

Charge-Transfer in Fullerene Complexes*

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Spectral investigations of fullerene charge-transfer complexes with planar and spatial electron-donor molecules are reported. The results of this study indicate that the CT complexes of C₆₀ with planar donors are involved in polarization interactions of van der Waals type. CT is very weak in these compounds and is hindered by unfavourable steric factors. As a result, the CT rate does not correlate with the ionization potential of the donor. Contrary to the planar donors, the spatial ones form complexes with CT rate approaching 1.

Key words: fullerene, CT complexes, IR spectra, VIS-NIR spectra

Introduction

Fullerene, C₆₀ is the most intensively studied molecule of the past ten years. This remarkable interest in the fullerenes results from their unusual structure, interesting chemical and physical properties and potential applications [1,2]. Most of the investigations have been concerned with the C₆₀ carbon cluster though higher fullerenes, in particular C₇₀, are also the subject of interest in material science. C₆₀ molecule is a π -acceptor with some unusual features. It consists of hexagonal and pentagonal rings, which build up a practically spherical surface of the molecule [1]. Thus, the molecular structure of C₆₀ is completely different from the structure of other π -acceptors. The electron affinity, E_a of the C₆₀ is rather small – adiabatic E_a is 2.1 ÷ 2.2 eV [3]. On the other hand, C₆₀ molecule exhibits a very high polarizability, about 85 Å³ [4], and, therefore, the contribution of van der Waals polarization interactions is substantially higher for C₆₀ than for other π -acceptors. Recently, many donor-acceptor complexes involving fullerenes have been prepared.

C₆₀ complexes with planar donors

The complexes of C₆₀ form a special class of new materials with planar donors of the tetrathiafulvalene, pyranilidene or dithiadiazafulvalene family. It is known that charge-transfer (CT) complexes and ion-radical salts of these donors with

*Dedicated to the memory of Professor Krzysztof Pigoń.

strong, planar, π -acceptors or inorganic anions exhibit very interesting properties, especially a low-dimensional electron structure. The donor-acceptor interaction in these complexes occurs without any steric hindrances: donor and acceptor molecules are able to approach quite close to each other and their molecular orbitals can effectively overlap. Therefore, the charge-transfer rate δ is mainly dependent on the ionization potential, I_p of the donor and electron affinity of the acceptor. In the case of the spherical acceptor as C_{60} , conditions for the charge transfer are entirely different. The shape of the molecular orbital of C_{60} is nearly spherical and therefore close approach of the donor and C_{60} as well as parallel alignment of their molecular orbitals, leading to an effective overlap, are out of question. In this case, the CT rate is mainly determined by steric compatibility between the shape of donor and fullerene molecules.

IR spectroscopy is considered to be a good technique for an estimation of CT rate in the C_{60} complexes [5,6]. There is a simple relation between the electron density of a certain bond and its force constant [7,8]. It results in a linear dependence of the frequency of some vibrational modes of the donor or acceptor molecules on δ . This dependence is described by the following equation:

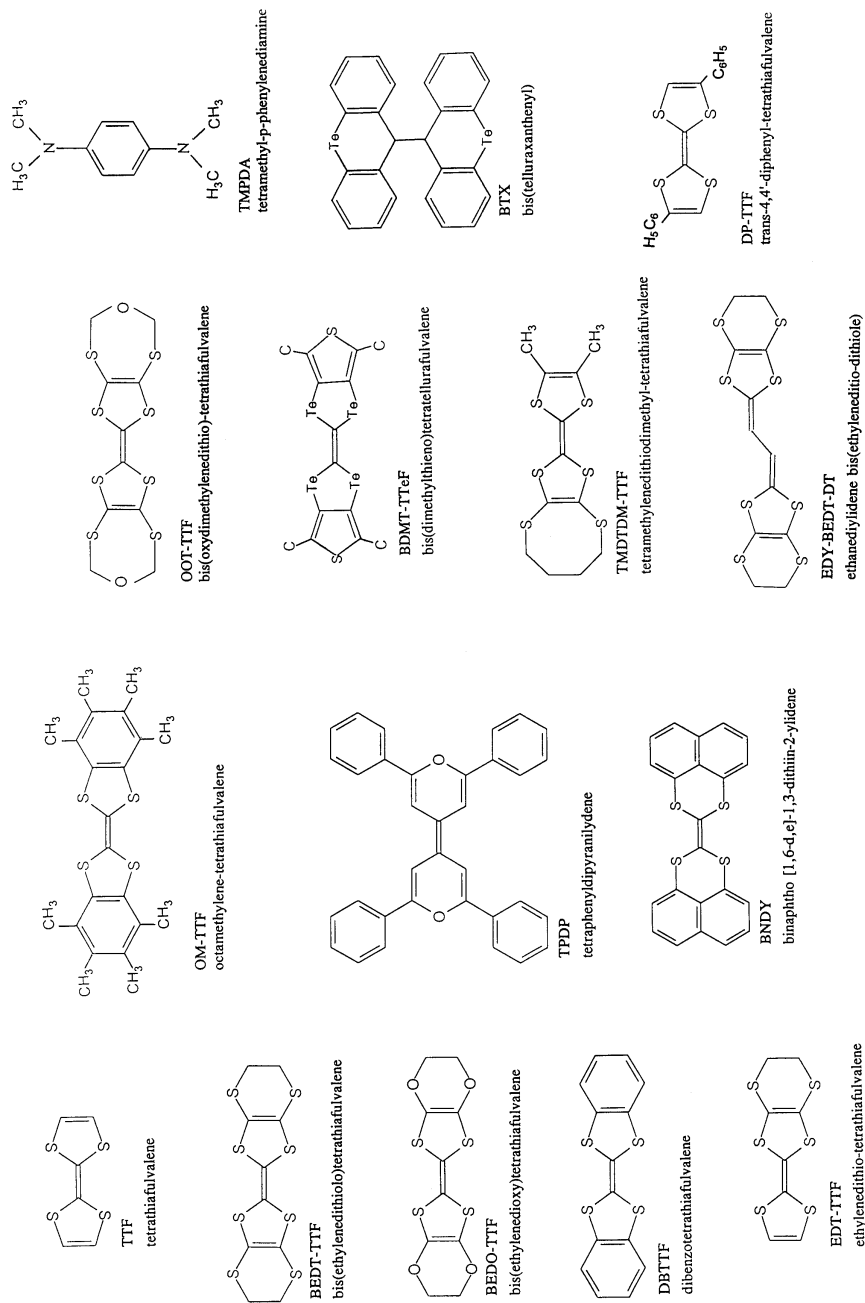
$$\delta = 2\Delta v/v_0(1 - v_1^2/v_0^2) \quad (1)$$

where v_0 is the mode frequency for a neutral molecule, v_1 is the same mode frequency of the anion or cation radical, and Δv is the difference between the mode frequency for a neutral molecule and the corresponding frequency of the CT complex, v_N [8,9].

Formula (1) can be used to characterize C_{60} complexes with various donors. The charge transfer to C_{60} leads to linear frequency changes *vs.* δ for F_{1u} (4) IR active mode of the fullerene. The frequency of the F_{1u} (4) mode shifts from 1429 cm^{-1} for the neutral C_{60} to 1393 cm^{-1} for C_{60}^- monoanion [10]. The correlation is quite linear for the complexes with $\delta < 1$. Entering these numbers to Eq. 1 an approximate relation can be derived:

$$\delta = 0.03\Delta v \quad (2)$$

Tens of the C_{60} complexes with planar donors of various structure and properties have been investigated recently by Konarev *et al.* [8,9,11–13]. Some of the used donors are shown in Scheme 1. The IR absorption spectrum of BEDO-TTF· C_{60} · C_6H_6 in a KBr matrix, characteristic for C_{60} complexes with planar donors, is shown in Fig. 1; for comparison the spectrum of the neutral C_{60} is also displayed. The spectrum of the complex reflects the effects common for all the investigated compounds. It consists of several bands: four of them (1429 cm^{-1} , 1183 cm^{-1} , 576 cm^{-1} and 527 cm^{-1}) are attributed to F_{1u} modes, which are IR active in the C_{60} molecule of I_h point symmetry. There are also numerous bands of donors and solvents used for the crystal growth. The spectra contain numerous, weak bands characteristic of the broken symmetry of the fullerene molecule [9].



Scheme 1. Chemical names, acronyms and structural formulae of the typical donor molecules.

Charge transfer from the donor to C_{60} most strongly affects the frequency of F_{1u} (4) mode of the fullerene [8–12]; this mode is usually slightly downshifted in the CT complexes under study. The frequency shifts are approximately 1 cm^{-1} , *e.g.* the parameter δ is below 0.03 for C_{60} complexes with planar donors, and is practically independent on the ionization potential of the donor. The CT absorption band observed usually between 700 and 1000 nm is very weak too, but their position depends on I_p (Fig. 2). From our spectral studies it results that C_{60} forms only weak CT complexes with planar donors, even with such for which the I_p is as low as about 5 eV. This is caused not only by weak acceptor properties of the fullerene but mainly by its unfavourable steric factors for charge transfer. As a result, the degree of CT is very low and the CT band is weak. The main contribution to the binding energy of the complex is made by van der Waals polarization interactions. Under these conditions, the formation and stabilization of the CT complexes are defined mainly by molecular polarizability of the donor molecule and the steric compatibility between the planar donor and spherical C_{60} molecule. Energetically favourable are the donors, which do not require deformation of the molecule in their coordination with C_{60} . Therefore, the donors which reveal a peculiar spatial structure, *e.g.* the donors with a “butterfly”, “double butterfly” or cup-like type form more stable complexes with C_{60} . Charge transfer is also more effective for small donor molecules [9]. In solution, the CT energies for C_{60} and C_{70} complexes with various, planar TTF-derived donors are similar and almost independent on a solvent polarity. In addition, it was shown that the CT energy of the complex in the solid state is $0.15 \div 0.20\text{ eV}$ lower than those in the solution [13].

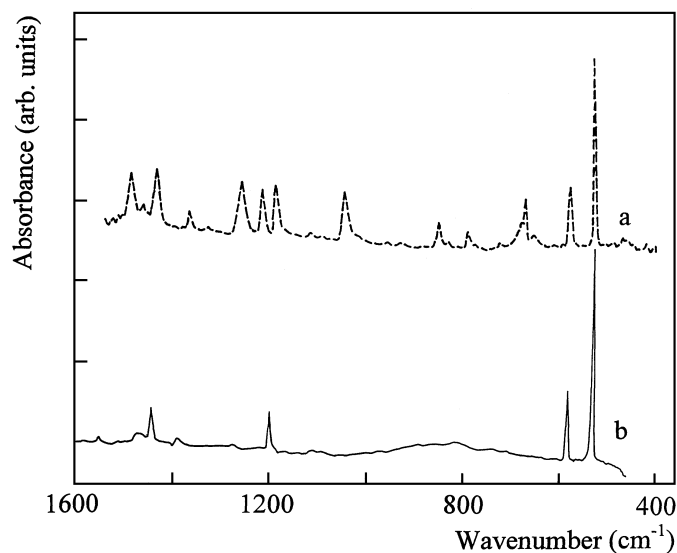


Figure 1. IR absorption spectrum of the BEDO-TTF· C_{60} · C_6H_6 complex characteristic for C_{60} complexes with planar donors (a); IR spectrum of the neutral C_{60} molecule is shown for comparison (b).

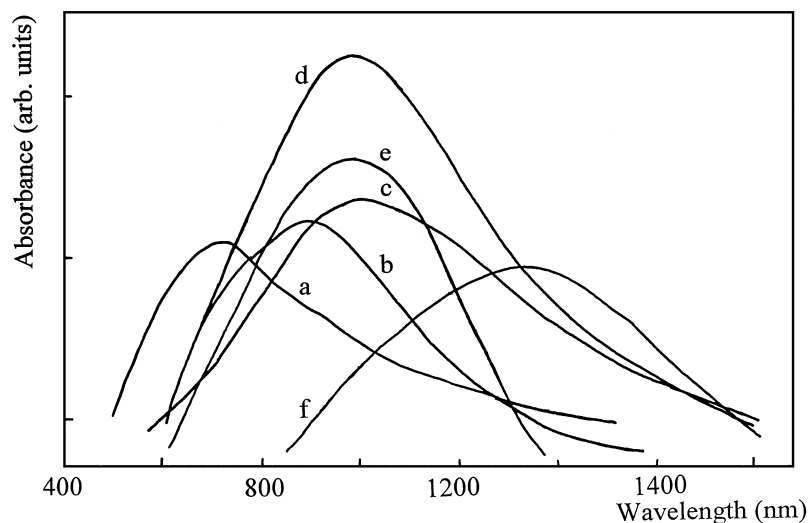


Figure 2. Charge transfer bands observed for C_{60} complexes with various planar electron-donor molecules: OOT-TTF· C_{60} · C_7H_8 (**a**), DP-TTF· C_{60} · C_6H_6 (**b**), TMPDA· C_{60} (**c**), OMTTF· C_{60} ·Py (**d**), (EDT-TTF) $_2$ · C_{60} · CS_2 (**e**), TPDP·(C_{60}) $_2$ (CS_2) $_4$ (**f**) in KBr pellets, at room temperature.

C_{60} complexes with spatial donors

The radical anion salts C_{60} ·tetraphenylphosphonium halides $(Ph_4P)_2 \cdot C_{60} \cdot Y$, where $Y = Cl, Br$ or I are unusual members of the fullerite family: in these compounds $\delta = 1$, namely the acceptor molecule (C_{60}) appears in monoanionic form $-C_{60}^-$. The C_{60} monoion is stable in these salts because it is surrounded by eight phenyl rings of the $(Ph_4P)^+$ cations [14]. In such type of C_{60} complexes the fullerene ions are isolated and checked in the crystal lattice. The occurrence of C_{60} monoanions has been discovered in the single crystals of $(Ph_4X)_2 \cdot C_{60} \cdot Y$ family, where $X = P, As$ and $Y = Cl, Br$ or I [15]. The electronic absorption spectrum, which point to the presence of C_{60}^- consists of a strong band at 1101 nm, two weaker bands at 1025 and 953 nm and a shoulder at about 1050 nm (Fig. 3). Similar absorption has been observed for chemically (in solution) or electrochemically obtained monoanions [16].

In the spectral range of the four IR active F_{1u} modes a very interesting phenomena have been observed [15]. The $F_{1u}(4)$ mode at 1428 cm^{-1} (in the neutral C_{60}) is downshifted in these salts by about 35 cm^{-1} with a strong enhancement of the linewidth and the oscillator strength as well as a change of the line shape. This distinct modification of the IR spectrum of the salts of the $(Ph_4X)_2 \cdot C_{60} \cdot Y$ family has been attributed to an onset of charged phonon behaviour or, in other words, to the coupling of electronic excitations to intramolecular vibrations of the C_{60} molecule. Similarly, the Raman spectra of $(Ph_4P)_2 \cdot C_{60} \cdot Y$ salts reveal a strong broadening and a characteristic down-

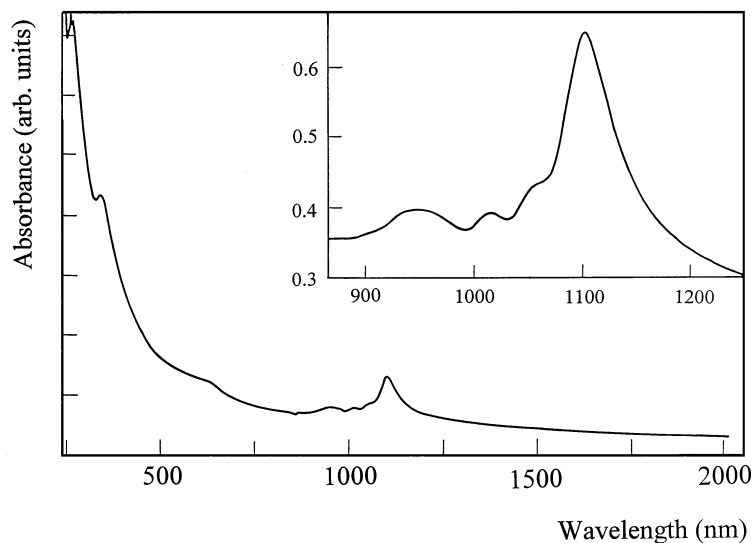


Figure 3. Optical absorption spectrum of $(\text{Ph}_4\text{P})\cdot\text{C}_{60}\cdot\text{I}$ taken at room temperature in KBr matrix. The inset shows the absorption due to the C_{60}^- monoanion.

shift of the H_g radial modes. They split into five components (Fig. 4). The electron-molecular vibration coupling has been suggested as a reason for the broadening and shift of the lines [17]. Recently, the electron-phonon coupling constants have been evaluated by us for low-frequency H_g and A_g modes of the fullerene monoanion in $(\text{Ph}_4\text{P})_2\cdot\text{C}_{60}\cdot\text{I}$ [18]. The obtained coupling constants are in good agreement with recent results obtained with various experimental methods and theoretical evaluations

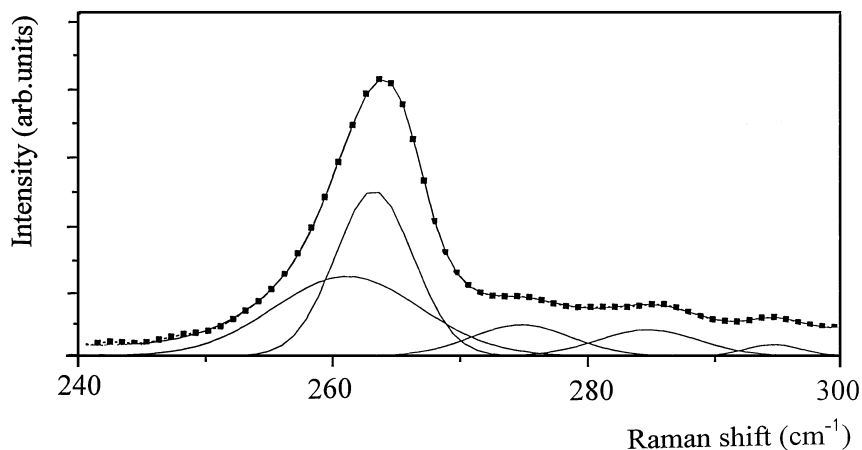


Figure 4. Raman band $\text{H}_g(1)$ (dotted line) of the $(\text{Ph}_4\text{P})\cdot\text{C}_{60}\cdot\text{I}$ complex and its decomposition for five components.

on the monovalent and multi-charged C_{60} molecules in fullerites intercalated with alkali metals [19].

The structure of the $(Ph_4X)_2 \cdot C_{60} \cdot Y$ fullerides enhances their stability and suggests that they are stabilized either through electrostatic interactions or the interactions between the π -orbitals of the carbon atoms of C_{60} and matching phenyl rings of the cations. Taking into consideration the properties of these fullerides and attempting to site the C_{60} in an asymmetric environment, complexes of C_{60} and C_{70} with chloro-(triphenylphosphine)gold, $(Ph_3P)AuCl$ were grown and spectrally characterized [20–22]. In these crystals the fullerene molecule is surrounded on four sides by phenyl rings of the $(Ph_3P)AuCl$, so that π electrons of the phenyl rings interact with the fullerene electron system. This interaction stabilizes the structure and hinders the rotation of acceptor molecules. However, the charge transfer from the electron donor molecule to the acceptor is very small: the compounds are molecular crystals in which van der Waals interactions are predominant. It takes mainly from the IR spectral studies: very small modifications of the IR spectra of the compounds with respect to the spectra of parent substances testify to weak intermolecular interactions and $\delta \approx 0$ in both $C_{60} \cdot 2[(Ph_3P)AuCl]$ and $C_{70} \cdot 2[(Ph_3P)AuCl]$ [21,22]. This conclusion is confirmed by very low electrical conductivity, smaller than $10^{-8} S \cdot cm^{-1}$, and electron spin resonance (ESR) investigations. ESR spectrum of $C_{60} \cdot 2[(Ph_3P)AuCl]$ consists of two lines: a narrow line with $g = 2.0020$ and $\Delta B_{pp} = 4.4 G$ and a broad one characterized by $g = 1.9974$ and $\Delta B_{pp} = 45.3 G$ [21]. The narrow ESR line could be attributed to the isolated fullerene; interactions between $(Ph_3P)AuCl$ and C_{60} molecules produce a small charge on the C_{60} site. This charge is delocalized on the carbon atoms of the C_{60} cage, so that the contributions to the ESR line are dynamically averaged over all the site lo-

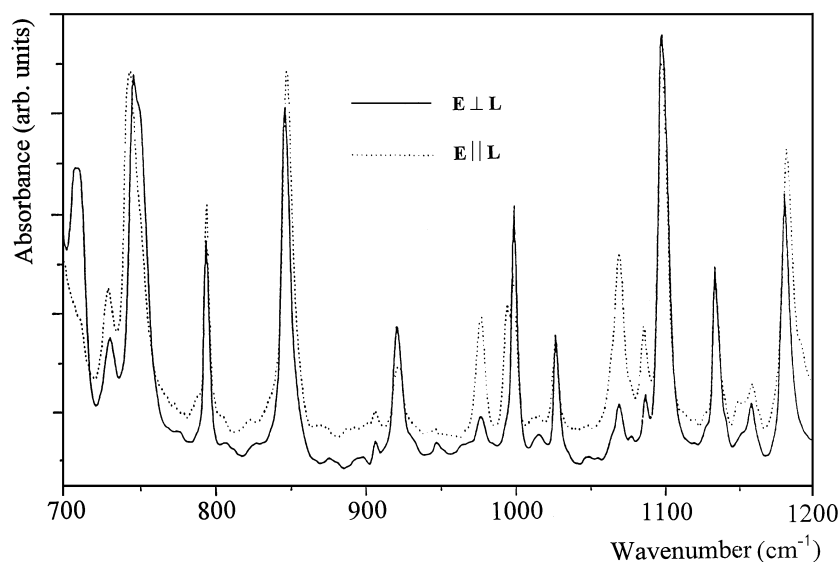


Figure 5. IR polarized spectra of the single crystals of $C_{70} \cdot 2[(Ph_3P)AuCl]$ at room temperature, for two perpendicular light polarizations.

cations of the C_{60} . The broad line is attributed to the $(Ph_3P)AuCl$ system modified by the interaction with fullerene molecule [21].

IR spectra of $C_{70} \cdot 2[(Ph_3P)AuCl]$ (Fig. 5) are strongly anisotropic – they reflect the crystal structure organization mainly caused by an elongated form of the fullerene C_{70} . In particular, the bands attributed to the normal vibrations of the donor exhibit an anisotropy. Besides, the IR and ESR studies reveal an anomaly in the temperature dependence of the spectral parameters at about 160 K; this anomaly has been corroborated by temperature variation of the unit cell a parameter [22]. It was concluded that $C_{70} \cdot 2[(Ph_3P)AuCl]$ undergoes a first-order phase transition at $T \approx 160$ K. Singularities in the IR spectra at $T \approx 250$ K in $C_{70} \cdot 2[(Ph_3P)AuCl]$ and at $T \approx 200$ K in $C_{60} \cdot 2[(Ph_3P)AuCl]$ are not caused by a structural phase transitions but rather reflect the changes of oscillator forces occurring at this temperature or by some redistribution of the charges on the donor molecule, if not by changes in the molecular dynamics of the phenyl rings [20–22]. Comparing the electron structure of the $(Ph_4X)_2 \cdot C_{60} \cdot Y$ salts and $C_{60}/C_{70} \cdot 2[(Ph_3P)AuCl]$ complexes, deduced from IR spectral investigations, one may conclude, that the electron properties of both groups of com-

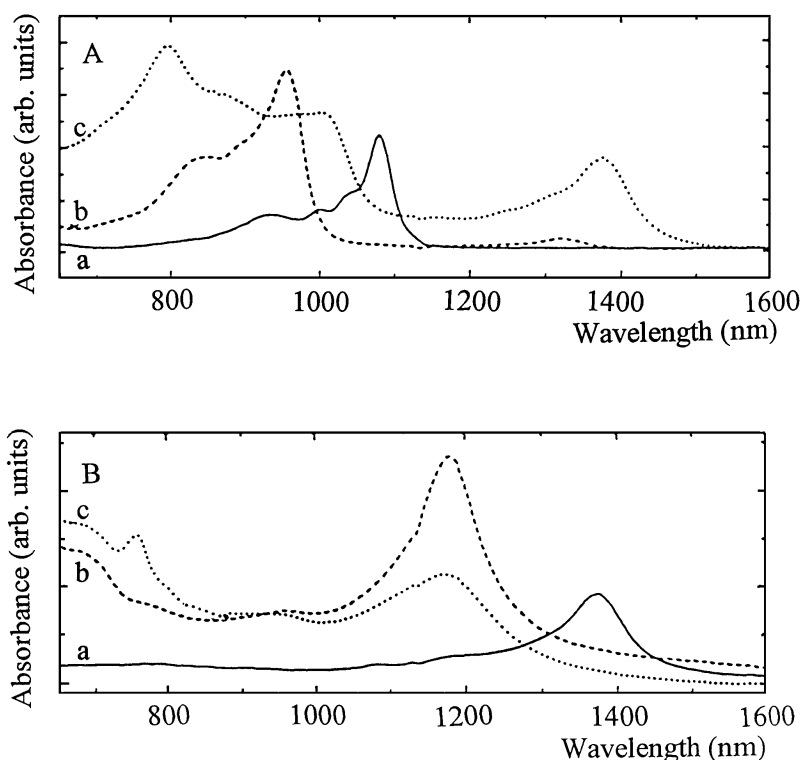


Figure 6. Optical absorption spectra of the C_{60} anions (A) generated in the benzonitrile solution (a – 72% of the C_{60} molecules in the monoanion state, b – 100% of the dianions C_{60}^{2-} , c – 100% of the trianions C_{60}^{3-}) and of the C_{70} anions (B) (a – 85% of C_{70}^{-} , b – 100% of C_{70}^{2-} , c – 100% of C_{70}^{3-}).

pounds are completely different: the former are ionic salts with $\delta = 1$ but the latter are weak van der Waals complexes with $\delta \approx 0$.

As reported earlier [16] the NIR spectroscopy provides us with information on the degree of ionization of C_{60} or C_{70} species. In this report, the spectra of the fullerene anions C_{60}^{n-} and C_{70}^{n-} , for $n = 1, 2$ and 3 , in benzonitrile, in presence of three reducing agents: Na, K and TDAE were studied for the first time. It proves that the chemically generated fullerene anions reveal characteristic, NIR absorption bands (Fig. 6) similar to those observed in electrogenerated anions. Bands attribution is based on schematic molecular orbital and optical transition diagrams for C_{60}^{n-} anions proposed by Lawson *et al.* [23]. These diagrams suggest the origin of the observed absorption bands in the solution of generated anions.

Conclusions

Some possible applications of vibrational and electronic spectroscopies in characterizing the electronic processes in the fullerene complexes with various donor molecules as well as in the fullerene anions were discussed. The changes in the spectral parameters of the complexes, in comparison with those of the neutral fullerene molecules, were attributed to redistribution of the charges and changes of the electron structure of the C_{60} molecules in their compounds. It was shown that spectral methods are useful in the determination of the electron structure of fullerenes C_{60} and C_{70} and their ions. It was shown also that the spectroscopy is not only a viable method of the investigation of the electron structure of fullerene anions but also provides some information on the symmetry of the charge distribution in the fullerene cage and on the fullerene reduction processes in oxygen-containing solvents.

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