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Mendeleev Commun., 2009, **19**, 200–202

Mendeleev Communications

Background paramagnetism in fullerene C_{60} and its low-temperature radiolysis

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DOI: 10.1016/j.mencom.2009.07.009

The radiation-chemical yield of paramagnetic centres during fullerene C_{60} low-temperature (77 K) γ-irradiation in a vacuum has been found (G_{PMC} = 0.001±0.00015 1/100 eV); in solid solutions, fullerene C_{60} acts as a sensitizer.

The effect of γ-irradiation on nanomaterials at low temperatures is of interest from both fundamental and practical points of view since irradiation may be used for modification of nanomaterials. However, information on paramagnetic centres (PMCs) formed during the low-temperature radiolysis of fullerene and its solutions is scarce.[1,2] The goal of this work was to investigate the background PMCs in pristine C_{60} powder, as well as to study the low-temperature radiolysis of fullerene and its 0.1% solid solutions in isopropylbenzene (IPB) and *N*-vinylpyrrolidone (NVP).†

The ideal molecular structure of fullerene should not show paramagnetic features. In fact, when fullerene has been strongly purified no signal has been observed.[3] Nevertheless, it is known that commercial fullerene samples demonstrated paramagnetism giving two narrow singlets: one with the overall width ΔH = = 0.13–0.2 mT (g = 2.0021–2.0025) and the other with ΔH = = 0.05–0.2 mT (g = 1.9978–2.0012).[4,5] The former singlet was attributed[6,7] to PMCs formed in reactions with oxygen or to an unpaired electron[4,8] delocalized along the conjugated system or quasi-localized state in positive radical-ion $C_{60}^{\cdot+}$. The latter signal of ΔH = 0.05–0.2 mT (g = 1.9978–2.0012) was assigned[4,5] to the radical-anion $C_{60}^{\cdot-}$.[4,5] The anisotropic components of g (g_x, g_y, g_z) in the range of 2.000–1.998 have been distinguished for $C_{60}^{\cdot-}$ analogue (methanofullerene radical-anion).[9]

The background ESR spectra of pristine C_{60} powder (in a vacuum) are shown in Figure 1 (spectra *1*, *2*). Spectrum *1* constitutes an isotropic singlet of Lorentzian form with ΔH = 0.2 mT and g = 2.0023. In high fields and at low microwave power, an additional singlet with ΔH = 0.12 mT and g = 1.998 was detected. The latter singlet was not detected in every sample (see also ref. 4). It can be assumed that a singlet with ΔH = 0.12 mT and g = 1.998 is an inherent component of complex spectrum *2*. To prove this belief the curves of saturation for both singlets (at g = 2.0023 and g = 1.998) have been obtained (Figure 2, curves *1*, *2*). Their different behaviours confirmed that spectrum *2* is a superposition of two singlets derived from the PMC of different nature. Oxygen does not influence the widths of both singlets. The concentration of background PMC is about

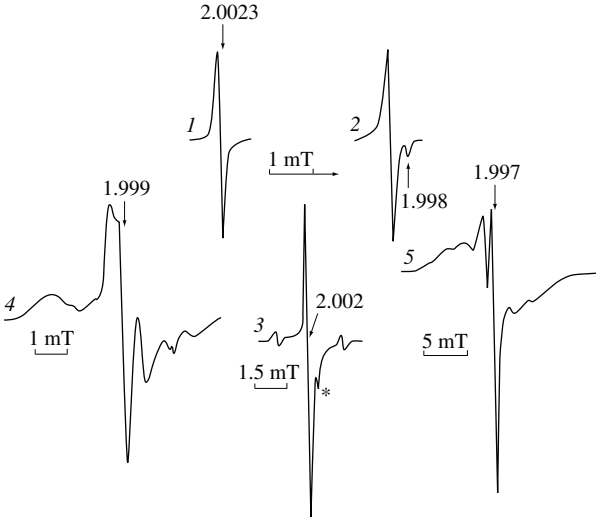

Figure 1 ESR spectra of fullerene C_{60}: (*1*), (*2*) background spectra of fullerene powder in a vacuum, (*3*) after γ-irradiation by dose 500 kGy in the presence of oxygen, asterisk points the line with g = 1.998; γ-irradiation of solid 0.1% C_{60} solutions in (*4*) IPB and (*5*) NVP. Irradiation and spectra registration have been carried out at 77 K.

4×10^{15}–3×10^{17} spin g^{-1}. In the range of experimental accuracy, the temperature dependence of C_{60} background ESR signal at g = 2.0023 corresponds to Curie law (Figure 3). The number of PMCs does not depend on temperature, and the ground state is paramagnetic.

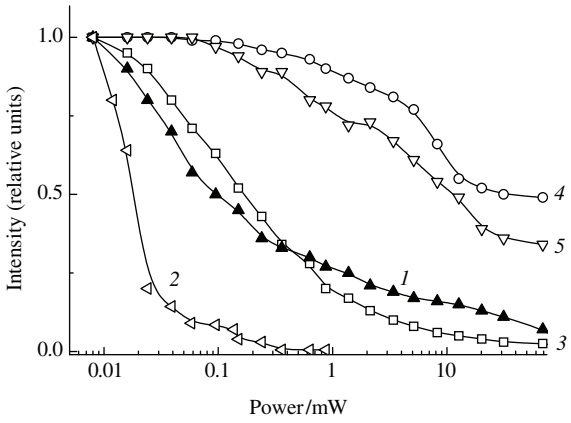

Figure 2 Saturation curves of ESR signals at 77 K: (*1*) C_{60} background singlet with ΔH = 0.2 mT at g = 2.0023; (*2*) C_{60} background singlet with ΔH = 0.12 mT at g = 1.998; (*3*) photooxidated polysterene; (*4*) coal; (*5*) fullerene containing soot (~10% C_{60}).

† Fullerene of 99.5% purity produced by an electroarc method was used. Samples (~0.05 g) were placed in ampoules made of special glass, which does not give an ESR signal after irradiation, evacuated and γ-irradiated. The γ-irradiation was performed on a Gamma-tok 100 setup with a power of 1.7 kGy. The ESR spectra were recorded on an ESR-21 (3 cm, X-band) spectrometer at a microwave power of 10^{-5} W at 77 K. PMC concentrations were determined from ESR spectra using a standard stable radical sample. The accuracy of determination including the double integration of spectra was ±15%.

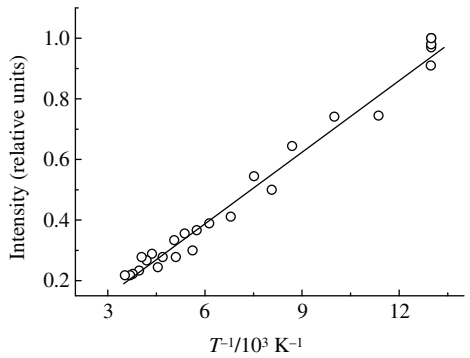

Figure 3 Intensity of C_{60} background singlet with $\Delta H = 0.2$ mT at $g = 2.0023$ as a function of the temperature.

To analyze the background spectra of pristine C_{60} powder, *g*-factor was used. The *g*-factor determines the resonance value of a magnetic field, and it characterizes ESR singlet lines. Narrow singlet lines with *g*-factors close to that of a free electron can result from PMCs with unpaired electron, which is on strongly delocalized molecular orbital with very weak spin-orbital coupling or PMC where electron is on localized orbital. Both variants are possible for C_{60} molecule: (1) molecular orbital, which includes the system of conjugated bonds with delocalized unpaired electron or (2) insulated on vacancy electron, which is on localized orbital where no magnetic nuclei (including H and others) are present.

The C_{60} carbon net holds 30 double bonds. At the same time, the conjugated π-system of C_{60} is not completely delocalized; as a consequence, this cluster is similar in reaction abilities to alkenes. Fullerenes can absorb a sufficient amount of free radicals to form new stable radicals.[10] For example, the interaction between double bonds of conjugated systems and active radicals can occur during C_{60} synthesis or its thermal oxidation. In that case an appearance of free valence on partly delocalized molecular orbital will result in spin paramagnetism. Obviously, this peculiarity of conjugated systems is responsible for a fullerene background singlet with $g = 2.0023$ close to that of free electron (like in hydrogenous and stone coals, graphite, soot, and other carbonized systems).

The conjugated character of background PMC is confirmed by saturation curve *1* of singlet with $g = 2.0023$ (Figure 2), behaviour of which is very similar to that (curve *3*) for polyene radicals of photooxidized polysterene (PS). PS polyene radical conjugated system contains four phenyl groups in addition to olefin bonds of main chain.[11] This is evidence that an aromatic component participates sufficiently in the fullerene conjugated system.

As the background signals and the character of saturation are practically the same for fullerenes of different origin, we can leave the PMC derived from impurities (by-products of synthesis and purification) out of consideration (this is in a good agreement with published data[12]) and assume that background PMC are connected with C_{60} molecule nature. Saturation curves *1*, *2* for pristine fullerene (Figure 2) sharply differ from those for purification products such as coal and soot (curves *4*, *5*). Thus, for the first time, it has been shown that, in spite of the identity of ESR signals, their relaxation characteristics (saturation curves) have specific information about PMC molecular orbital structure. This enables one to identify individual C_{60} spectra in the presence of carbon-containing impurities.

The radicals of high level of conjugation demonstrate high stability and chemical inertness. They cannot be oxidized into the radical ROO$^{\cdot}$, and their participation in fullerene chemical conversions is unlikely. Indeed, chemical inertness of PMC with $g = 2.0023$ has been confirmed by low-temperature fullerene halogenation: both the ESR spectrum and the background PMC concentration do not vary at molecular fluorination or chlorination.

At the same time, the radical-cation $C_{60}^{+\cdot}$ (ref. 8) or other PMC with a quasi-localized electron are also detected supposedly as a narrow singlet with *g*-factor close to that of free electron. It is very hard to make spectral distinction of these centres by ESR spectroscopy. Therefore, further investigations are necessary for the interpretation of background singlet with $g = 2.0023$ including ESR investigations using 2 mm range spectrometer, which has high spectral resolution in *g*-factor magnitude.

The second observed singlet ($\Delta H = 0.12$ mT and $g = 1.998$) has practically the same parameters like in refs. 4, 5 where it has been attributed to $C_{60}^{-\cdot}$. The appearance of a singlet with the parameters $\Delta H = 0.07$ and $g = 2.000$ (near the singlet with $g = 2.0023$) has been detected[1] after the γ-radiolysis of fullerene C_{60} powder and also has been attributed to $C_{60}^{-\cdot}$. It is believed that $C_{60}^{-\cdot}$ as a background paramagnetic particle can arise under extreme conditions of electroarc synthesis of fullerene when fullerene inner cavity is able to trap the electron. This may also be a reason for the high thermostability of radical-ions. Fullerene cage transparency to spin density ('spin leakage') has been predicted.[13] Koltover *et al.*[14] found the partial transfer of electron spin density from paramagnetic atom located in fullerene sphere out of the latter. 'Spin leakage' can also take place in the opposite direction.

The fact that the *g*-factor of $C_{60}^{-\cdot}$ is different from that of free electron may be caused by orbital magnetism; *i.e.*, there is some kind of trapped electron delocalization on orbital, which envelops significant part of C_{60} sphere. As a consequence, the spin-orbital coupling appeared. The *g*-factors of $C_{60}^{-\cdot}$ obtained by fullerene solution electrolysis have been discussed.[15,16] The theoretical justification of *g*-value of $C_{60}^{-\cdot}$ using the Jan–Teller effect is given in ref. 17.

The γ-irradiation of C_{60} samples leads to PMC formation, but in a vacuum the spectrum shape does not change until large doses (500 kGy). Obviously, at γ-irradiation the same PMCs are produced in fullerene molecules as under the extreme conditions of C_{60} synthesis. This result is in a good agreement with published data.[2] Using the data for very small doses (where conversion is proportional to dose) the radiation-chemical yields (*G*) of the PMC, characteristic of the radiation stability of substances, have been estimated. The value has appeared to be 0.001±0.00015 PMC per 100 eV (and 8±1.5 for soot, for example). The low value of *G* for fullerene indicates the high radiation stability of the C_{60} molecule. Through the comparison of *G* for fullerene with *G* for well-known polymer–monomer systems it has been established that fullerene *G* most closely corresponds to that ($G = 0.0025 \pm 0.0004$) for plasma-treated polypropylene, in which a large amount of aromatic conjugated systems has formed.[18]

Irradiation in the presence of oxygen does not change the rate of PMC formation but it causes changes in the shape of ESR spectra. From the both sides of singlet with $g = 2.0023$ at a distance of 1.6–1.7 mT two satellite lines with width ~0.2 mT have appeared to convert the whole spectrum into a triplet (Figure 1, spectrum *3*). Such signals observed during fullerene solutions electrolysis have been assigned to radical-ion $C_{120}O^{3\cdot-}$ derived from the dimer $C_{120}O$, which is an impurity in fullerene.[7,19] Obviously, in our case, the dimer forms during fullerene irradiation in the presence of oxygen and stabilized electrons reduce it into $C_{120}O^{3\cdot-}$.

Having a very low value of *G* (0.001±0.00015) being as a powder the fullerene shows in its solid solutions a capacity to sensitizing. The radiation-chemical yield of PMCs in 0.1% solutions of C_{60} in NVP and IPB turned out to be twice larger than that for pure solvents irrespective of their polarity. The

Table 1 Radiation-chemical yields of PMCs at 77 K in fullerene powder, its solutions and solvents.

Compound	G_{PMC}
Fullerene C_{60}	0.001±0.00015
Fullerene black (~10% C_{60})	8±1.5
Isopropylbenzene	0.15±0.03
Isopropylbenzene + fullerene	0.30±0.05
Isopropylbenzene + fullerene [$C_{60}^{\cdot-}$]	0.024±0.004
N-vinylpyrrolidone	0.30±0.05
N-vinylpyrrolidone + fullerene	0.70±0.01
N-vinylpyrrolidone + fullerene [$C_{60}^{\cdot-}$]	0.003±0.0005

radiation-chemical yield of $C_{60}^{\cdot-}$ also has increased exceeding G_{PMC} for fullerene powder.[20] In Figure 1, the spectra of γ-irradiated C_{60} solid solutions in NVP and IPB are given (spectra *4*, *5*). In the central part of solvent complex spectra one can see narrow (ΔH = 0.5 mT) singlet lines with g = 1.997–1.999 which have been attributed to the radical-ion $C_{60}^{\cdot-}$ (g-value for pure solvents are in the range of 2.004–2.002). Thus, in solutions C_{60} demonstrates itself as a sensitizer like multi-walled nanotubes.[21] The radiation-chemical yields of PMCs and $C_{60}^{\cdot-}$ in fullerene powder, its solutions and solvents are given in Table 1.

This work was partially supported by the Programme of Fundamental Research of Presidium of the Russian Academy of Sciences (no. 2).

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Received: 5th September 2008; Com. 08/3212