

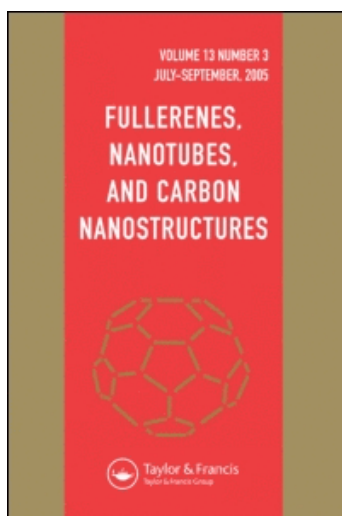
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ESR STUDY OF  $C_{60}^{n-}$  ANION RADICALS IN DMSO SOLUTION

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ABSTRACT

With the aim to stabilize reduced  $C_{60}$  molecules of solid fulleride as free anion radicals in solution,  $Na_xC_{60}$  ( $x=1, 10$ ) was dissolved in DMSO. The  $Na_xC_{60}$  was chosen among the other alkali-metal fullerides due to the possibility to increase a number of intercalated Na atoms in a f.c.c. lattice of  $C_{60}$ . A sufficiently high concentration of  $C_{60}$  anion radicals of an order of magnitude larger than that usually achieved in solution by an electrochemical reduction was obtained. The sharp resonances with the linewidths of order of 0.1 G and with  $g=2.0004(6) - 2.0012(8)$  of the room temperature ESR spectra of fluid solution were assigned from mono- to pentaanions of  $C_{60}$ . An appearance of additional sharp peaks at  $g=2.0016-2.0019$  in the spectra of solution of nominal  $Na_{10}C_{60}$ , but  $Na_1C_{60}$ , tentatively related to  $C_{60}^{n-}$  with  $n>6$ . The results of this study showed a simple approach in an accomplishment of highly concentrated solutions of free anion radicals  $C_{60}^{n-}$ , as well as in stabilization of the anion radicals with increased  $n$ . In this way a homogeneity of alkali metal intercalation and characteristics of the solvent will be important.

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## 1. Introduction

For fullerene molecule the lowest unoccupied molecular orbital (LUMO) of  $C_{60}$ ,  $t_{1u}$ , should be able to accept six electrons<sup>1-3</sup>. A possibility of a reduction of  $C_{60}$  up to twelve electrons involving the next  $t_{1g}$  orbital has been also predicted<sup>3</sup>. To date systematic reduction by up to six electrons have been done, mainly in electrochemical experiments<sup>4-12</sup>. Among them,  $C_{60}^{n-}$  with  $n=1, 2$ , and  $3$  have been stabilized in frozen solutions and studied by ESR technique<sup>5,7-10,12</sup>. A chemical route, when a reducing agent interacts with  $C_{60}$  in an appropriate solvent, was widely applied along with the electrochemical reduction. In this case reducing agent may represent either some complex compound<sup>13</sup>, or simply the alkali-metals<sup>14</sup> or their alloys<sup>15</sup>. A subsequent removing of solvent leads to a formation of various  $C_{60}^-$  fullerides where residual solvent molecules are/or not incorporated into the system<sup>13,16,17</sup>. A reduction of  $C_{60}$  in solutions by means of  $\gamma$ -irradiation have been also reported<sup>18</sup>.

In  $M_xC_{60}$  compounds (where  $M$  represent alkali metals Li, Na, K, Rb, and Cs or their alloys),  $C_{60}^{n-}$  anion radicals with  $1 \leq n \leq 6$  are formed as a result of intercalation of alkali metals into the  $C_{60}$  lattice<sup>19</sup>. The number of intercalated metal atoms,  $x$ , in  $M_xC_{60}$  is limited by their ionic radius and by a volume of interstitial sites. For K, Rb, and Cs a maximal number have been shown to be six<sup>19</sup>. An intercalation changes the lattice structure from a f.c.c. (face-centered-cubic) of pristine  $C_{60}$  to a b.c.t. (body-centered-tetragonal) and a b.c.c. (body-centered-cubic). On the other hand, a maximal number of Na atoms have been increased up to ten, and the compound at an intercalation retained a f.c.c. lattice structure<sup>20,21</sup>. In saturated  $K_6C_{60}$ ,  $Rb_6C_{60}$ , and  $Cs_6C_{60}$  phases intercalants are the isolated  $K^+$ ,  $Rb^+$ , and  $Cs^+$  ions. Hence, a number of electrons transferred to  $C_{60}$  is equal to the number of intercalated ions. In heavily doped  $Na_xC_{60}$  two

intercalants of two tetrahedral interstitial sites are isolated  $Na^+$  ions, while the other Na atoms are intercalated into the octahedral interstitial site as clusters, respectively, in  $Na_6C_{60}$  as a 4-atom tetrahedron and in  $Na_{10}C_{60}$  as a 8(9)-atom cube<sup>20,21</sup>. Yildirim et al.<sup>21</sup> have proposed that clusters are neutral or charged partially. It means that the ionic state of  $C_{60}$  might be defined mainly by the tetrahedral site  $Na^+$  ions. On the other hand, on the basis of theoretical calculation Andreoni et al.<sup>22</sup> have predicted that the Na tetrahedron in the octahedral site of  $Na_6C_{60}$  phase must be highly ionized. Thus, a number of electrons transferred to  $C_{60}$  in  $Na_xC_{60}$  is unpredictable, and the question on ionic states of  $C_{60}$  and Na atom clusters in  $Na_xC_{60}$  remains open. One of the ways to solve the problem would be an isolation of  $C_{60}$  ions somehow from solid  $Na_xC_{60}$  preserving their ionic state. For example, it would be a dissolution of the fulleride in some plausible solvent, followed by the characterization of resulting solution by spectroscopic techniques. At the same time, this route itself would be an alternative way for a formation in solution of  $C_{60}^{n-}$  anion radicals with increased  $n$ . In present paper  $Na_xC_{60}$  fulleride ( $x=1, 10$ ) was dissolved in a highly polar solvent (DMSO), and ESR and NIR spectra in solution assigned to  $C_{60}^{n-}$  anion radicals were studied in the temperature range 77-320 K. One of the purposes of the study was to try to form stable  $C_{60}^{n-}$  anion radicals with increased  $n$  in solution by an alternative to electrochemical reduction way.

## 2. Methods

**Preparation of  $Na_xC_{60}$  fullerides.**  $C_{60}$  (of 99.9% purity) and  $NaN_3$  (of >99% purity) were used as purchased, respectively, from Material and Electrochemical Research Corporation (Arizona, USA) and from Merck, without further purification. The Na metal vapor doping (Preparation A)<sup>20</sup> and the thermal

decomposition of  $\text{NaN}_3$  in a mixture with  $\text{C}_{60}$  followed by an annealing (Preparation B)<sup>23,24</sup> were used for a preparation of  $\text{Na}_x\text{C}_{60}$  compounds which further were dissolved in solvents.

**The choice of the solvent.** A number of organic solvents were tested to find out the highest solubility for Na-intercalated polycrystalline  $\text{C}_{60}$ . Dimethylsulfoxide (DMSO) purchased from Merck was distilled with anhydrous  $\text{CaSO}_4$  in vacuum. Tetrahydrofuran (THF) of Merck was distilled with metallic Na in nitrogen atmosphere. Dimethylformamide (DMF) was purchased from Ishizu Pharmaceutical (Japan). DMSO- $d_6$  and DMF- $d_7$  were purchased from Isotec Inc. and Aldrich Chemical, respectively. Other solvents ( $\text{CH}_2\text{OH}$ ,  $\text{CH}_2\text{Cl}_2$ , acetone, dioxan, toluene) were used as purchased from Merck. First, about 1 mg of the sample with maximal Na content (nominal composition  $\text{Na}_{10}\text{C}_{60}$ ) was mixed with 1 ml of solvents in a following consequence: DMSO, DMF,  $\text{CH}_3\text{OH}$ , acetone,  $\text{CH}_2\text{Cl}_2$ , dioxane, THF, and toluene. Solubility was monitored visually during several hours by the change of solution color and quantity of undissolved powder. The best solubility was demonstrated by DMSO, those color was immediately changed to the dark red-brown, while the solvents with lower polarity showed low solubility, i.e., the material was insoluble in solvents such as toluene or THF. It has been shown recently that an increase of a dielectric constant,  $\epsilon$ , of solvent from 2.27 (benzene) to 36.71(DMF) promote a reduction of  $\text{C}_{60}$ <sup>6</sup>. A highest six electron reduced state has been achieved in acetonitrile<sup>11</sup> ( $\epsilon=37.5$ , Ref. 25). A  $\epsilon=46.68$  of DMSO<sup>25</sup>, larger than those of above mentioned solvents, and the solubility test led us to use DMSO for  $\text{Na}_x\text{C}_{60}$  compound. At the following step, all manipulations were carried out under nitrogen atmosphere in a glove box. The reaction tube with  $\text{Na}_x\text{C}_{60}$  was opened, about 1-10 mg of the powder samples were transformed into the flask, and 1 ml DMSO was added to the sample. A

suspension was stirred at room temperature by ultrasonic mixer for 0.5 hour. Final solution was filtrated and centrifuged using Millipore filters with average pore size of 2.2  $\mu\text{m}$ ; about 20  $\mu\text{l}$  was transferred into the quartz capillary for ESR measurements, several cycles of freeze-and-thaw method has been performed, and finally capillary was sealed off in vacuum. In some cases solutions prepared in inert atmosphere were sealed off in pyrex capillaries without later treatment. The ESR spectra from both type of capillaries were identical to each other in details. As prepared solutions used in ESR were diluted for NIR experiments. Solutions in sealed capillaries were kept in liquid  $N_2$  before NIR and ESR measurements.

**Instruments.** Near-IR (NIR) optical absorption spectra were recorded on Shimadzu UV-3101P UV-VIS-NIR Scanning Spectrophotometer. ESR spectra were measured on the X-band ESR spectrometer Bruker ESP-300E. The 2,2-diphenyl-1-picrylhydazyl (DPPH) with  $g=2.0036$  attached outside the capillary was used as a  $g$ -value reference. Magnetic field was measured by NMR Gaussmeter, Bruker ER035. The temperature was varied within the range 100-320 K by  $N_2$  gas flow cryostat (the spectra at 77 K were written in a liquid  $N_2$  dewar). The air saturated 0.9 mM solution of peroxilamine disulfonate dianion (PADS) for calibration of microwave field  $H_1$  was prepared by dissolving potassium peroxyamine disulfonate in 0.05 M aqueous solution of  $K_2CO_3$ . The concentration of the solution was measured optically. The molar extinction coefficients of 1690  $\text{cm}^{-1}\text{M}^{-1}$  at 248 nm absorption and of 20.8  $\text{cm}^{-1}\text{M}^{-1}$  at 545 nm absorption were used<sup>26</sup>.

### 3. Results.

**Near-IR optical absorption.** NIR optical absorption spectroscopy is a good tool for identification of ionic state of  $C_{60}$  in solution<sup>27</sup>. Figure 1a shows room

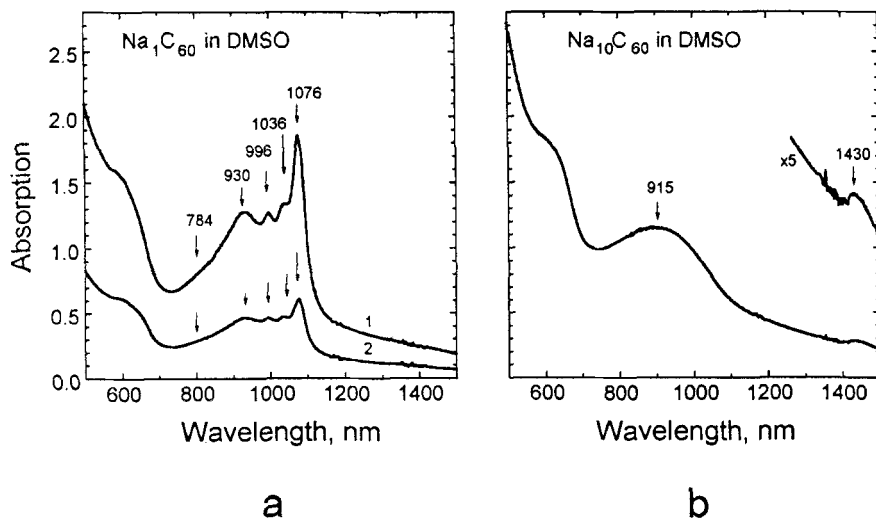


FIG 1 - The room temperature Near-Infrared (NIR) optical absorption spectra measured in solutions of nominal Na<sub>x</sub>C<sub>60</sub> in DMSO: a) spectra taken for nominal Na<sub>1</sub>C<sub>60</sub> fulleride dissolved in DMSO, where upper spectrum (1) is for the fulleride intercalated from Na metal vapor (Preparation A), and lower spectrum (2) is for the fulleride intercalated by the sodium azide decomposition (Preparation B); b) spectrum taken for nominal Na<sub>10</sub>C<sub>60</sub> fulleride intercalated by the former procedure (Preparation A).

temperatures NIR spectra of two samples with initial nominal composition Na<sub>1</sub>C<sub>60</sub> prepared by two different doping ways and then dissolved in DMSO. Both spectra, the upper one of the sample doped from Na metal vapor (Preparation A) and the lower one of the sample doped by decomposition of NaN<sub>3</sub> (Preparation B), are identical to each other in features. They exhibit four maxima sequentially at 930 nm, 996 nm, 1036 nm and 1076 nm. These values are in a good agreement with previous reports for C<sub>60</sub><sup>-</sup> anion radical in solutions<sup>4,9,10,12,14,27</sup>. The 1076 nm absorption is due to the transition from the singly occupied t<sub>1u</sub> orbital to the next highest unoccupied orbitals t<sub>1g</sub><sup>4,27</sup>. The other three absorptions are separated

from the former one, respectively, by  $1460\text{ cm}^{-1}$  for 930 nm, by  $800\text{ cm}^{-1}$  for 996 nm, and by  $400\text{ cm}^{-1}$  for 1036 nm. Absorption at 930 nm and the shoulder detected in the spectra at about 784 nm are within one group with fundamental  $1460\text{ cm}^{-1}$ . The second group, including 996 nm and 1036 nm absorptions, has  $400\text{ cm}^{-1}$  fundamental. Two possibilities have been taken in literature into consideration to explain the origin of these absorptions: a Jahn-Teller mechanism<sup>9</sup>, and intramolecular vibrations<sup>4</sup>. To evaluate a concentration of monoanions we have used an extinction coefficient  $2.0 \times 10^4\text{ cm}^{-1}\text{M}^{-1}$  for the peak at 1076 nm<sup>12,14,28</sup>. The value of absorbance at 1076 nm of the upper spectrum of Fig. 1a corresponded to a  $C_{60}^-$  concentration of 0.93 mM, while an absorbance of the lower spectrum corresponded to 0.46 mM. To conduct NIR measurements the dark red-brown solutions used in ESR measurements were diluted by a factor of three to ten to discolor the solutions into transparent yellow. Using concentrations evaluated from NIR we have calculated corresponding concentrations of the initial non-diluted dark red-brown solutions derived by dissolving of  $Na_1C_{60}$  and directly used in ESR measurements to be 9.3 mM for sample of Preparation A and 1.3 mM for the second one of Preparation B. These concentrations of monoanions derived by dissolving of fulleride were about an order of magnitude higher than that of the electrochemical reduction<sup>12</sup>.

Whereas, no evidence for the next redox states of  $C_{60}$ <sup>12,27</sup> was found in NIR spectra of  $Na_1C_{60}$  solutions, a solution of nominal  $Na_{10}C_{60}$  obtained by Preparation A showed a NIR spectrum of higher redox states (Fig. 1b). The spectrum yields a broad absorption with maximum at 915 nm and a very weak narrow one at 1431 nm. The former value is close to 934 nm of  $C_{60}^{4-}$ , while the latter one at 1431 nm is close to the peak at 1440 nm of  $C_{60}^{6-}$  reported in Ref. 27. However, there would not be only  $C_{60}^{4-}$  or  $C_{60}^{6-}$  because these radicals should be



an ESR-silent, and the same solution, as one can see below, have showed strong ESR signal (Fig.2c). Though no pronounced maxima related to the other anions were found in the spectrum, broad and smooth absorption of 915 nm most probably was a superposition of several unresolved peaks.

**Electron Spin Resonance spectroscopy.** ESR spectra of  $\text{Na}_x\text{C}_{60}$  powder samples measured before dissolution showed strong single line with  $g$ -values 2.0008-2.0010 in nominal  $\text{Na}_1\text{C}_{60}$  and 2.0013-2.0016 in nominal  $\text{Na}_{10}\text{C}_{60}$ , and linewidth, respectively, 5.0-6.5 G and 1.0-1.6 G. This observation was in a good agreement with results reported in Ref. 29, where ESR linewidth was narrowed and  $g$ -value increased with large  $x$  in nominal  $\text{Na}_x\text{C}_{60}$ .

*The ESR spectra of fluid solutions.* For the sake of completeness a few room temperature ESR spectra of fluid solution of nominal  $\text{Na}_1\text{C}_{60}$  (denoted *a* and *b*) and  $\text{Na}_{10}\text{C}_{60}$  (denoted *c*, *d*, *e* and *f*) are presented in Fig.2. The spectra of the solution of nominal  $\text{Na}_{10}\text{C}_{60}$  taken at different time after preparation are presented in Fig. 3. The main features of the spectra as follows. All of them exhibited several narrow resonances lying within the field range of about 10 G. All resonances had  $g$ -value less than 2.0023 free electron  $g$ -value. Each spectrum had two kind of lines: the broad one in high-magnetic field with  $g=2.0001$  and linewidths 0.50-0.70 G, and a few sharp lines in low-magnetic field with  $g$ -values in the range of 2.0004-2.0019 and linewidth 0.12-0.15 G. Although a peak-to-peak amplitude of the resonances was varied from spectrum to spectrum, positions of the resonances in a  $g$ -value scale were surprisingly fixed for all the samples under study (Fig.2). The number of the sharp resonances as well as their peak-to-peak amplitude in a low-field part of the spectra for solution of  $\text{Na}_{10}\text{C}_{60}$  (Fig.2c-f) were larger comparing to solution of  $\text{Na}_1\text{C}_{60}$  (Fig.2a-b). The main spectral features remained when DMSO was diluted by THF in a ratio 1:2, or when DMSO- $d_6$  and DMF- $d_7$  were used as the solvents.

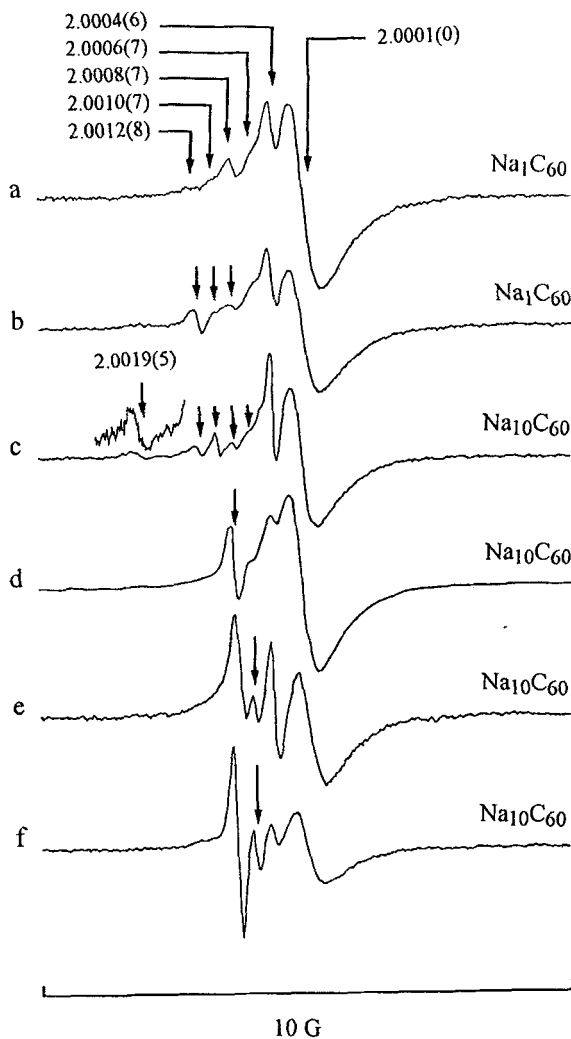


FIG 2 - The room temperature ESR spectra of solution of  $Na_xC_{60}$  fulleride in DMSO. Two upper spectra (*a* and *b*) are for the nominal  $Na_1C_{60}$ : spectrum (*a*) is for solution of the fulleride of a Preparation A, spectrum (*b*) is for the fulleride of a Preparation B. Four lower spectra (denoted *c*, *d*, *e*, and *f*) are for the nominal  $Na_{10}C_{60}$ : spectra (*c*) and (*d*) are for the fullerides of a Preparation A, and spectra (*e*) and (*f*) are for the fullerides of a Preparation B.

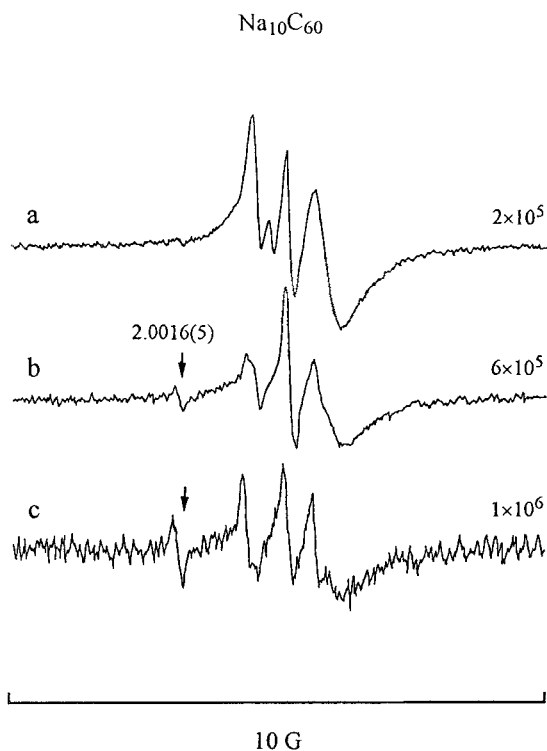


FIG 3- Evolution of ESR spectrum of fluid solution of nominal  $\text{Na}_{10}\text{C}_{60}$  at the room temperature exposition of the sealed in vacuo capillary for several days: (a) spectrum was measured just after dissolving of the fulleride; (b) two days later; (c) four days later. New resonance of  $g=2.0016(5)$  and  $\Delta H_{pp}=0.13$  G appeared at the exposition. See text for further discussion.

Figure 4 shows typical dependences of the peak-to-peak amplitude of the sharp resonance at  $g=2.0004(6)$  and of the broad one at  $g=2.0001(0)$  measured for nominal  $\text{Na}_1\text{C}_{60}$  (ESR spectrum of this solution is presented in Fig.2a). The sharp resonances were easily saturated by incident microwave power level of about 10 mW. The broad resonance was not saturated at the highest power level available on the ESR spectrometer (200 mW), though the dependence has deviated from the

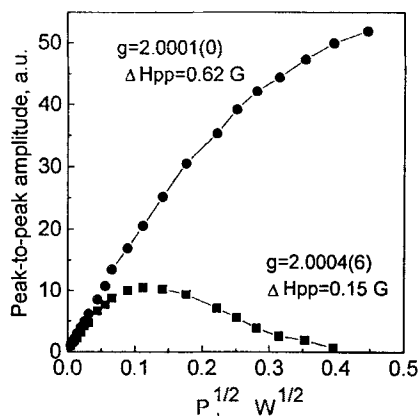


FIG 4 - A peak-to-peak amplitude of the narrow resonances of fluid solution of nominal  $Na_1C_{60}$  in DMSO versus the square root of 2 of microwave power level: the dependence showed apparent saturation at microwave power level of about 10 mW is for sharp resonance with  $g=2.0004(5)$  and  $\Delta H_{pp}=15$  G, while the dependence slightly deviated from the linearity is for the broader resonance with  $g=2.0001(0)$  and  $\Delta H_{pp}=0.62$  G.

linearity at maximal power level (Fig.4). The room temperature longitudinal electron-spin relaxation time,  $T_1$ , was evaluated by continuous-wave saturation method assuming a lorentzian line shape<sup>30</sup>. The transverse electron-spin relaxation time,  $T_2$ , was evaluated directly from the linewidth. The microwave field,  $H_1$ , at the sample position was calibrated by a comparison with the air saturated 0.9 mM solution of peroxilamine disulfonate dianion (PADS)<sup>31</sup>. A PADS reference and the sample under study were placed simultaneously in both cavities of the Bruker double resonator, so the spectra at different microwave power levels were taken at the same experimental conditions. The sharp resonance at  $g=2.0004(5)$  was evaluated to have  $T_1=(6.5\pm 0.5)\times 10^{-7}$  sec and  $T_2=(5.0\pm 0.3)\times 10^{-7}$  sec. The broad resonance at  $g=2.0001(0)$  was evaluated to have  $T_1=(5.7\pm 0.5)\times 10^{-7}$  sec and  $T_2=(1.1\pm 0.3)\times 10^{-7}$  sec.

A multicomponent structure of the spectra of Fig.2, i.e., inherent sharp resonances became apparently observable at 250-260 K when temperature was running to grow (or similarly, was vanished below 250-260 K, when temperature was decreasing). These temperatures were lower than a temperature of the melting point of pure DMSO (291.7 K, Ref.<sup>25</sup>). It is demonstrated most clearly in Fig.5 which presents the linewidth versus temperature in the temperature range of 77-320 K (properties of the spectra in frozen solution will be described below). To determine the melting point of the solution, a proton NMR measurement was performed for the nominal  $\text{Na}_1\text{C}_{60}$  in DMSO in the same sealed capillary used in ESR experiment. A narrow line of the protons of DMSO broadened and disappeared in NMR spectrum below 290 K, but 260 K. Therefore, one could conclude that a melting point of DMSO consisting of dissolved material was very close to that of pure solvent. In turn, the insets of Fig.5 show that in the vicinity of the melting point the temperature dependence of the ESR linewidth showed the extrema. Generally speaking, the narrow resonances first appeared at 250-260 K narrowed up to 290-300 K, and broadened again with temperature up to 320 K. The broadening in between 290-320 K was linear, and hence the increase of the linewidth might be thermally activated. The temperature-independent intrinsic linewidth can be evaluated from the temperature dependence of the linewidth by the extrapolation of the temperature-dependent linewidth to 0 K<sup>7</sup>. The  $\Delta H_{pp}(0)=0.11$  G was found for a broad resonance ( $g=2.0001(6)$  and  $\Delta H_{pp}(\text{RT})=0.63$  G) of a nominal  $\text{Na}_{10}\text{C}_{60}$  from the plot presented in Fig.6a. A corresponding plot of the natural log of the increase of the temperature dependent part of the linewidth versus temperature is presented in Fig.6b. Activation energy,  $E$ , for this resonance was evaluated from the equation  $\ln(\Delta H_{pp}(T)-\Delta H_{pp}(0))=A-E/kT$  to be 0.025 eV (2.4 kJ/mol). Because of a very short temperature range

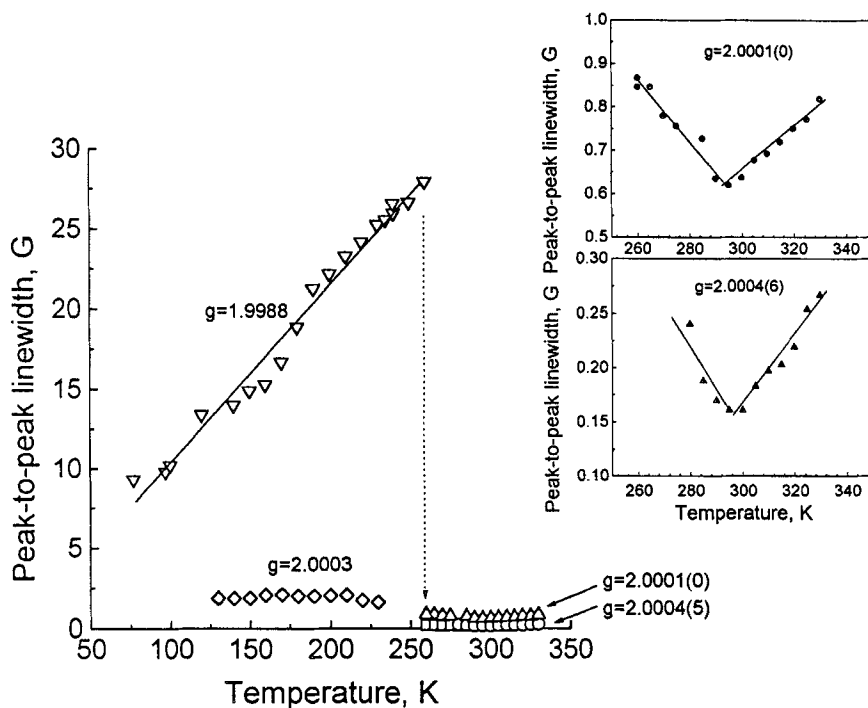


FIG 5 - A peak-to-peak linewidth versus temperature taken for solution of nominal  $Na_1C_{60}$  in DMSO. Two temperature regions, below and above 260 K, are seen clearly. At the low temperature range spectra had two components, respectively, the broad one with  $g=1.9988$  and linewidth linearly increasing with temperature from 9.3 G at 77 K to 28 G at 260 K, and the second narrow one with  $g=2.0003$  and linewidth of about 2 G. Two insets show the dependencies in the temperature range of 260-320 K in enlarged scale. The top inset presents the linewidth of the broader resonance with  $g=2.0001(0)$ ; the bottom inset presents the linewidth of the one of the sharp resonances with  $g=2.0004(5)$ .

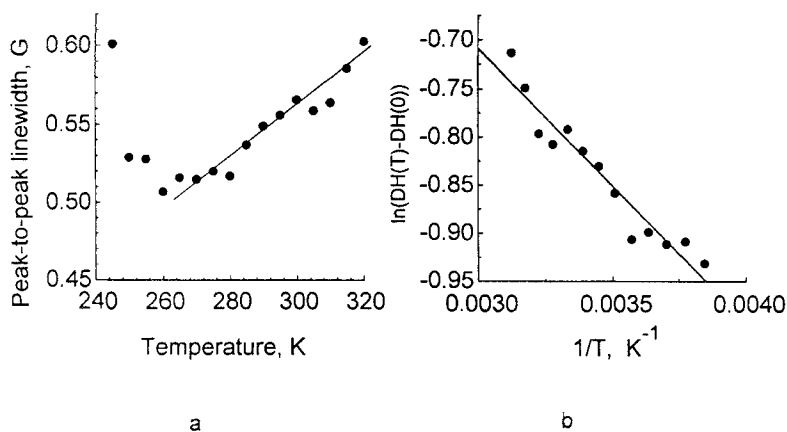


FIG 6 - The left plot (a) shows a peak-to-peak linewidth versus temperature for the broader resonance with  $g=2.0001(8)$  of fluid solution of nominal  $Na_{10}C_{60}$ ; the right plot (b) shows the natural log of the increase of the linewidth versus  $1/T$  for the same resonance.

(290-320 K) and a big distance to 0 K, an attempt to find out the temperature independent portion of the linewidth of the sharp resonances gave unacceptable (negative) intercept at 0 K. Only a rough estimate of the activation energy of within 0.05-0.12 eV (4.8-11.5 kJ/mol) was made assuming  $\Delta H_{pp}(0)=0$  G.

Paramagnetic specieses in fluid solution showed quite good stability. Integral intensities of ESR spectra decreased only by order of two or three times after two months when sealed capillaries were kept in a freezer, while all the features of the spectra were almost remained. Signal were detectable after exposition of the sealed capillaries at room temperature for several days (Fig.3). After exposition of some solutions to air for days, a broad intensive axially symmetric resonance was detected in the spectra with  $g_{\perp}=2.0029$  and  $g_{\parallel}=2.0051$ , while narrow resonances of  $g<2.0023$  disappeared completely.

*The ESR spectra of frozen solution.* Figure 7 shows ESR spectra of nominal  $Na_1C_{60}$  (left side) and  $Na_{10}C_{60}$  (right side) in DMSO depending upon temperature (corresponding room temperature spectra of these samples in expanded scale of magnetic field were presented in Fig.2a,c). The spectra of frozen solution were much broader than those of fluid solutions. The narrow resonances of order of a few tenths of Gauss were not detected. The spectra of nominal  $Na_1C_{60}$  in frozen solution had exhibited two components. One of them was sufficiently broad, with  $g=1.9988$  and linewidth varying linearly with temperature from 9.3 G at 77 K to 28 G at 260 K (Fig.5 and Fig.7a). The increase of the temperature dependent part of the linewidth for this component was found to be thermally activated. Activation energy,  $E$ , was evaluated for the temperature range of 77-260 K to be 0.014 eV (1.3 kJ/mol). The second narrow component emerged clearly in the spectra above 120 K, had  $g=2.0003$  and linewidth of order of 2 G up to 240 K. Frozen solution of nominal  $Na_{10}C_{60}$  showed only a single symmetric resonance of  $g=2.0003$  and linewidth of order of 2 G slightly depending on temperature (Fig.7b).

## Discussion

**Electron Spin Resonance in fluid solution.** The following results should be discussed: the origin of extremely narrow resonances, the discrepancy between NIR and ESR measurements, and the mechanism of the linewidth narrowing in comparison with more broad linewidths reported by the other groups. A non-monotonous behavior of the linewidth and a linear broadening in the temperature range of 290-320 K.

A hyperfine interaction with the solvent protons or the  $^{23}Na$  nuclear spin of  $I=3/2$ , the exchange processes with dissolving oxygen, and, finally, the  $C_{60}^{n-}$  anion radicals or complexes of  $C_{60}$  and Na, can be taken sequentially into consideration



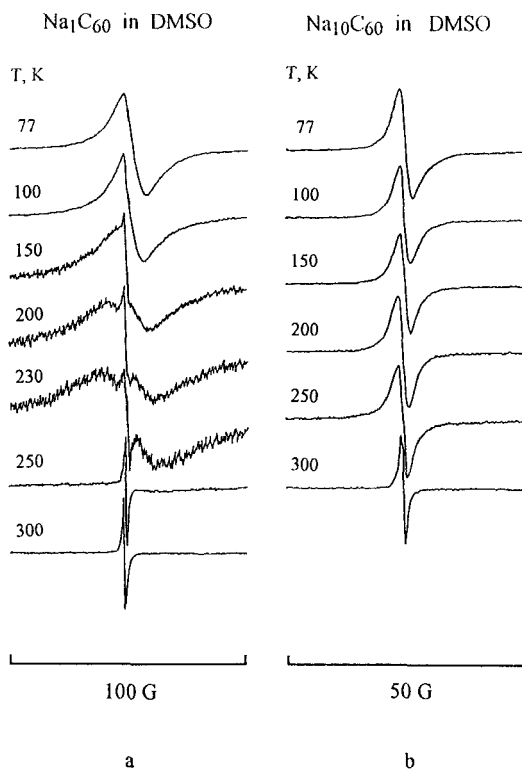


FIG 7 - Temperature dependence of the ESR spectra taken for two solutions prepared by dissolution of nominal  $\text{Na}_1\text{C}_{60}$  (a) and  $\text{Na}_{10}\text{C}_{60}$  (b) in DMSO.

to explain a multicomponent structure of the ESR spectra of fluid solution. Since very similar spectra were detected when  $\text{DMSO-d}_6$  and  $\text{DMF-d}_7$  were used as the solvents, a hyperfine interaction with the solvent protons are ruled out. The unequal spacing and random intensity pattern of the sharp resonances could rule out the splitting due to Na nuclear spin. Solutions were treated by freeze-and-thaw technique and sealed off in vacuo, and then any exchange processes between dissolving oxygen are unlikely as well. Because a precursor comprised only Na and  $\text{C}_{60}$ , it seems, no any species could be referred to the paramagnetic centers of

fluid solution except anions of  $C_{60}$  and complexes of the anions with Na. A NIR spectra of solution of nominal  $Na_1C_{60}$  (Fig.1a) showed exclusively  $C_{60}^-$  anion radical of fairly high concentration, so this monoanion must obviously be in the solution and appear in ESR spectra. Further, the anion radicals of  $C_{60}$  have been reported to yield  $g$ -values less than 2.0023 free electron  $g$ -value<sup>9</sup>, and the low  $g$ -value different from  $g$ -values of all organic radicals was shown to be an unique characteristic of reduced  $C_{60}$ <sup>7,8,12,27</sup>. And finally, multicomponent ESR spectra very similar to those of Fig.2 have been recently reported by Kukolich et al.<sup>15</sup> for  $C_{60}$  reduced by NaK amalgam in a mixture of dimethoxyethane and benzene, where the narrow resonances with the linewidths of order of a few tenths of Gauss at  $g=2.0006$ ,  $g=2.0009$ , and  $g=2.0014$  were assigned to mono-, tri- and pentaanions, respectively. Taking into account of these reasons, the sharp resonances of fluid solution of  $Na_xC_{60}$  in DMSO can be referred to free  $C_{60}^{n-}$  anion radicals. We have assigned them, consequently, at  $g=2.0004(6)$  to  $C_{60}^-$ , at  $g=2.0008(7)$  to  $C_{60}^{2-}$ , at  $g=2.0010(7)$  to  $C_{60}^{3-}$ , and at  $g=2.0012(8)$  to  $C_{60}^{5-}$  (Fig.2a-d). Peak at  $g=2.0006(7)$  with a weak peak-to-peak amplitude (Fig.2e-f) detected only in solution of  $Na_{10}C_{60}$ , where concentration of paramagnetic centers was enhanced, would be tentatively assigned to some electron exchange between anions. The peaks of most interest seemed to be the sharp resonances with  $g=2.0019(5)$  in Fig.2c and  $g=2.0016(5)$  in Fig.3c. They were detected in solutions of nominal  $Na_{10}C_{60}$ , but  $Na_1C_{60}$ . They had  $g$ -value still less than 2.0023 and linewidth of the same order as of the other sharp resonances. Therefore, they might be related to some highest reduced state of  $C_{60}$  though the other unknown sources are likely. The broad resonance can be assigned to  $Na_xC_{60}^{n-}$  complexes remaining in solution.<sup>15</sup> Disintegration of the complex occurred during room temperature exposition of solution in sealed capillaries for a couple of days

released  $C_{60}^{n-}$  anions which were associated with the complex. That resulted the decrease of the peak-to-peak amplitude of the broad line and an appearance of the sharp line of  $g=2.0016(5)$  (Fig.3). A discrepancy observed between NIR and ESR spectra (Figs.1 and 2) was due to high sensitivity of ESR technique. Analogous discrepancy between NIR and ESR has been noted, for example, in Refs. 14 and 27.

Schell-Sorokin et al.<sup>14</sup> summarizing recently ESR data on a  $C_{60}$  monoanion have concluded that a sufficiently broad linewidth is inherent feature of the spectra of the radical approximately above 50 K. Actually, depending upon the host, a room temperature linewidth of  $C_{60}^-$  was published to be within 45-80 G<sup>14,16</sup>. Moreover, the linewidth of a monoanion in DMSO at 320 K was reported to have 55 G<sup>14</sup> which is nearly two order of magnitude larger than the linewidth of the broadest resonance in present study (Fig.2). On the other hand, that is not only a case. The linewidth of order of 0.2-0.4 G of monoanion in THF was published in Ref. 27. As mentioned above, the linewidth of a few tenths of Gauss were reported in Ref. 15 for mono-, three-, and pentaanions. Most authors have observed a sharp spike superimposed the broad resonance in ESR spectra of monoanion, as well. A number of explanations of that spike were presented so far<sup>4,7,12</sup>. For example, Greaney and Gorun<sup>4</sup> suggested that a broad signal was related to the ion-paired  $C_{60}^-$  and the sharp spike to a free  $C_{60}^-$ . One of the reasons of such remarkable difference in linewidth may be connected to what kind of energetic levels of a reduced  $C_{60}$  molecule an electron occupies. According to the calculations of Koga and Morokuma<sup>32</sup> and Adams et al.<sup>33</sup> addition of an electron to the triply degenerate LUMO of  $C_{60}$ ,  $t_{1u}$ , will result in Jahn-Teller distortion that splits three orbitals ( ${}^2T_u$  state in  $I_h$  symmetry of  $C_{60}$  molecule) into one at lower energy and a pair at higher energy ( ${}^2A_{2u}$  state of the  $D_5$  symmetry of the molecule). The other

configuration is when two orbitals have lower energy and one has higher energy ( ${}^2E_{1u}$  state of the  $D_5$  symmetry). Stinchcombe et al.<sup>33</sup> associated the broad ESR signal of  $C_{60}^-$  to  ${}^2E_{1u}$  doubly degenerate ground state and the narrow spike to a low-lying  ${}^2A_{2u}$  excited state. Thus, there is a possibility for a monoanion to have a narrow linewidth based on the electronic configuration under Jahn-Teller distortion. Another source of extremely narrow linewidths may be a tumbling of free  $C_{60}^{n-}$  anion radicals in fluid solution. The plot of the peak-to-peak intensity versus square root of 2 of microwave power (Fig.4) showed for the sharp resonances with linewidths of order of 0.1 G a typical saturation behavior of homogeneously broadened signal. Unsaturated curve of the broader resonance of 0.5-0.7 G was typical for an inhomogeneously broadened signal. Mentioned difference has supported the assignment of the sharp signals to free  $C_{60}^{n-}$  and the broader signal to the  $Na_xC_{60}^{n-}$  complexes. The relaxation times of order of  $10^{-7}$  sec found for the narrow lines in this study are comparable with typical relaxation times of organic radicals with nondegenerate electronic ground states tumbling fast in fluid solution. A motional narrowing possibly determined a decrease in linewidth in the temperature range 260-290 K (insets in Fig.5), a little below but close to the melting point of the solvent, when DMSO start to soften. Meanwhile, a contribution of the processes of the excitation between energetic levels of the electronic state of free  $C_{60}^{n-}$  was enhanced above melting point. Activation energies of order of 0.05-0.12 eV (4.8-11.5 kJ/mol) evaluated from the linear broadening of the peak-to-peak linewidths of the sharp resonances in between 290-320 K are within the same values of the energy differences between excited states of the internal multiplet electronic structure of free  $C_{60}^{n-}$  ions<sup>35</sup>. The broadening of the linewidth above 290 K (insets in Fig.5) can be explained by a variation of the relative populations of two nearest energetic levels with increase of temperature.

**Electron Spin Resonance in frozen solution.** Opposite to the room temperature result, the spectra of nominal  $\text{Na}_1\text{C}_{60}$  below 250 K showed typical signal reported in literature for monoanion of  $\text{C}_{60}$  in frozen solution. A broad resonance of  $g=1.9988$  can be instantaneously assigned to  $\text{C}_{60}^-$ . The temperature dependence of its linewidth in the range of 77-250 K showed in Fig.4 was very similar to that of monoanion in DMSO presented in Fig.3 of Ref. 14. Analysis of the temperature dependence of the broad linewidth showed that within 77-260 K range the linewidth was thermally activated. The activation energy of 0.014 eV (1.3 kJ/mol) evaluated from Fig.6 was about three times smaller than that reported by Dubois et al.<sup>7</sup> for a monoanion in frozen THF,  $\text{CH}_2\text{Cl}_2$ , pyridine, and benzonitrile. The difference obtained is probably associated with the solvent, which makes an energetic gap between the levels, responsible for the activation behavior, smaller comparing with the mentioned solvents. The origin of the narrow resonance of  $g=2.0002$  with the linewidth of order of 2 G (Fig.7) might be related to one of those appeared in literature.<sup>4,7,12,34</sup> However, it should be noted that solutions in this study had an enhanced concentration. A distance between neighbor anion radicals in the matrices of the frozen solvent was enlarged. Exchange processes between anions, which are negligible in frozen solution with a low concentration of the anions<sup>7</sup>, in this case would contribute to the spectral linewidth narrowing. Analogously, the exchange processes between anion radicals in frozen solution of nominal  $\text{Na}_{10}\text{C}_{60}$  determined dominantly observed ESR linewidths (Figs.5 and 7).

### Conclusion Remarks.

In conclusion we have tried to stabilize free anion radicals of  $\text{C}_{60}$  in solution by dissolving of alkali metal fulleride in aprotic solvent, DMSO. The  $\text{Na}_x\text{C}_{60}$  fulleride

was chosen due to the possibility to enlarge a number of intercalated Na atoms in a f.c.c. lattice of  $C_{60}$ , and consequently, to enhance, in some sense, an electron transfer to  $C_{60}$  molecule. At the following dissolution of  $Na_xC_{60}$  in DMSO one could expect a stabilization of free  $C_{60}^{n-}$  anion radicals of the highest reduced state in solution. An apparent result of this attempt was a sufficiently high concentration of anion radicals of  $C_{60}$  of an order of magnitude larger than of that usually achieved in solution by an electrochemical reduction. However, at this stage of the study we could not obtain homogeneous solution consisted of any one anion radical but not several ones. For example, though the room temperature NIR optical absorption spectra of solution of nominal  $Na_1C_{60}$  showed an existence of only a monoanion, ESR spectra exhibited a few narrow resonances assigned to different anion radicals of  $C_{60}$ . It should be noted, that a role of the solvent in stabilization of  $C_{60}^{n-}$  anion radicals, i.e., of the half-wave-potential of the  $C_{60}^{n-}/C_{60}^{(n-1)-}$  redox couple in given solvent can not be ignored<sup>6</sup>. A distribution of the reduced  $C_{60}$  molecules in solid precursor, which was reached after intercalation, may change in fluid solution for a short time after dissolving depending upon the potential. A probability of a  $C_{60}^{n-} \rightarrow C_{60}^{(n-1)-}$  process should be higher than of the reverse one. An observation in fluid solution of  $C_{60}^{5-}$  (in ESR) and  $C_{60}^{6-}$  (in NIR) along with the other ones means that these radicals already existed in solution just after dissolving, and consequently, the highest reduced state of  $C_{60}$  in solid precursor might be close to from five- to six-electron transfer. It seemed a solvent with dielectric constant higher than of DMSO might stabilize the reduced  $C_{60}$  at dissolving much better. However, tentative experiments using N-Methylformamide with  $\epsilon=182.4$  (Ref.<sup>25</sup>) showed for  $Na_{10}C_{60}$  a room temperature ESR spectrum of poorly resolved multicomponent structure with  $\Delta H_{pp}=1.5$  G and  $g=2.0001(9)$ , while an optical absorption spectrum did not

show any absorbtion in near IR range. At the following an optimization of the method will be done. The results obtained will be presented in course of the work.

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