top, and blends with $PC_{61}BM$ are on the bottom. **Left.** Experimental cw X-band spectra (black), simulations of fullerene radical anions (blue, wine, green) and sum of simulations (red). The individual simulations are scaled for better visualization. **Right.** Experimental pulsed D-band spectra (black), simulations of fullerene radical anions (blue, wine, green) and sum of simulations (red). The individual simulations are scaled for better visualization. The D-band spectra have been pseudomodulated⁴⁵ to yield derivative-like EPR spectra and thus allow easier comparison with cw EPR spectra. For simulation parameters, see text and Table 1.

Figure 2.

cw X-band EPR spectra of C_{60} :P3HT blends in toluene at 20 K. Experimental cw X-band spectra of two samples frozen in the dark and illuminated at 20 K (black, blue); experimental cw X-band spectrum of a sample frozen in the dark, illuminated at 20 K, annealed in the dark at 130 K for 5 minutes, and measured in the dark at 20 K (red). Spectra have been shifted to adjust for differences in microwave frequency and scaled to be of comparable C_{60}^- signal intensity.

Figure 3.

Unpaired electron spin density plots of the monoanion C_{60}^- with an isosurface of $0.001 e/a_0^3$. **Left.** Orientation with the g_2 principal axis perpendicular to the plane. **Right.** Orientation with the g_3 principal axis perpendicular to the plane.

Figure 4.

Left. Effect of deformations along the normal mode q on the g -values and energies of the deformed conformations for the 344 cm^{-1} low frequency normal mode in the monoanion C_{60}^- . **Right.** Visualization of the 344 cm^{-1} low frequency normal mode in the monoanion C_{60}^- . The molecule is in the same orientation as the left panel of Figure 3 with the g_2 axis perpendicular to the plane. The normal mode vectors are shown in blue. Snapshots of the most positive q (blue) and most negative q (red) structures.

Figure 5.

Left. Effect of deformations along the normal mode q on the g -values and energies of the deformed conformations for the 480 cm^{-1} normal mode in the monoanion $\text{PC}_{61}\text{BM}^-$. **Right.** Visualization of the 480 cm^{-1} low frequency normal mode in the monoanion $\text{PC}_{61}\text{BM}^-$. The normal mode vectors are shown in blue. Snapshots of the most positive q (blue) and most negative q (red) structures.

Table 1.

Experimental and calculated principal values of the g-tensors of fullerene anion radicals C_{60}^- and $PC_{61}BM^-$.

g	C_{60}^-	C_{60}^-			$PC_{61}BM^-$	$PC_{61}BM^-$
	Calculated ^a	Experimental ^b			Calculated ^c	Experimental ^c
g₁	1.9985	1.9932	1.9948	1.9965	1.9995	1.9985
g₂	1.9986	1.9989	1.9975	1.9970	2.0008	2.0005
g₃	2.0008	2.0001	2.0001	2.0000	2.0009	2.0006
	Relative weight	0.4	0.3	0.3		

^a calculated using the EPRII basis set and B3LYP functional for the structures optimized at the B3LYP||6-31G+(d) level. Numbering of the g-values follows the scheme employed by the ORCA program package, $g_3 > g_2 > g_1$.

^b determined experimentally in frozen toluene solution of C_{60} :P3HT blends.

^c taken from ²⁹