

# RADIATION STABILITY AND PECULIARITIES OF BACKGROUND PARAMAGNETISM OF FULLERENE C<sub>60</sub>

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## Introduction

There is a lot of interest in  $\gamma$ -irradiation effect on fullerenes at low temperatures both from fundamental and practical points of view, since irradiation may be used for modification of fullerenes. The goal of this communication is to investigate the background paramagnetic centers (PMC) in pristine C<sub>60</sub> powder as well as to study low-temperature radiolysis of fullerene and its 0.1 % solid solutions in isopropylbenzene (IPB), N-vinylpyrrolidene (N-VP). Fullerene used has been produced by electro arc method and contained not less than 99.5% of essential substance. The  $\gamma$ -irradiation has been performed on a «Gamma-tok 100» setup with power 1.7 kGy/hour. The ESR spectra were recorded on an ESR-21 (3 cm, X-band) spectrometer at a microwave power of 10<sup>-5</sup> W at 77 K. PMC concentrations were determined from ESR spectra using as standard the sample of stable radical of certain concentration. An accuracy of determination including registration and double integration of spectra was  $\pm 15\%$ .

## Results and discussions

The background ESR spectra of pristine C<sub>60</sub> powder recorded in our experiments (in vacuum) are shown in Fig.1, spectra 1, 2. Spectrum 1 constitutes isotropic singlet of Lorentzian form with  $\Delta H=0.2$  mT and  $g=2.0023$ . In high fields and low microwave power additional singlet with  $\Delta H=0.12$  mT and  $g=1.998$  was registered (spectrum 2). Different behavior of signals 1 and 2 during saturation indicated that they are originated from two different paramagnetic centers. Oxygen presence does not effect on the width of background signals. The number of background PMC in investigated samples have been equal to  $4 \times 10^{15}$ - $3 \times 10^{17}$  spin/g.

The investigators attribute first singlet with  $g=2.0023$ - $2.0026$  to PMC, formed in reactions with oxygen [1], while other authors it is due to delocalized along conjugated system electron [2] or due to quasi-localized state of unpaired electron in positive ion-radical C<sub>60</sub><sup>+</sup> [3]. We attribute it to electron delocalized on conjugated system like in

paramagnetic centers in hydrogenous and stone coals, graphite, soot, and other carbonized systems.

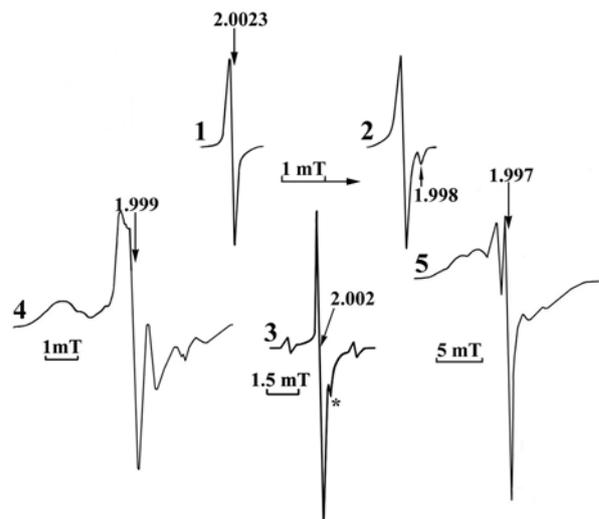


Fig.1. ESR spectra of fullerene C<sub>60</sub>: (1,2)-background spectra of fullerene powder in vacuum, (3)- after  $\gamma$ -irradiation by dose 500 kGy in the presence of oxygen, asterix points the line with  $g=1.998$ ;  $\gamma$ -irradiation of solid 0.1% C<sub>60</sub> solutions in IPB (4) and in N-VP (5). Irradiation and spectra registration have been carried out at 77 K.

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

The radicals of high level of conjugation demonstrate high stability and chemical inertness. They can not be oxidized into radical ROO<sup>·</sup> and their participation in fullerene chemical conversions is unlikely. Indeed, chemical inertness of PMC with  $g=2.0023$  has been confirmed by results on low temperature fullerene halogenation: both the ESR spectrum and background PMC<sup>·</sup> concentration do not vary at molecular fluorination or chlorination [4].

Saturation curves 1, 2 sharply differ from those for coal and soot (curves 4, 5), this may help to

identify individual spectra of  $C_{60}$  among possible carbon containing impurities.

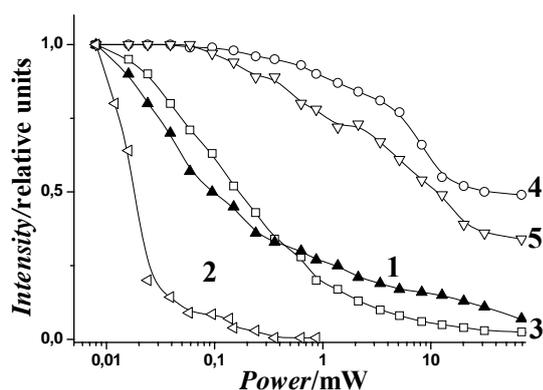


Fig.2. Saturation curves of ESR signals at 77 K:

1 -  $C_{60}$  background singlet with  $\Delta H=0.2$  mT at  $g=2.0023$ ; 2-  $C_{60}$  background singlet with  $\Delta H=0.12$  mT at  $g=1.998$ ; 3 - photooxidated polystyrene, 4 - coal; 5 - fullerene containing soot ( $\sim 10\%$   $C_{60}$ ).

According to its parameters second signal of  $\Delta H=0.12$  mT и  $g=1.998$  is assigned to anion-radical  $C_{60}^{\bullet-}$ . We assume it is formed during electro arc synthesis of fullerene. By localization of electron in fullerene's cage may be explained the high thermo stability of this particle. Divergence of its g-factor ( $g=1.998$ ) from  $g_e$  is caused by peculiar delocalization of electron on orbital of  $C_{60}$  frame with arising of spin-orbital interactions.

Using the data for very small doses (where conversion is proportional to dose) the radiation-chemical yields (G) of the PMC, characteristic for radiation stability of substances, have been estimated. The value has appeared to be  $\sim 0.001 \pm 0.00015$  PMC per 100eV of absorbed energy (and  $\sim 8 \pm 1.5$  for soot, for example). Low value of G for fullerene indicates high radiation stability of the  $C_{60}$  molecule.

The reason for very low value of  $G_{PMC}$  is obviously energy dissipation due to aromatic structures included in polyconjugated system of fullerene.

Irradiation in the presence of oxygen does not change the rate of PMC formation but it causes the 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  $\sim 0.2$  mT have appeared to convert the whole spectrum into a triplet (Fig.1, spectrum 3). Such signals observed during fullerene solutions electrolysis have been

assigned to ion-radicals  $C_{120}O^{2+}$ . Latter has been indicated in Ref. [1].

Having very low value of  $G_{PMC}$  ( $0.001 \pm 0.00015$ ) being as a powder the fullerene shows in its solid solutions a capacity to sensitizing. Radiation-chemical yield of the PMC in 0.1% solutions of  $C_{60}$  in N-VP and in IPB turned out to be twice larger than that for pure solvents without regard to their polarity. The radiation-chemical yield of  $C_{60}^{\bullet-}$  also has increased exceeding  $G_{PMC}$  for fullerene powder. In Fig.1 the spectra of  $\gamma$ -irradiated  $C_{60}$  solid solutions in N-VP and in IPB are given (spectra 4, 5). In the central part of solvent complex spectra one can see narrow ( $\Delta H=0.5$  mT) singlet lines with  $g=1.997-1.999$  (Fig.1, spectra 4, 5), which have been attributed to the ion-radical  $C_{60}^{\bullet-}$ .

## Conclusions

On the base of high thermostability and chemical inertness of background paramagnetic centers in fullerene  $C_{60}$  powder as well as taking in an account the singular characteristics of their ESR signals (saturation curves) the background singlet with  $g=2.0023$  has been attributed to stable radical where free electron is delocalized on conjugated system which includes aromatic bonds.

For the first time radiation-chemical yield of PMC formation during radiolysis of  $C_{60}$  powder has been determined which turned out to be equal to  $G_{PMC} = 0.001$  per 100 eV. Having low value of  $G_{PMC}$  in solid phase fullerene  $c_{60}$  in solutions has demonstrated itself as an effective sensitizer twice increasing radiation-chemical yields in comparison with pure solvents.

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## References

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