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Optical absorption spectra of chemically generated C_{60} and C_{70} anions

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RÉSUMÉ

Les spectres des anions des fullerènes C_{60}^{n-} et C_{70}^{n-}, où n = 1, 2 et 3 ont été étudiés pour la première fois en solution dans le benzonitrile et en présence de trois réducteurs: Na, K et TDAE. Les anions du fullerène montrent des bandes d'absorption caractéristiques en infrarouge proche, ressemblant aux bandes observées pour les anions générés électrochimiquement. Une augmentation des intensités des bandes à 1042 nm, 1001 nm et 940 nm en comparaison des bandes de $C_{60}Na$ ou $C_{60}K$ est observée pour le sel $C_{60}\cdot TDAE$. Cette augmentation peut être causée par des différences de symétrie de l'anion C_{60}^{-} de ces sels. Une oxydation de l'anion-radical du C_{60} et une apparition d'une bande neuve dans la région spectrale entre 900 et 1000 nm suivent une réduction du C_{60} dans une solution qui contient de l'oxygène.

Mots clés: fullerène, anions du C_{60}, anions du C_{70}, spectres optiques.

ABSTRACT

For the first time the spectra of the fullerene anions C_{60}^{n-} and C_{70}^{n-}, for n = 1, 2, and 3, in benzonitrile, in the presence of three reducing agents: Na, K and TDAE, were studied. The fullerene anions reveal characteristic, near IR absorption bands, similar to those observed in electrogenerated anions. In the normalised $C_{60}\cdot TDAE$ monoanion spectrum an increase of the intensities of 1042 nm, 1001 nm and 940 nm bands is observed when compared with $C_{60}Na$ or $C_{60}K$. This increase can be due to differences in the C_{60}^{-} anion symmetry in these salts. Reduction of C_{60} in oxygen-containing solvent showed an oxidation of C_{60} anion-radical with an appearance of a new absorption band in 900-1000 nm region.

Keywords: fullerene, C_{60} anions, C_{70} anions, optical spectra.

INTRODUCTION

The discovery of superconductivity in alkali-metal–doped fullerides [1] has put these materials at the centre of fullerene research. More recently it has been found that C_{60} can accept up to six electrons with formation of various anion radical salts with interesting electrical and magnetic properties. In the case of Na_xC_{60}, the compounds containing more than six Na atoms per C_{60} molecule have been obtained in a closed thermodynamic system [2]. On the other hand simple arguments based on the filling of one–electron orbitals suggest that C_{60} can accept up to 12 electrons; it was supported by calculations on a $Li_{12}C_{60}$ cluster [3].

The possibilities of reducing fullerenes have led to the preparation of novel molecular materials among them C_{60}–based molecular superconductors [1,4] (alkali metal doped C_{60}) and a 'soft' ferromagnets (e.g. C_{60}·TDAE complex [5], where TDAE is tetrakis(dimethylamino)ethylene). In the first group of solids the anions C_{60}^{3-} play the main role but in the second the anion C_{60}^{1-} is important. The highest C_{60}^{n-} fullerides known in solution are n=6 on the electrochemical timescale [6] and n=5 for low – temperature spectroscopic identification [7]. Electrochemically generated C_{60}^{n-} anions ($1 \leq n \leq 6$) have been spectrally characterised by many authors [6, 8 – 11]. Spectral studies of the anions prepared under high vacuum or inert gas atmosphere, in tetrahydrofuran (THF) or THF / toluene solution by contact on a potassium mirror have been also reported [12, 13]. Observation of an absorption spectrum of the C_{60}^{5-} anion, produced by a solution–phase technique using rubidium in liquid ammonia has been given by Fullager et al [7].

In general, the fullerenes anion radicals can be generated relatively easy by the electrochemical method in e.g. benzonitrile solution [14,15]. Contrary to the electrochemical method the chemical method is confined to only two solvents: THF or liquid ammonia. Small solubility of C_{60} and C_{70} in THF as well as of their anions C_{60}^{n-} and C_{70}^{n-} confines the chemical procedure to generation of monoanions or sometimes dianions. Only few papers report the successful synthesis and isolation of discrete salts of the highly reduced C_{60}^{n-} anions [16 – 18].

Benzonitrile, as a polar solvent (dipole moment: 4.18 D), could be used also for C_{60}^{n-} or C_{70}^{n-} preparation. This solvent has been successfully used for fullerene doping [19], but the reaction in this solvent has never been spectrally studied. TDAE is a strong electron-donor ($E_{½} = -0.75$ V vs. SCE [20]) which can selectively reduce fullerenes to monoanions (half-wave potentials of the C_{60} vs. SCE are: –0.44 V and –0.82 V; the potentials of the C_{70} are: –0.41 V and –0.80 V vs. SCE [8]). In this paper we perform a systematic spectral study of redox states of C_{60} and C_{70} produced in benzonitrile solution by contact on Na, K or TDAE. For the first time the generation of the two fullerene anions, in the same solvent, has been performed using the same procedure. The features of fullerene anions optical spectra in the near IR region are discussed.

EXPERIMENTAL

Electronic absorption spectra of the chemically generated anions C_{60}^{n-} or C_{70}^{n-} were recorded with a Perkin Elmer UV – VIS – NIR Lambda 19 spectrometer. All the spectra were analysed within the spectral range from 600 to 1600 nm, in solutions, at room temperature. The spectra, shown later in Fig. 2, are normalised to the amplitude of the most intense band of the anion at 1080 nm for C_{60}^{1-} and 1374 nm for C_{70}^{1-}. With this choice of co-ordinates, direct comparison of the spectra of the monoanions with the contribution of various electron donors becomes possible.

Absorption spectra of C_{60} or C_{70} solution in the benzonitrile, in the presence of Na, K or TDAE were recorded in the air–tight quartz cell of a path $l = 0.499$ cm and a volume $\upsilon = 1$ ml. In the reference beam the similar absorption cell with alkali metal solution in the benzonitrile was placed. Benzonitrile purchased from Aldrich (HCD grade) was vacuum distilled and degassed with a stream of argon for about 1 h. All the manipulations were carried out under the inert atmosphere conditions of a glovebox under argon. No substantial absorption of the benzonitrile in the investigated spectral range was observed.

Fullerene C_{60} or C_{70} (10 mg) was dissolved in freshly prepared benzonitrile (20 ml) at the heating during 4 h. The solution was filtered and poured into the quartz cell. The fullerene anions were prepared directly in the cell by contact on small pieces of alkali metals K or Na (10 – 20 mg) or by mixing with a solution of TDAE (0.1 ml) at room temperature. Progress of the reaction of the fullerene with a reducing agent was observed by spectral method, recording the absorption spectra every 5 to 20 minutes.

RESULTS AND DISCUSSION

Reaction of fullerene reduction by the alkali metal M (e.g. Na or K) in benzonitrile (BN) runs in two stages and can be described by a scheme [19]:

$$\underset{\textit{surface}}{\mathrm{M}} + \mathrm{BN} \rightarrow \underset{\textit{surface}}{(\mathrm{BN}^{\cdot-})} \rightarrow \underset{\textit{solution}}{(\mathrm{BN}^{\cdot-})}$$

$$\mathrm{BN}^{\cdot-} + C_{60} \rightarrow \mathrm{BN} + C_{60}{}^{1-} \rightarrow C_{60}{}^{2-} \rightarrow \text{ and so on}$$

On the first stage of the reaction the benzonitrile molecule receives an electron from an alkali metal and benzonitrile anion-radical forms on the alkali metal surface. Then the anion radical diffuse to the solution forming a salt with the alkali metal ($BN^{-}M^{+}$). This compound is red-coloured and strongly absorbs the light with an absorption maximum at 550 nm; the absorption decreases quickly in the 600-620 nm range. Thus the spectral study of the fullerene reduction in the benzonitrile is possible only for wavelengths longer than about 650 nm. In solution an electron transfer from $BN^{-}M^{+}$ to a fullerene molecule occurs leading to formation of the anion-radical fullerene salt.

Speed of the reaction of the $BN^{\cdot-}$ anion-radical formation depends mainly on quality of the alkali metal surface and square of the alkali metal surface and does not change during the reaction due to considerable abundance of alkali metal and benzonitrile quantities related to fullerene.

Rates of the reactions of fullerenes C_{60} and C_{70} reduction are nearly the same at room temperature and decrease with an increase of the number of charges on fullerenes. However, a calculation of kinetic data of the creation of fullerene anion-radicals is impossible on account of a used experimental method: the solution was stirred by the sample shaking while the spectra were recorded all the time. One can evaluate only a time of the creation of various anion-radicals. Production of the monoanions C_{60}^{1-} and C_{70}^{1-} was observed in 10 –15 minutes, C_{60}^{2-} and C_{70}^{2-} in 45 minutes – to one hour and C_{60}^{3-} and C_{70}^{3-} in about 3 – 4 h after start of the reaction. After C_{60}^{3-} and C_{70}^{3-} formation an accumulation of BN^- occurs and it leads to an increase of the absorption in the region of 550 – 650 nm. In the space of about 5–6 h the solution becomes not transparent at visible region and the spectra in 550 to 900 nm range become distorted. Thus, the fullerene anions spectra can only be analysed when the reaction is far from such saturation.

An evolution of the absorption spectra of the C_{60} anion generated in the benzonitrile solution by contact on sodium mirror is shown in Fig. 1. The C_{60}^{1-} fullerene monoanion exhibits strong absorption at 1081 nm together with additional fine structure at 1042 nm, 1001 nm and 940 nm. Upon charging to di-anion the C_{60}^{1-} bands disappear while strong absorption bands at 844 nm and 957 nm gain in intensity together with a weak band at 1322 nm. The next reduction state (C_{60}^{3-}) is characterised by a relatively intense NIR transitions at 1378 nm and 1012 nm with another band at 878 nm, while the dominant absorption is shifted to 796 nm. The obtained spectra are similar to the spectra of electrochemically generated C_{60} anions that have been observed by other authors [9-11]. Using extinction coefficients determined by Lawson et al. [14] the abundance of particular anions was evaluated. For the spectra of mixture of various anions (Figs 1B, 1D) the contributions of each component are shown as dotted curves. The wavelengths corresponding to the main and supplementary maxima in the spectra of C_{60} anions chemically generated by contact on three different reducing agents are collected in the Table 1.

All the maxima are observed at nearly the same wavelengths for K, Na and TDAE, but they are red–shifted by 5 – 20 nm in comparison with the spectra observed in other solutions. Obviously it is caused by universal solvent effect. The attribution of the bands has been given previously by many authors [e.g. 7, 9, 10, 12, 14].

Table 1

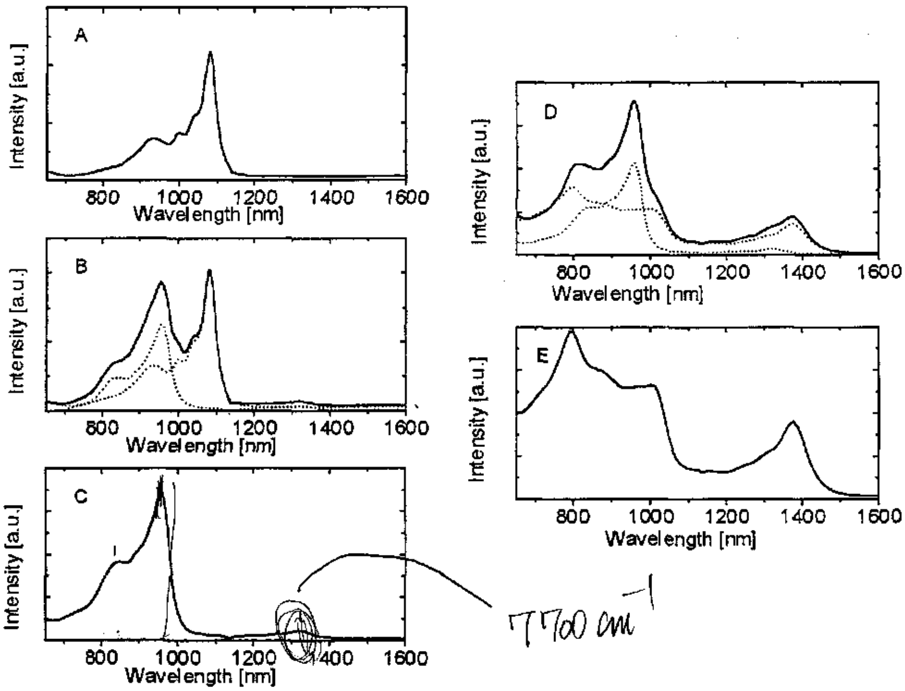
Wavelengths of the absorption bands of C_{60} and C_{70} anions chemically generated in benzonitrile solution by contact with various reducing agents.

SPECIES	WAVELENGTHS [nm]			SPECIES	WAVELENGTHS [nm]		
	REDUCING AGENTS				REDUCING AGENTS		
	Na	K	TDAE		Na	K	TDAE
C_{60}^{1-}	1081 1042 1001 940	1080 1042 1001 936	1080 1042 998 940	C_{70}^{1-}	1374	1373	1379
C_{60}^{2-}	1332 957 844	1321 955 840		C_{70}^{2-}	1182 670	1182 670	
C_{60}^{3-}	1378 1012 878 796	1378 1002 868 796		C_{70}^{3-}	1172 759 675	1171 759 670	
				C_{70}^{4-}		1160 759 674	

Lawson et al.[14] have proposed the schematic molecular orbital and optical transition diagrams for C_{60}^{n-} anions; these diagrams suggest the origin of the observed absorption bands in the solution of chemically generated anions.

Figure 2 shows the spectra of the C_{60} monoanions produced chemically with three various agents. The spectra are normalised with respect to the amplitude of the strongest band at 1080 nm. The spectra of C_{60}^{1-} in solutions containing alkali metals are nearly the same whereas the spectrum for TDAE reduction shows a supplementary absorption between 750 and 1050 nm. It is known [4], that the symmetry of HOMO – LUMO transition in C_{60}^{1-} is $t_{1u} - t_{1g}$. Both orbitals split by a

Jahn – Teller distortion and an electron-vibrational coupling into a_{2u} and e_{1u} (the LUMO) and e_{1g} + a_{2g} (for HOMO), respectively. The additional electron in C_{60}^{1-} occupies the lower a_{2u} state and the maximum 1080 nm can be identified as $a_{2u}\rightarrow e_{1g}$ allowed transition. The maxima of 1042 nm, 1001 nm and 940 nm are weaker and can be attributed to vibrational structure of a forbidden $a_{2u}\rightarrow a_{2g}$transition. The maxima of this vibrational structure, shown in Fig. 2, have considerably higher intensity in the C_{60}^{1-} with TDAE spectrum than in C_{60}^{1-} with Na and K spectra. Since in this region of the spectrum the absorption of TDAE and C_{60} is absent, this additional intensity can be interpreted as absorption of C_{60}^{1-}. An intensity increase of



7700 cm^{-1}

Figure 1: Optical absorption spectra of the C_{60} anions generated in the benzonitrile solution by contact on the sodium mirror; the abundances of particular anions are given: (A) – 72% of the C_{60} molecules in the monoanion state, (B) – mixture of about 65% of C_{60}^{1-} and 35% of C_{60}^{2-}, (C) – 100% of the di-anions C_{60}^{2-}, (D) – mixture of about 50% of C_{60}^{2-} and 50% of C_{60}^{3-}, and (E) – 100% of the tri-anions C_{60}^{3-}. The dotted curves (Figs B and D) show contributions of C_{60}^{1-}/C_{60}^{2-} and C_{60}^{2-}/ C_{60}^{3-}, respectively.

this vibrational structure can be explained when the donors geometry is taken into account. Small atom radii sodium and potassium cations can affect the C_{60}^{1-} geometry to a lesser extent than the larger TDAE molecule. The interaction of TDAE with C_{60}^{1-} lowers the symmetry of the fullerene ion and leads to an increase of the probability of the forbidden transitions.

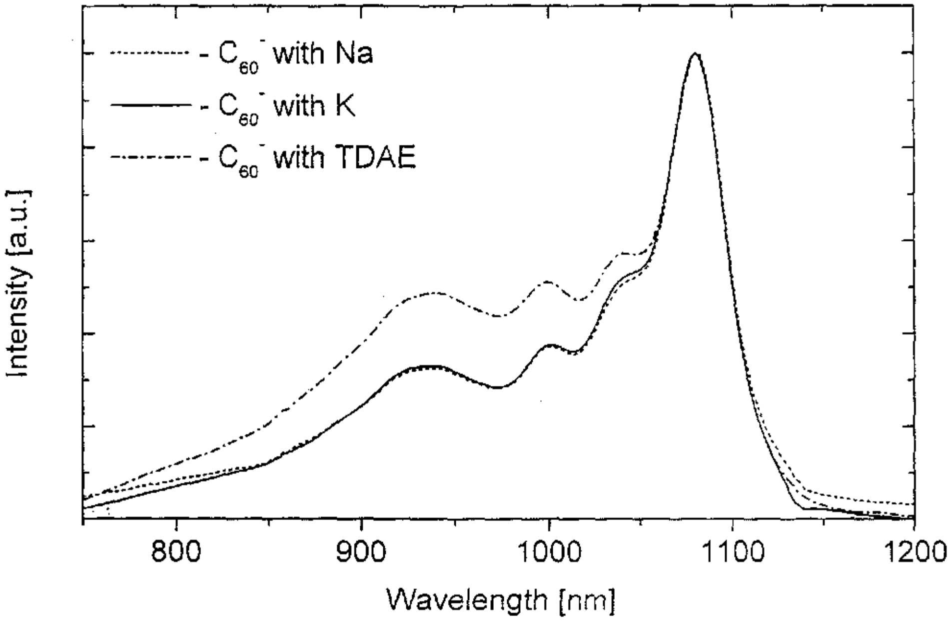


Figure 2: Absorption spectra of the C_{60}^{1-} monoanions chemically generated in the benzonitrile solutions by contact with various reducing agents.

The spectra of the C_{70} anions produced under the same conditions as C_{60}^{n-} are shown in Fig. 3; their maxima are listed also in Table 1 for comparison with the data of C_{60} anions. Monoanion C_{70}^{1-} shows an absorption band at 1374 nm. Further reduction of C_{70} reduces the intensity of this band, and a new strong band at 1182 nm and a weak one at 670 nm gain their intensities. Mono- and di-anion bands of C_{70} that are 5 – 17 nm red-shifted from these positions have been reported [15], similarly as it is in the C_{60} spectra and it can also be attributed to the universal solvent effect. With C_{70}^{3-} formation the band at 1182 nm shifts to 1172 nm and its width considerably increases. Simultaneously a distinct band at 769 nm appears. It is necessary to realise that the compounds of the benzonitrile anion-radical with alkali metal cations absorb strongly below about 650 nm in the concentrated solutions. This is why we cannot attribute unmistakably the strong absorption below 800 nm seen in Fig. 3F; it is only suggested that this absorption is mainly due to the tetra-anions C_{70}^{4-}; a suggested contribution of C_{70}^{3-} is shown at Fig.3F (a full decomposition of the spectrum is impossible because the C_{70}^{4-} spectrum is unknown). The obtained spectra are similar to the spectra of C_{70} reduced electrochemically in benzonitrile [15]. The C_{70}^{4-} spectrum differs considerably from the analogous spectrum obtained for C_{70} reduced in THF by contact on a potassium mirror which shows only one maximum at 1048

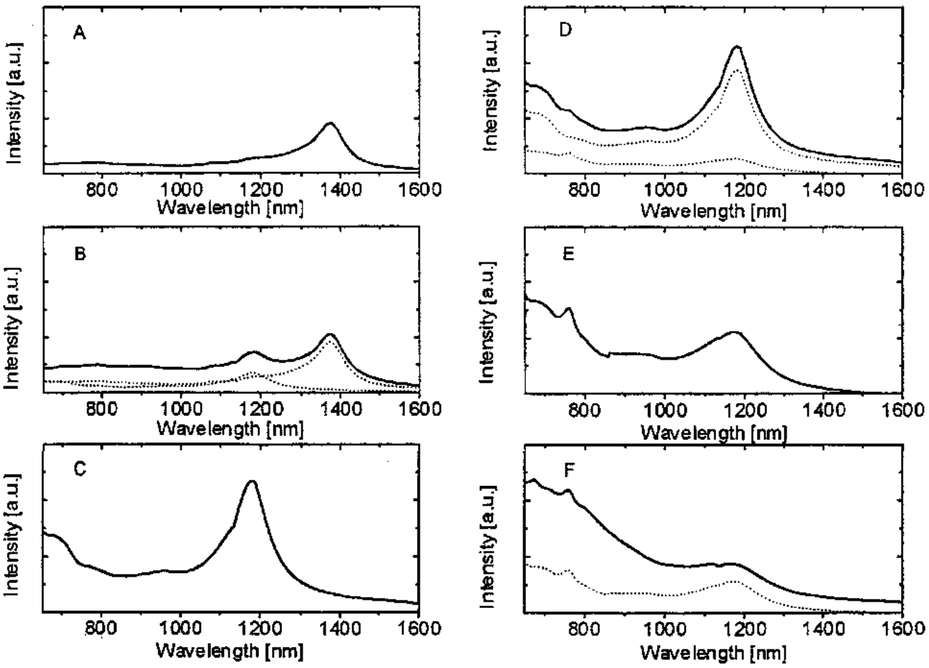


Figure: 3 Optical absorption spectra of the C_{70} anions, generated in the benzonitrile solution by contact with the sodium mirror; contents of particular anions are given: (A) – 85% of the C_{70} molecules in the monoanion state, (B) – mixture of about 85% of C_{70}^{1-} and 15% of C_{70}^{2-}, (C) – 100% of the di-anions C_{70}^{2-}, (D) – mixture of about 80% of C_{70}^{2-} and 20% of C_{70}^{3-}, (E) – 100% of tri-anions C_{70}^{3-}, (F) – mixture of about 50% of C_{70}^{3-} and C_{70}^{4-}, probably. The dotted curves (Figs B and D) show contributions of C_{70}^{1-}/C_{70}^{2-} and C_{70}^{2-}/C_{70}^{3-}, respectively.

nm [13]. The intensities of the low-energy transitions from the region of 1100-1400 nm decrease but intensities of the high-energy transitions from the region 650-800 nm increase in the spectra of higher C_{70} anion-radicals.

Figure 4 shows the monoanions spectra of both fullerenes with TDAE as reducing agent in the range 800-1600 nm. It is symptomatic that only the spectrum of C_{60}^{1-} exhibits the vibrational structure on the short-wave shoulder of the band; the origin of it was discussed earlier.

It is known that the fullerene anions can oxidise in the oxygen-containing atmosphere [17-18]. This reaction can be described by a following scheme

$$C_{60}^{n-} + O_2 \rightarrow C_{60}^{(n-1)-} + O_2^- \rightarrow C_{60}\ (O_2^-)_n.$$

The oxidation reaction for C_{60} and C_{70} monoanions is thermodynamically unfavourable as for redox pair O_2/O_2^- the reduction potential at aprotic environment is - 0.8 V and for fullerene monoanions the reduction potential for redox pair is - 0.44 V and - 0.41 V for C_{60} and C_{70}, respectively [19]. Some solvents can shift the balance to oxidation of fullerene monoanions by stabilisation of di-anion for example, by proton H^+. The oxidation reaction of the fullerene di-anions is thermodynamically favourable and it can easily occur in the presence of atmospheric oxygen. We have obtained the optical spectra of anion-radicals C_{60}^{2-} degradation in the benzonitrile containing oxygen. All remaining conditions of the fullerene reduction reaction were the same; these spectra are shown in Fig. 5.

As quickly as in 10 minutes after the contact on sodium mirror a formation of C_{60} monoanion can be observed almost without any oxidation effects. After 30 minutes (Fig. 5) the C_{60}^{1-} peak intensity goes down considerably and the band 957 nm, characteristic for C_{60}^{2-}, comes up. Simultaneously, the absorbance in the region of 900 – 1000 nm increases. It shows that di-anion formation is accompanied with the onset of C_{60} anion oxidation. Nearly in an hour (Fig. 5C) all monoanions are reduced to di-anions (the band at 1080 nm is absent) which subsequently are transformed to oxidation reaction products, apparently $C_{60}(O_2^-)_n$ that showing a broad absorption band in the 900-1000 nm region. Thus, the reaction of C_{60}^{2-} oxidation means not only the electron transfer from fullerene to oxygen but also a formation of a new chemical compound containing oxygen and fullerene exhibiting a new optical absorption band in NIR-spectra. The analogous compound $C_{60}O_2^-$ is proposed for monoanion C_{60}^{1-} oxidation reaction under oxygen treatment [21]. The details of the oxidizing mechanism need supplementary studies.

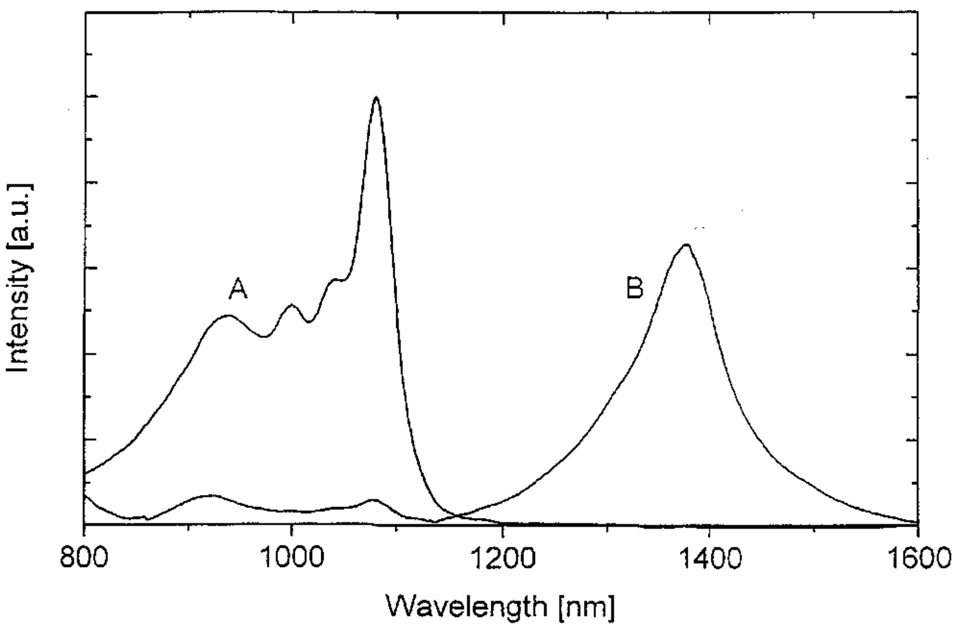


Figure 4: Comparison of the spectra of fullerene monoanions: (A) – C_{60}^{1-} and (B) – C_{70}^{1-} generated in the benzonitrile solution with TDAE reducing agent.

In conclusion, we would like to stress, that in this paper the chemically generated anions of the fullerenes C_{60} and C_{70} in the benzonitrile solution of three reducing agents (Na, K, and TDAE) were spectrally characterised. It was demonstrated that the spectra of chemically generated anions are similar to that observed for the electrochemically produced fullerene anions; small shifts of the absorption bands (5-20 nm compared to the analogous spectra of anions in other solvents) can be due to solvent effect. In the normalized C_{60} TDAE monoanion spectrum if compared with $C_{60}Na$ and $C_{60}K$ an increase of intensities of 1042 nm, 1001 nm and 940 nm peaks is observed; these peaks are identified with the vibrational structure of the forbidden transition $a_{2u} \rightarrow a_{2g}$. It could mean that TDAE reduces the C_{60}^{1-} symmetry far more effectively than alkali-metal cations hence it increases the forbidden transitions probability. Reduction of C_{60} in oxygen-containing solvent showed that the monoanion is relatively stable against oxidation while its dianion is oxidised quickly with formation of $C_{60}(O_2^-)_n$, leading to a broad absorption band in 900-1000 nm region.

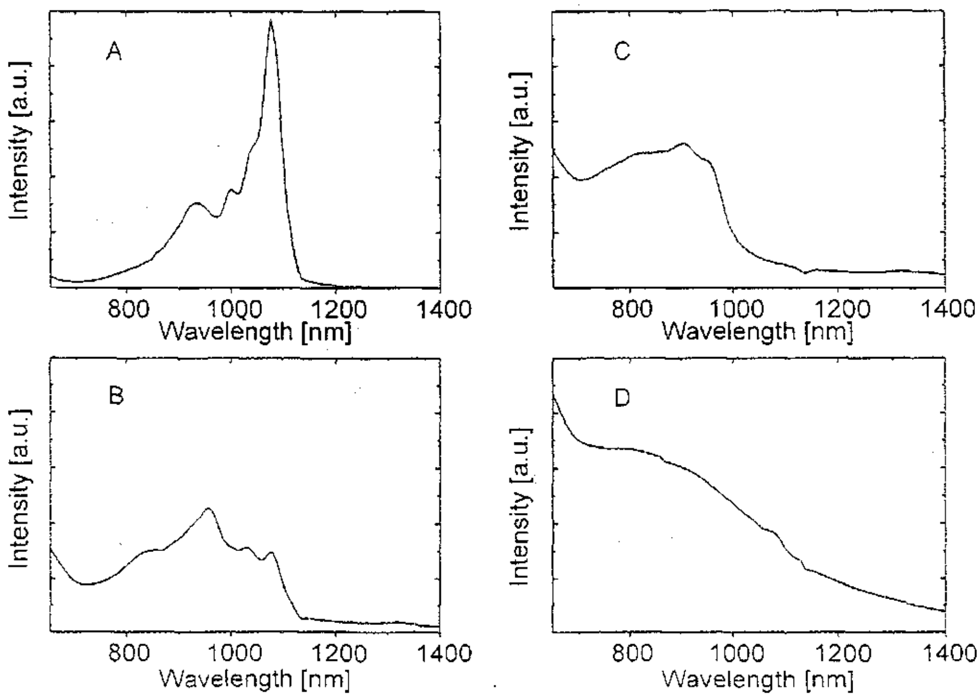


Figure 5: Evolution of the optical spectrum of the C_{60}^{1-} during anion degradation in the oxygen containing atmosphere: (A) – monoanion spectrum just after preparation, (B) – after 10 minutes, (C) – after 30 minutes, (D) – after 1 h.

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REFERENCES

1 Hebard A F, Rosseinsky M J, Haddon R C, Murphy D W, Glarum S H, Palstra T T M , Ramirez A P , Kortan A R (1991) Nature **350**, 600 – 601

2 Yildirim T, Zhou O, Fischer J E, Bykovetz N, Strongin R A, Cichy M A, Smith III A B, Lin C L, Jelinek R (1992) Nature **360**, 568 – 570

3 Kohanoff J, Andreoni W, Parrinello M (1992) Chem Phys Lett **198**, 472 – 477

4 Dresselhaus M S, Dresselhaus G, Eklund P C (1996) *Science of Fullerenes and Carbon Nanotubes.* Academic Press, San Diego - Boston - New York - London - Sydney - Toronto, 616 p

5 Allemand P-M, Khemani K C, Koch A, Wuld F, Holczer K, Donovan S, Grüner G, Thompson J D (1991) Science **253**, 301 – 303

6 Xie Q, Perez – Cordero E, Echegoyen L (1992) J Am Chem Soc **114**, 3978 – 3980

7 Fullagar W K, Gentle I R, Heat G A, White W (1993) J Chem Soc, Chem Commun, 525 – 527

8 Dubois D, Kadish K M (1991) J Am Chem Soc **113**, 4364 – 4366

9 Greaney M A, Gorun S M (1991) J Phys Chem **95**, 7142 – 7144

10 Heath G A, McGrady J E, Martin R L (1992) J Chem Soc, Chem Commun 1272 – 1274

11 Khaled M M, Carlin R T, Trulove P C, Eaton G R, Eaton S S (1994) J Am Chem Soc **116**, 3465 – 3474

12 Baumgarten M, Gügel A, Gherghel L (1993) Adv Mater **5**, 458 – 461

13 Gherghel L, Baumgarten M (1995) Synth Met **70**, 1389 – 1390

14 Lawson D R, Feldheim D L, Foss C A, Dorhout P K, Elliott C M, Martin C R, Parkinson B (1992) J. Electrochemical Soc **139**, L 68 – L 71

15 Lawson D R, Feldheim D L, Foss C A, Dorhout P K, Elliott C M, Martin C R, Parkinson B (1992) J Phys Chem **96**, 7175 – 7177

16 Bhyrappa P, Paul P, Stinchcombe J, Boyd P D W, Reed C A (1993) J Am Chem Soc **115**, 11004 – 11005

17 Boyd P D W, Bhyrappa P, Paul P, Stinchcombe J, Bolskar R D, Sun Y, Reed C A (1995) J Am Chem Soc **117**, 2907 – 2914

18 Sun Y, Reed C A (1994) J Chem. Soc, Chem Commun 747- 748

19 Wang H H, Schlueter J A, Cooper AC, Smart J L, Williams J M, Welp U, Dudek J D, Caleca M A (1993) J Phys Chem Solids **54**, 1655 – 1666

20 Kuwata K, Geske D H (1964) J Am Chem Soc **86**, 2101 – 2105

21 Hwang Y L, Yang C C, Hwang K C (1997) J Phys Chem A **101**, 7071 – 7976