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Infrared and visible spectra of the complexes of fullerene-70 and its salt

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Abstract

Electronic and vibrational spectroscopies were used to investigate the electron processes in neutral C_{70} fullerene and its complexes with crown-shaped sulfur and 9,9′-bis-*trans*-(telluraxanthenyl) donors; spectral properties of the salt $[(C_6H_5)_4P]_2C_{70}Br$ are discussed also. It is concluded that the complexes are weak, molecular complexes of the van der Waals type. The activation of silent modes of C_{70} as well as distinct changes of the donor IR spectra have been discovered in the $[(C_6H_5)_4P]_2C_{70}Br$ salt. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The fullerenes are the most intensively studied molecules of the past ten years. This remarkable interest in the fullerenes results from their unusual structure, interesting chemical and physical properties and potential applications [1–4]. Most of the investigations have been concerned with the C_{60} carbon cluster. At present, understanding of its properties is relatively good. The chemistry and physics of C_{70} have developed more slowly than that of C_{60} and currently numerous effects and properties of the molecule are being studied.

In contrast to the C_{60} molecule with I_h symmetry, the C_{70} molecule has the lower symmetry, D_{5h} and lacks the inversion symmetry. Although the electronic absorption spectrum [5,6] as well as IR [7,8] and Raman [8,9] spectra of C_{70} have been described several times, the data are not complete. The quantum chemical calculations of normal vibrational modes have led to inconsistent results. Some progress has been made; however, the calculations based on the C_{60} model, with an addition of a small perturbation to account for the weakening of the force constants of the belt atoms, have led to satisfactory agreement between the theory and the experimentally determined frequencies. Namely, 31 IR-active and 53 Raman-active modes out of the total number of 122 possible vibrational mode frequencies have been assigned [8,10]. It was also found that the neutral C_{70} exhibits a dominant visible band at 469 nm, whereas upon electrochemical reduction new absorption arises at 1369 nm [11].

Although there is more strain in the C_{70} molecule than in C_{60} and fewer pyracylene bonds in the former molecule, it exhibits the same first reduction wave potentials in various solvents [12]. However, despite the similar chemical nature, materials made out of C_{70} differ very much in their properties from their C_{60} analogues. Similarly, the number of reports on the physical properties of both groups of derivatives is quite different. For example, it seems that only $C_{70}S_{48}$ [13,14] and $C_{70}\cdot BTX(CS_2)_{0.5}$ [15] complexes and $[(C_6H_5)_4P]_2C_{70}I$ salt [16] are characterized by X-ray diffraction.

Since visible, near-IR and IR spectroscopies have proven to be a useful tool for the investigation of the CT process, molecular ionization, electronic and vibrational states and inter- and intramolecular interactions, we performed spectral studies of C_{70} in solution and KBr pellets, C_{70} complexes with crown-shaped sulfur, S_8 and 9,9′-bis-*trans*-(telluraxanthenyl) (BTX) donors as well as C_{70} salt $[(C_6H_5)_4P]_2C_{70}Br$. There are two reasons for such a choice of donors. Firstly, they have differentiated forms: the S_8 ring of crown-shaped form is a small, compact molecule, BTX consists of two non-planar telluraxanthene fragments in a ‘double butterfly’ conformation, whereas tetraphenylphosphonium cations are big species but the difference in size of $[(C_6H_5)_4P^+]_2Br^-$ and C_{70} is compensated by the orientation

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of the phenyl groups. Secondly, C_{60} analogues of all the compounds investigated here have been studied by us previously [17–20] — thus offering a possibility for comparisons.

In this paper we characterize spectrally the three C_{70} complexes and the salt. The aim of these investigations is a selection of the spectral effects typical for C_{70} complex or salt formation; the evolution of the spectra, from solution, through a solid state to complexes and salts is also at the centre of our interest.

2. Experimental

The complexes of C_{70} with S_8 of two stoichiometries, $(S_8)_2$ and $(S_8)_6$, as well as BTX were grown from solutions of stoichiometric amounts of C_{70} and appropriate donors in C_6H_6 and CS_2. Small single crystals were obtained by slow evaporation of the solvents. Single crystals of $[(C_6H_5)_4P]_2C_{70}Br$ were grown by electro-crystallization from a solution containing C_{70} and $(C_6H_5)_4PBr$. More detailed descriptions of the synthesis of the investigated compounds are given elsewhere [16,21–23]. A study of the thermal stability of the complexes and the salt was carried out. Thermogravimetric analysis under argon by using a Thermograph Q calorimeter shows that all investigated compounds are stable up to 400 K at least. Some of them, e.g. $C_{70}\cdot BTX\cdot CS_2$ lose carbon disulfide molecules in the 473–505 K temperature range; partial decomposition of the donor occurs in the 613–653 K range [22].

Single crystals of $C_{70}\cdot BTX\cdot CS_2$ were grown as elongated prisms of typical dimensions 0.8×1.5 mm^2, with black and shiny surfaces. Crystals of $C_{70}(S_8)_6$ show two forms: thin plates of about 1.5×1.5 mm^2 or needles of typical lengths up to 10 mm and thickness about 0.1 mm. The faces of well-formed single crystals of the complex are black and shiny. Single crystals of $[(C_6H_5)_4P]_2C_{70}Br$ salt exhibit a shape of a regular pile with plate surfaces of typical dimensions 0.5×0.5 mm^2 and thickness of 0.2–0.3 mm.

Electronic absorption spectra of the fullerene, C_{70}, in n-heptane solution and KBr pellets containing dispersed samples with concentrations from 1:2000 to 1:16 000, were recorded with a Perkin-Elmer UV–Vis–NIR Lambda 19 spectrometer. Reflectance spectra of single crystals of the C_{70} complexes and salt were recorded with a custom-made microspectra-reflectometer (ultraviolet and visible regions). Standard extrapolation of the reflectivity data to the spectral range where the data are not available was performed [24]. Transmission spectra of single crystals in the IR region were obtained using a Perkin-Elmer 1725X FT-IR spectrometer. Both instruments were fitted with dedicated microscopes. The investigations were performed for polarized light, for various crystal orientations. The spectra were measured for well-developed faces, with two polarizations of light: along the long axis of the sample and in the perpendicular direction. All spectral measurements were taken at room temperature. The spectra of the C_{70} complexes, C_{70} salt and pristine donors and C_{70} were additionally recorded for powdered samples, in the KBr matrix. In addition, some test electron spin resonance (ESR) studies were performed.

3. Results and discussion

3.1. Electronic spectra of C_{70} adducts

The excellent quality of the single crystals of C_{70} complexes with crown sulfur donor, with two different compositions, $(S_8)_2$ and $(S_8)_6$, enables us to measure the anisotropy of their electronic absorption spectra. For the first time these unique investigations have brought to light the anisotropy of some electronic excitations in the complexes of C_{70}. The electronic absorption of CT complexes of C_{70} with crown sulfur donor, for two light polarizations (parallel and perpendicular to the long single crystal axis), is shown in Fig. 1. The spectrum of the $C_{70}\cdot BTX\cdot CS_2$ complex, for one light polarization, is also shown. For comparison, the absorption spectrum of the pristine C_{70} single crystal is given. All the spectra have been recorded from 200 to 1100 nm. Similar investigations of powdered samples in a KBr matrix were performed up to 2500 nm, but between 700 and 2500 nm no absorption was found.

Strong absorption centred at 290 nm, typical for neutral C_{70} crystals, has its counterparts in the spectra of all the investigated complexes. The bands of $C_{70}(S_8)_2$, for both polarizations, are situated at the same wavelengths, about 290 nm. Their intensities are also the same, for ⊥ and ∥ polarizations; however, their linewidth is distinctly larger than the linewidth of the C_{70} band. The respective bands for $C_{70}(S_8)_6$ show but an insignificant down-shift for the perpendicular light polarization and significantly larger shift, down to 280 nm, for the parallel polarization; some changes of the intensities and a broadening of the bands are also seen. The absorption spectrum of $C_{70}\cdot BTX\cdot CS_2$ consists of a number of overlapped and strongly broadened bands. Nevertheless the down-shift of the band corresponding to that of 290 nm is observable.

Much more interesting effects are observed in the region above 370 nm. Counterparts of the band at 420 nm, for pristine C_{70}, show distinct shifts and strong anisotropies for both C_{70} complexes with crown sulfur donor. The bands for the light polarization perpendicular to the long crystal axes, for $C_{70}(S_8)_2$ and $C_{70}(S_8)_6$, are shifted to about 410 and 400 nm, respectively. For the parallel polarization these bands disappear for the two C_{70} complexes. The absorption of the light of parallel polarization is significantly lower than the absorption of perpendicularly polarized light up to about 600 nm in $C_{70}(S_8)_2$ and 530 nm in $C_{70}(S_8)_6$; above these wavelengths of radiation, the opposite effects are observed. In particular, the absorption at the parallel polarization increases with wavelength, and even shows a broad maximum centred at about 840 nm, for $C_{70}(S_8)_6$ complex.

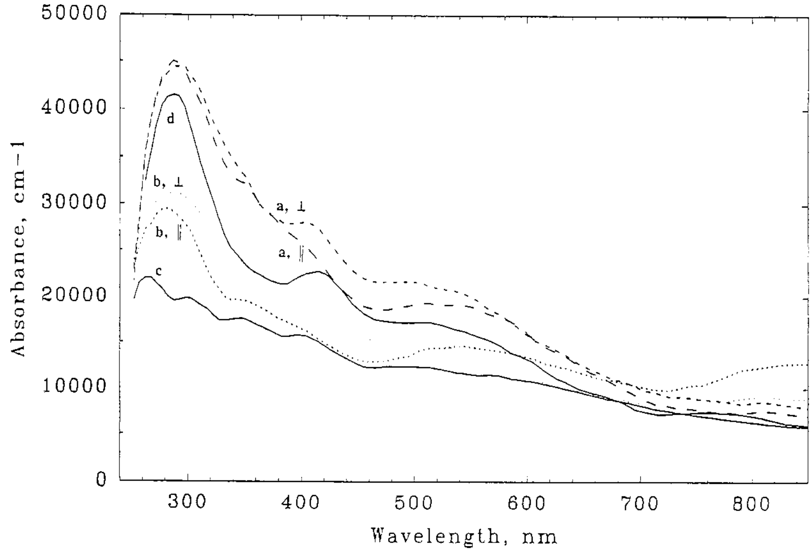

Fig. 1. UV–Vis electronic absorption spectra of single crystals of $C_{70}(S_8)_2$ (a), $C_{70}(S_8)_6$ (b), C_{70}•BTX•CS_2 (c) and C_{70} grown from C_6H_6 (d). The spectra of the C_{70} complexes with crown sulfur donor were recorded for light polarizations parallel (∥) and perpendicular (⊥) to the crystal axes. All the spectra are taken at room temperature.

The observed spectral anisotropy is consistent with the crystal structure of the investigated complexes. According to Roth and Adelmann [13] the structure of $C_{70}(S_8)_6$ consists of planes of closely packed C_{70} molecules perpendicular to the *c*-axis interleaved by a complex array of S_8 rings. The long axes of all C_{70} molecules (five-fold molecular rotation axis) point along the *b*-direction. It was also found that platelets of $C_{70}(S_8)_6$ show a pronounced anisotropy of light absorption and are ruby-red along the *b*-axis and black along the *a*-axis [13]. This anisotropy is determined exactly in our investigation and is shown in Fig. 1.

Unfortunately, the crystal structure of $C_{70}(S_8)_2$ has not been determined as yet. However, it is known that there are large cavities in the form of hexagonal channels parallel to the *c*-axis, containing S_8 species in the crystals of $C_{60}(S_8)_2$ [25]. One can expect that a similar organization of the donor's chains occurs in $C_{70}(S_8)_2$; it should effect an axial ordering of the C_{70} molecules. Thus, the spectral anisotropy of $C_{70}(S_8)_2$ may also be consistent with the anticipated crystal structure. A similar crystal structure, with C_{70} layers interleaved by layers of BTX and CS_2, has been found for BTX•C_{70}•$(CS_2)_{0.5}$ [15].

The electronic absorption spectrum of the salt $[(C_6H_5)_4P]_2C_{70}Br$ is completely different from the spectra of C_{70} complexes and it does not even resemble the spectrum of pristine C_{70}; it is shown in Fig. 2. The spectrum of the salt consists of two strong and relatively narrow bands at about 265 and 340 nm and weak and broad absorption centred at 460 nm; the absorption for the longer wavelengths, up to 2500 nm, is weak and does not show any bands or anomalies. On the other hand, the spectrum resembles the electronic absorption spectra of the salts of the $[(C_6H_5)_4P]_2C_{60}Y$ family, where Y = Cl, Br or I [20]. These spectra consist of two distinct bands at 263 and 338 nm and a broad and weak feature at 630 nm. The two strong bands were attributed to simultaneous absorption given by the opposite ion $(C_6H_5)_4P^+$ and the monoanion of C_{60}. It suggests that the electronic absorption spectrum of the salt $[(C_6H_5)_4P]_2C_{70}Br$ is dominated by the absorption of the opposite ion. The bands at 265 and 340 nm are well separated because there is no overlap with the absorption of the anion C_{70}^-. On the other hand, the broad absorption at 460 nm could be assigned to absorption at 500–580 nm observed for solid C_{70}. It seems that a shoulder near 420 nm on the slope of the 340 nm band could be related to the C_{70} band at 420 nm.

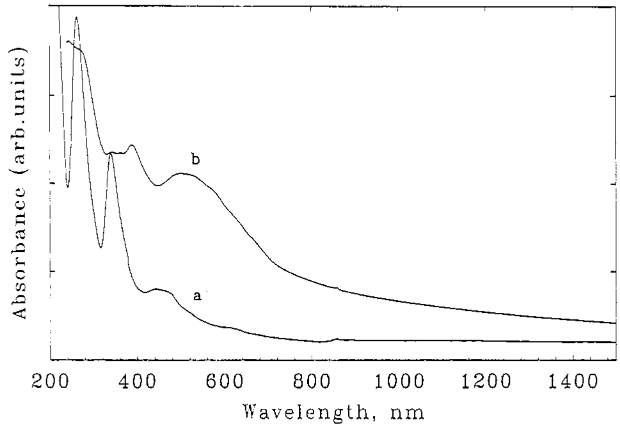

Fig. 2. UV–Vis–NIR absorption spectra of the salt $[(C_6H_5)_4P]_2C_{70}Br$ (a) and the pristine C_{70} (b). Both spectra are recorded for KBr pellets containing powdered samples at room temperature.

According to the electrochemical procedure of growing the $[(C_6H_5)_4P]_2C_{70}Br$, the complete formula should be $[(C_6H_5)_4P^+]_2C_{70}^-Br^-$; thus, the product is a radical-ion salt. ESR and our IR spectral investigations confirm the presence of the C_{70} radical anion generated in the electrochemical reduction of C_{70} and electrocrystallization of $[(C_6H_5)_4P]_2$-$C_{70}Br$. Pénicaud et al. [16] using the same conditions of electrocrystallization produced single crystals of the salt $[(C_6H_5)_4P^+]_2C_{70}^-I^-$. Their ESR and magnetic susceptibility measurements, similar to our data for $[(C_6H_5)_4P]_2C_{70}Br$, have proved the electron transfer from the donor to C_{70} molecule; as a result the acceptor transforms into the C_{70}^- radical anion. On the other hand, it was shown that, upon reduction of C_{70} in tetrahydrafuran solution by contact on a potassium mirror, a new near-IR (NIR) absorption arises at 1369 nm [26]. The absorption band has been ascribed to C_{70}^-. The intensity of the band is a couple of times smaller than that of C_{70} absorption below 400 nm.

Unfortunately, our effort to observe the monoanion absorption for the salt $[(C_6H_5)_4P]_2C_{70}Br$ was not successful; the absorption of the salt in the NIR range is completely featureless and flat. Bearing in mind the arguments from the electrochemical method of preparation of the salt, our evaluation of the degree of CT from the IR spectra and the onset of the ESR line characteristic for C_{70}^-, one can reject the argument about the lack of the C_{70} monoanions in the structure of the salt. Hence, we suggest that the electronic transitions typical for C_{70} anion excitations are not detectable by the NIR spectral method because of a peculiar mechanism of the dissipation of the C_{70}^- anion excitation. This effect and the electronic structure of the C_{70} monoanion in the solid state are under investigation.

3.2. Vibrational spectra of C_{70} adducts

Vibrational IR spectra of the single crystal complexes of C_{70} with crown-shaped sulfur donor as well as BTX have been recorded at room temperature, for two mutually perpendicular light polarizations; they are shown in Fig. 3 for one of the polarizations. It is necessary to emphasize that the IR spectra of the single crystals of C_{70} complexes have been studied for the first time; on the other hand, the spectra of their C_{60} counterparts have been investigated for $C_{60}\cdot S_{16}\cdot 0.5C_6H_5Cl$ [18] and $BTX\cdot C_{60}$ [19]. The vibrational spectra of the sulfur-containing C_{70} complexes exhibit very weak anisotropy; the wavenumbers and the shapes of the absorption bands are the same for both polarizations but the intensities of some bands show only minor polarization dependence. The effect is seen for the bands at, e.g., 905, 922, 1134, 1430, 1463, 1527 and 1534 cm^{-1}. Only two of them (1134 and 1430 cm^{-1}) can be assigned to the stronger C_{70} bands observed by us in the IR spectra of the C_{70} powdered sample in KBr; the other one, at 1463 cm^{-1} could also be attributed to vibrations of C_{70} [27]. The remaining polarized bands are much weaker and could be assigned to vibrations of C_{70} which are not usually observed at C_{70} pellets because of their low intensity. Some absorption bands can be attributed to activated silent modes and higher order combination modes of C_{70} — a contribution of the sulfur donor vibrations has not been ruled out.

In contrast to the spectra of $C_{70}(S_8)_2$ and $C_{70}(S_8)_6$, the IR spectrum of the single crystal of $C_{70}\cdot BTX\cdot CS_2$ shows numerous bands given by the BTX donor: those recorded at 721, 748, 824, 863, 935, 1021, 1029, 1048, 1202, 1273, 1292, 1349 and 1560 cm^{-1} are of particular significance. The strong and complex absorption between 1400 and 1540 cm^{-1} is produced by superposition of the donor, acceptor and solvent bands.

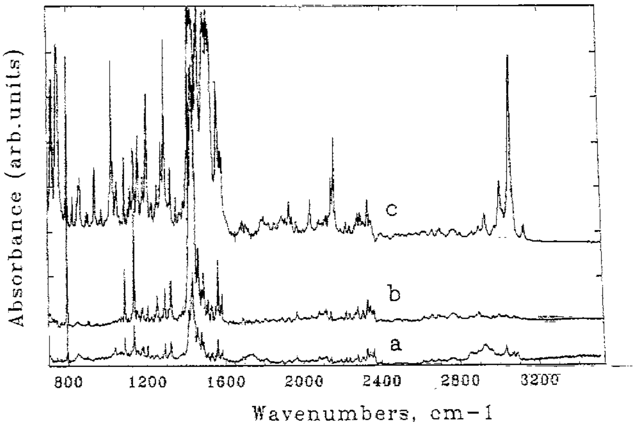

Fig. 3. IR absorption spectra of the single-crystal complexes of C_{70} with crown-shaped sulfur $(S_8)_6$ (a) and $(S_8)_2$ (b) as well as BTX (c) recorded for polarized light at room temperature.

In general, the wavenumbers of both the donor and the acceptor bands are insignificantly shifted in the investigated complexes. The strongest band of C_{70} observed at 1430 cm^{-1} in its IR spectrum is found nearly at the same frequency (1430 ± 1 cm^{-1}) in the C_{70} complexes. According to Jishi et al. [8] this band is assigned to the E_1' mode of C_{70}. On the other hand, according to a force-constant model for the vibrational modes in C_{70} [10] this mode should be shifted down to 1387 cm^{-1} for C_{70}^{6-} in solid M_6C_{70}, where M represents an alkali-metal atom. Assuming that the frequency shift, $\Delta\nu$, in the C_{70} derivatives is directly proportional to the degree of CT, as already found for C_{60} complexes [28,29], the CT ρ in the C_{70} complexes and salts can be evaluated from the formula:

$$\rho=0.14\,\Delta\nu \qquad (1)$$

in which $\Delta\nu$ is in cm^{-1}.

Our spectral data for three C_{70} complexes with S_8 and BTX show that $\rho=0\pm0.14$ in these complexes. The evaluation confirms our earlier suggestion that the CT complexes of C_{70} with crown sulfur and BTX donors are weak, molecular complexes of the van der Waals type. The same can been stated for the appropriate complexes of C_{60} [17–19,29]. Hence, the complexes of both C_{70} and C_{60} with various donors, independently of their ionization potentials and structural properties, are complexes with very small degrees of CT and are neutral complexes in their ground state.

Fig. 4 shows the vibrational spectrum of the single crystal of the salt $[(C_6H_5)_4P]_2C_{70}Br$; for comparison, the spectra of the salt $[(C_6H_5)_4P]Br$ and the C_{70} acceptor dispersed in KBr matrix are also displayed. The single crystal spectrum of the C_{70} salt is very rich. Apart from the strongest bands of the fullerene C_{70} and the opposite ion $(C_6H_5)_4P^+$ one can find a multitude of new lines. In comparison with the spectra of the

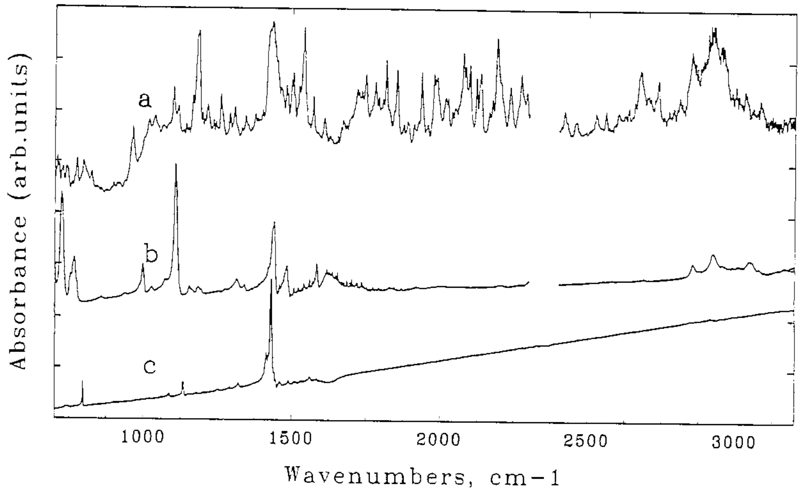

Fig. 4. IR absorption spectra of the single crystal $[(C_6H_5)_4P]_2C_{70}Br$ salt (a) recorded with polarized light at room temperature as well as the absorption spectra of the $[(C_6H_5)_4P]Br$ salt (b) and the fullerene, C_{70} (c), both in KBr pellets at room temperature.

complexes shown in Fig. 4, in particular with the spectrum of the complex of C_{70} with BTX (c), the IR spectrum of the salt is richer for the frequencies above 1600 cm^{-1}. Not only the number of the observed lines but also their intensities are unique for the investigated salt. According to experimental data and model calculations [8,10,27] all the normal vibrations of the C_{70} molecule are between 300 and 1600 cm^{-1}; above these frequencies some combination modes could be expected. On the other hand, the opposite ion with four phenyl groups has some normal vibrations in this spectral range. In particular, between 2850 and 3050 cm^{-1}, the vibrations of CH groups are seen. The characteristic modification and enhancement of these vibrations were recently observed by Świetlik et al. [30] for numerous solvated crystals of the fullerene C_{60}. It was suggested that there is a significant interaction between the π clouds of C_{60} and the solvent molecules. This effect has an influence on the position and shape of the IR bands assigned to the CH stretching vibrations of the guest molecules, as well as the slight frequency changes of the vibrational C_{60} bands. It seems that a similar effect is observed for C_{70} adducts, e.g. for $[(C_6H_5)_4P]_2C_{70}Br$.

The IR spectrum of the investigated salt differs strongly from that obtained by superposition of the spectra of C_{70} and the opposite ion. Several new or strongly deformed and shifted bands (e.g. 672, 775, 963, 1182, 1423 and 1539 cm^{-1}) appear in the single crystal spectrum of $[(C_6H_5)_4P]_2C_{70}Br$. The shift of the frequency of the E_1' mode of C_{70}, from 1430 cm^{-1}, for the neutral C_{70}, to 1423 cm^{-1} in the salt shows that the degree of the CT, according to Eq. (1), is about one for $[(C_6H_5)_4P]_2C_{70}Br$. Unusually strong bands are observed also in the region between 1600 and 2300 cm^{-1}. These observations show strong interaction between the salt $(C_6H_5)_4PBr$ and the C_{70}. It seems that such strong effects cannot be caused by relatively weak dispersive interactions but must be given by much stronger effects. For example, the electron–molecular vibration coupling could be responsible for the spectral modification of the salt. A similar effect has been observed by Kuzmany and co-workers [28] in the IR reflectivity measurements of alkali-metal-doped C_{60}: A_xC_{60} phases for $x = 1, 3, 4$ and 6, as well as by us [20] for the fullerides of the general formula $(Ph_4X)_2C_{60}Y$, where X = P or As, and Y = Cl, Br or I. The changes in the line positions, linewidths and oscillatory strengths were explained theoretically as the coupling of the additional carriers in the t_{1u}-derived conduction band to the selected vibrational modes of C_{60} by a virtual transition to the next highest band which has t_{1g} symmetry [28,31]. The frequency shift is strongly dependent on the degree of CT, ρ. The parameter $\rho \approx 1$ for the $[(C_6H_5)_4P]_2C_{70}Br$ salt and this is why the coupling of the electrons and intramolecular vibrations of C_{70} should be significant. It seems that some combination modes of C_{70} are also coupled, which might explain the strong absorption bands between 1600 and about 2300 cm^{-1}. Next, it is possible that characteristic complex absorption between 2850 and 3050 cm^{-1} is also influenced by the electron–phonon coupling, as for the interaction of C_{60} with organic molecules in solvate crystals [30]. However, the electron–molecular vibration coupling has never been observed for C_{70} compounds and we are not able to give convincing arguments supporting our suspicion. The subject is under investigation.

In addition, the spectral study of $[(C_6H_5)_4P]_2C_{70}Br$ versus temperature was performed by heating the salt up to 370 K. The salt is stable in this temperature range and its vibrational spectra change monotonically and reversibly within the temperature range. It proves also that no anomalies occur up to 370 K.

4. Conclusions

The study provides spectral information on the selected charge-transfer complexes and the radical-ion salt of the fullerene, C_{70}; these materials have been spectrally characterized for the first time. Electronic and vibrational spectroscopies were used to investigate the electron processes in neutral C_{70} fullerene and its charge-transfer complexes with crown-shaped sulfur and BTX donors; spectral properties of the salt $[(C_6H_5)_4P]_2C_{70}Br$ were also studied and discussed. Some investigations were performed on single-crystal samples using polarized light.

It is concluded that the complexes of C_{70} with the donors are weak, molecular complexes of the van der Waals type. Although the charge transfer from the donors to C_{70} is negligible, a broadening of some absorption bands has been observed. The interesting and unique properties of both electronic and vibrational spectra of the C_{70} salt were discussed. We have to emphasize that, according to our knowledge, this is the first time that an analysis of the spectral properties of C_{70}-derived materials is presented. An evolution of the C_{70} spectra, from the C_{70} solutions in neutral solvents, through the solid state to the crystalline C_{70} charge-transfer complexes and radical-ion salts is presented and discussed.

Acknowledgements

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References

[1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.

[2] R.C. Haddon, A.F. Hebard, M.J. Rosseinsky, D.W. Murphy, S.J. Duclos, K.B. Lyons, B. Miller, J.M. Rosamilia, R.H. Fleming, A.R. Kortan, S.H. Glarum, A.V. Makhija, A.J. Muller, R.H. Eick, S.M. Zahurak, R. Tycko, G. Dabbah, F.A. Thiel, Nature 350 (1991) 320.

[3] P.M. Allemand, K.C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, J.D. Thompson, Science 253 (1991) 301.

[4] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, Science of Fullerenes and Carbon Nanotubes, Academic Press, San Diego, 1996.

[5] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, Nature 347 (1990) 167.

[6] H. Ajie, M.M. Alvarez, S.J. Anz, R.D. Beck, F. Diederich, K. Fostiropoulos, D.R. Huffman, W. Krätschmer, Y. Rubin, K.E. Schriver, D. Sensharma, R.L. Whetten, J. Phys. Chem. 94 (1990) 8630.

[7] D.S. Bethune, G. Meijer, W.C. Tang, H.J. Rosen, Chem. Phys. Lett. 174 (1990) 219.

[8] R.A. Jishi, M.S. Dresselhaus, G. Dresselhaus, K.A. Wang, P. Zhou, A.M. Rao, P.C. Eklund, Chem. Phys. Lett. 206 (1993) 187.

[9] D.S. Bethune, G. Meijer, W.C. Tang, H.J. Rosen, W.G. Golden, H. Seki, C.A. Brown, M.S. Derries, Chem. Phys. Lett. 179 (1991) 181.

[10] R.A. Jishi, R.M. Mirie, M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, Phys. Rev. B 48 (1993) 5634.

[11] L. Gherghel, M. Baumgarten, Synth. Met. 69–71 (1995) 1389.

[12] P.-M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M.M. Alvarez, S.J. Anz, R.L. Whetten, J. Am. Chem. Soc. 113 (1991) 1050.

[13] G. Roth, P. Adelmann, J. Phys. I France 2 (1992) 1541.

[14] H.A. Romberg, M. Knupfer, J.F. Armbruster, G. Roth, Synth. Met. 69–71 (1995) 1379.

[15] B.Z. Narimbetov, L.V. Zorina, S.S. Hasanov, L.P. Rozenberg, R.P. Shibaeva, D.V. Konarev, R.N. Lyubovskaya, Kristallografia (in Russian), submitted for publication.

[16] A. Pénicaud, A. Peréz-Benitez, R. Escudero, C. Coulon, Solid State Commun. 96 (1995) 147.

[17] N.D. Kushch, I. Majchrzak, W. Ciesielski, A. Graja, K. Woźniak, T.M. Krygowski, J. Phys. I France 3 (1993) 1987.

[18] N.D. Kushch, I. Majchrzak, W. Ciesielski, A. Graja, Chem. Phys. Lett. 215 (1993) 137.

[19] D.V. Konarev, V.N. Semkin, R.N. Lyubovskaya, A. Graja, Synth. Met. 88 (1997) 225.

[20] V.N. Semkin, N.G. Spitsina, S. Król, A. Graja, Chem. Phys. Lett. 256 (1996) 616.

[21] A.V. Talysin, V.V. Ratnikov, P.P. Syrnikov, Solid State Phys. (St. Petersburg) 38 (1996) 2263.

[22] D.V. Konarev, R.N. Lyubovskaya, O.S. Roschupkina, Y.M. Shul'ga, M.G. Kaplunov, I.N. Kremenskaya, L.P. Rozenberg, S.S. Hasanov, R.P. Shibaeva, Mol. Mater. 8 (1996) 79.

[23] B. Miller, J.M. Rosalmilia, J. Chem. Soc., Faraday Trans. 89 (1993) 273.

[24] F. Wooten, Optical Properties of Solids, Academic Press, New York, 1972.

[25] O.A. Dyachenko, E.B. Yagubskii, S.V. Konovalikhin, N.D. Kushch, G.V. Shilov, N.G. Spitsina, Mol. Mater. 4 (1994) 133.

[26] L. Gherghel, M. Baumgarten, Synth. Met. 69–71 (1995) 1389.

[27] R. Meilunas, R.P.H. Chang, S. Liu, M. Jensen, M.M. Kappes, J. Appl. Phys. 70 (1991) 5128.

[28] T. Pichler, R. Winkler, H. Kuzmany, Phys. Rev. B 49 (1994) 15 879.

[29] D.V. Konarev, V.N. Semkin, A. Graja, R.N. Lyubovskaya, J. Mol. Structure, accepted for publication.

[30] R. Świetlik, P. Byszewski, E. Kowalska, Chem. Phys. Lett. 254 (1996) 73.

[31] M.J. Rice, H.Y. Choi, Phys. Rev. B 45 (1992) 10 173.