Aggregation of Some TTF Derivatives and Their Adducts with C_{60}[*]

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Spectral investigations of selected tetrathiafulvalene-derived donor molecules (TTFs) and the fullerene-derived adducts with these donors linked to them were performed. The main attention has been devoted to studies of possible intermolecular interactions, in particular to aggregation processes in these materials.

Key words: fullerene C_{60}, tetrathiafulvalene derivatives, aggregation, optical spectroscopy

The preparation of covalently attached C_{60} – electron-donor systems (C_{60} adducts) is an area of increasing interest of fullerene chemistry [1]; for recent review see [2]. These new materials have become very interesting from the viewpoint of improving the fullerene stability, processibility, and other properties. A wide variety of donor moieties such as ferrocene [3], phthalocyanine [4], porphyrin [5], aniline [6] or tetrathiafulvalene (TTF) [7–9] derivatives (named here as TTFs) have been bounded to C_{60} in order to obtain materials of unique structure and properties. On the other hand, studies of the intramolecular electron-transfer mechanisms and intermolecular interactions in these materials are important from the point of view of chemical and biological reactions. The intermolecular interactions lead to aggregation of adducts, which can show particular characteristics.

The strongest organic donor molecules that can be covalently linked to C_{60} skeleton are TTF and its derivatives. To promote electronic interaction, the strategy of linking C_{60} and TTFs by a rigid bridge have been developed [7,8]. TTF-C_{60} systems have been designed in such a way that the C_{60} acceptor and TTF donor are directly attached by two rigid σ-bonds, forming a cyclohexane ring. In this way, the fusion of the two electroactive centres with a six-membered ring provides not only a short distance, but also a controlled rigidification between the donor and the acceptor, giving rise to well-defined relative spacing and orientation of both moieties [10].

Recently, we have studied the optical properties, mainly electron and vibrational spectra of several polyadducts of TTFs linked to C_{60} [11–13]. It was shown that the charge redistribution on C_{60} and TTFs depends not only on the nature of a substituent

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[*] Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.
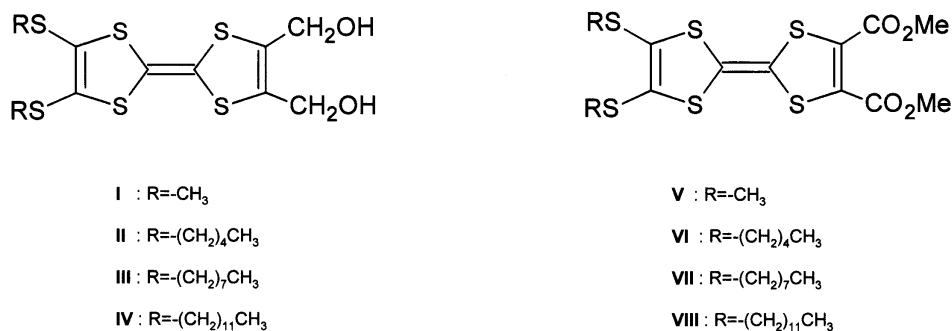[**] Author for correspondence.

but first of all on the number of bounded donors to C_{60}. Changes of the energy of electronic levels of the C_{60} moiety and broadening of electronic excitations are the main consequences of redistribution of charge; this effect increases with the number of the attachments. Strong effect was observed in the IR spectra of the double-substituted fullerene molecules, where a new very strong and broad band appears at about 1100 cm^{-1}. The resonant origin of this band was suggested [11–13].

The aim of the present work is to provide supplementary information on vibrational properties of selected TTF-derived electron-donor molecules and *bis*-linked adducts of C_{60} with TTFs with two alkylsulfanyl (-SC$_N$H$_{2N+1}$) groups (N = 1, 5, 8 or 12). In particular, the goal of the paper is to study the aggregation both TTF-derived donors and adducts having these donors linked to C_{60}. An analysis of their vibrational spectra (IR and Raman) is completed with model simulations.

EXPERIMENTAL

TTF-derived donor molecules chosen for our investigations contain two alkylsulfanyl groups on one side and two hydroxymethyl (-CH$_2$OH) (**I** – **IV**) or methoxycarbonyl (-CO$_2$CH$_3$) (**V** – **VIII**) function groups on another side (see Scheme 1). These donors were linked to C_{60} forming a set of polyadducts (**IX** – **XI**) containing alkylsulfanyl groups of various lengths (1 < N < 12) (see Scheme 2). According to methodology described elsewhere [7,14], the TTFs-C_{60} adducts were synthesized by Hudhomme and co-workers using successive cycloadditions.

I : R=-CH$_3$	**V** : R=-CH$_3$
II : R=-(CH$_2$)$_4$CH$_3$	**VI** : R=-(CH$_2$)$_4$CH$_3$
III: R=-(CH$_2$)$_7$CH$_3$	**VII** : R=-(CH$_2$)$_7$CH$_3$
IV: R=-(CH$_2$)$_{11}$CH$_3$	**VIII**: R=-(CH$_2$)$_{11}$CH$_3$

Scheme 1. Chemical formulae of the TTF-derived donor molecules **I** – **IV** and **V** – **VIII**.

Vibrational absorption spectra of the donors and adducts in the spectral range 400–7000 cm^{-1} were recorded with a FT IR Perkin Elmer 1725 X spectrometer, in KBr pellet containing dispersed compounds with typical weight concentration 1:1000. Similar samples were prepared for Raman scattering investigation. The Raman spectra excited with 1064 nm radiation (1.16 eV) from a Nd:YAG laser were recorded with a Bruker IFS 66 FRA 106 spectrometer; the laser power was limited to 50 mW. The absorption of carbon disulphide solutions of the donors were measured with a FT IR Bruker EQUINOX 55 spectrometer. All spectral investigations were performed at room temperature. A standard PeakFit computer program was used for analysis of the complex absorption in the region of stretching vibration of OH groups. Lorentzian functions were assumed for individual components of the absorption profiles. The line positions and their integral intensities were analysed.
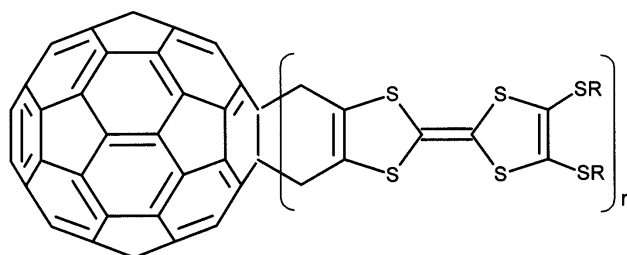
IX : R=-CH$_3$ with n=1,2 or 3

X : R=-(CH$_2$)$_4$CH$_3$ with n=1,2 or 3

XI : R=-(CH$_2$)$_{11}$CH$_3$ with n=1

Scheme 2. Chemical formulae of the *bis*-linked TTF-derived donors to fullerene C$_{60}$ (compounds **IX** – **XI**).

Molecular modelling of the studied molecules has been performed using molecular mechanics method supplied within the commercially available HyperChem package (by Hypercube Inc., Canada). The same method was used for discussion of possibilities of the aggregation of donor molecules and their adducts. In all calculations, full geometry optimization was performed with Polak–Ribiere conjugate gradient algorithm [15] until RMS gradient 0.5 kcal Å mol^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectrum of the compound **I** in the region of its intramolecular vibrations recorded in KBr pellet, at room temperature. This spectrum is typical for the compounds **I** – **IV** containing hydroxymethyl groups. The strongest absorption bands between 2820 and 2980 cm^{-1} are assigned to CH stretching modes. The broad and unsymmetrical band centered at about 3300 cm^{-1} is due to the stretching of hydrogen-bonded OH groups. This absorption will be discussed later. Generally, the spectra of the compounds **I** – **IV** are similar to the spectra of TTF and other TTF-derived molecules [11–13]. Counterparts of the strongest absorption lines of **I** in the spectral range 1650–600 cm^{-1} can be found in the spectrum of *bis*(ethylenedithio)tetrathiafulvalene (BEDT-TTF). Taking into account an assignment of BEDT-TTF vibrations given by Kozlov *et al.* [16] and Eldridge *et al.* [17] we can suggest the following attribution of the main vibrations of the compound **I**: 1611 cm^{-1} – stretching of the C=C (ring) bonds, 1422 cm^{-1} – stretching of the C=C (central and ring) bonds, 1048 cm^{-1} – stretching of the C–S and C–C bonds, 1004 cm^{-1} – stretching of the C–O coincident with the stretching of the C–S and C–C bonds and bending of the CCS bonds, 984 cm^{-1} – stretching of the C–C and C–S bonds, 777 cm^{-1} – stretching of the C–S bonds and bending of the CSC bonds, and 625 cm^{-1} – stretching of the C–S bonds. These bands are significantly red-shifted in comparison
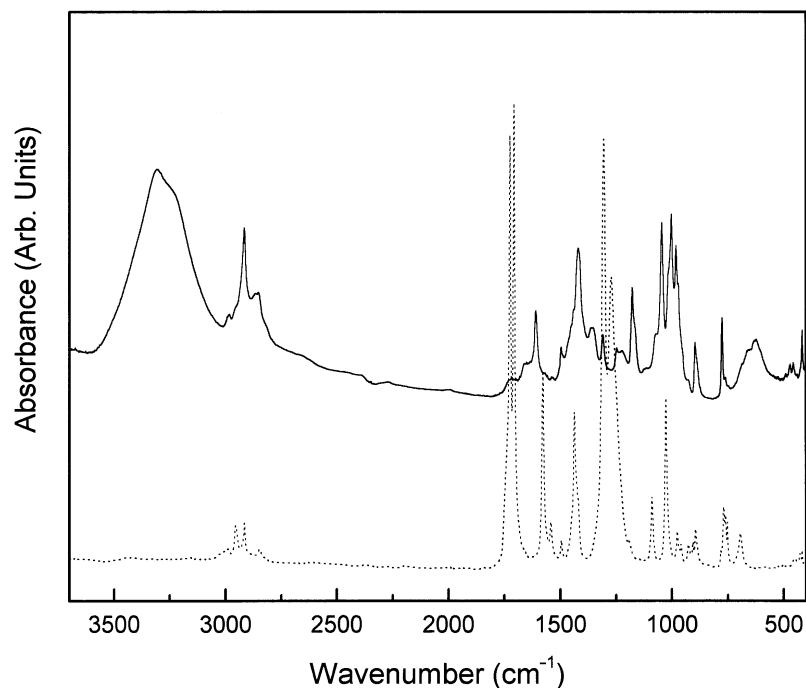
Figure 1. IR spectrum of the compound **I** in the region of its intramolecular vibrations recorded in KBr pellet, at room temperature. For comparison, the spectrum of the compound **V** is shown as a dashed line.

to the respective bands of BEDT-TTF. The large substituents in the compounds **I – IV** cause a shift of the electron density towards peripheries of the molecules and finally a weakening of the stretching vibrations of the TTF core.

An essential difference between the spectra of the above discussed compounds and compounds with methoxycarbonyl groups (**V – VIII**) resolves into a lack of an absorption centred at about $3300\ cm^{-1}$; it is shown as a dashed line in Fig. 1. Here, it is necessary to mention that a general appearance of these spectra differs from the spectra of compounds **I – IV**; nevertheless, the strongest absorption lines of **V – VIII** can be assigned to vibrations of BEDT-TTF molecule. Differences in the molecular structure of both groups of donors are responsible for observed shift of the bands assigned to corresponding vibrations and considerable changes in the band intensities.

Figure 2 gives a detailed presentation of the broad absorption between 3000 and $3600\ cm^{-1}$ in the solid compound **I**. This absorption can be decomposed into two bands, centred at $3310\ cm^{-1}$ (band $\nu_1(OH)$) and $3204\ cm^{-1}$ (band $\nu_2(OH)$). Similarly, the absorption of three remaining donors (**II – IV**) with hydroxymethyl groups can be approximated by two Lorentzian lines, which wavenumbers increase linearly with the parameter N describing the length of the alkylsulfanyl substituents. For example,
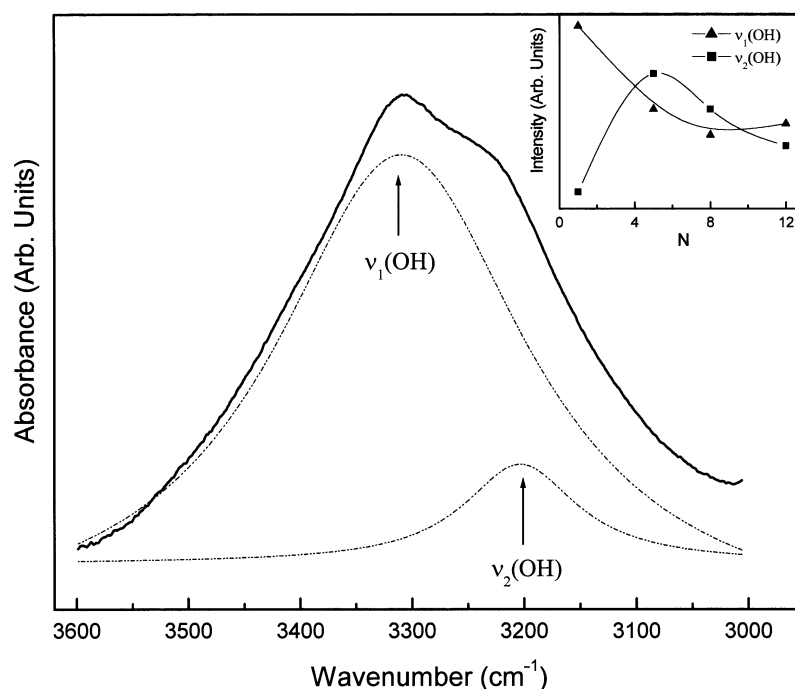
Figure 2. Broad IR absorption between 3000 and 3600 cm^{-1} in the solid compound **I** recorded in KBr pellet, at room temperature; the band decomposition is shown by dashed lines. The variation of the normalized integral intensity of the stretching vibrations of H-bonded OH groups with *N* is presented in the insert. The solid lines are a guide to the eye.

the wavenumbers of the component bands of the compound **IV** (with $N = 12$) are: 3336 and 3227 cm^{-1}, respectively. Variation of the integral intensity of these bands with *N* is shown in the insert of Fig. 2. The intensity was normalized to the same molar concentration of the compounds **I – IV**. Note a strong dominance of the band v_1(OH) (3310 cm^{-1} in the compound **I**). The intensities of both v_1(OH) and v_2(OH) components become similar with an increase of *N*.

In support of the component bands assignments we have performed IR absorption study of CS_2 solutions of the compounds **I – IV**. For some of the compounds, with suitable concentration, one can observe relatively narrow band at about 3600 cm^{-1} (band v_0(OH)) and at least two overlapping broad bands centred at about 3420 cm^{-1} (band v_1(OH)) and 3295 cm^{-1} (band v_2(OH)) (Fig. 3). These bands are red-shifted by 180 and 305 cm^{-1}, respectively in relation to v_0(OH) and these shifts are the same for compounds **I – IV**. Based on the computer decomposition of the bands, there are supplementary weak features at about 3380 and between 3450 and 3500 cm^{-1}. These bands probably reflect the appearance of OH groups involved in non-conventional, constrained hydrogen bonds [18–20]. Unfortunately, such weak features are not suitable for quantitative analysis, which could result in large errors of all the calculated band parameters. The band v_0(OH) observed in solutions is assigned to
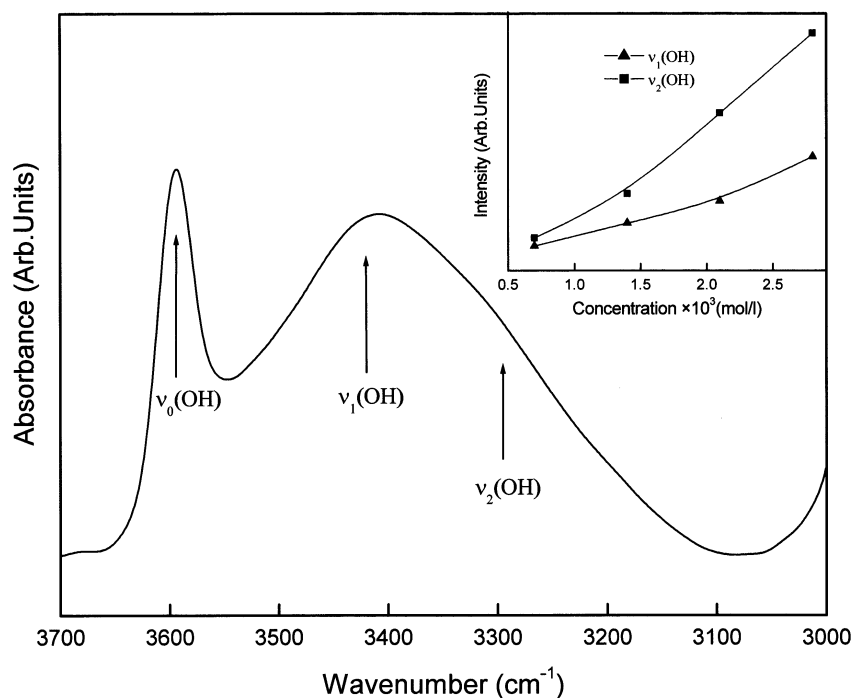
Figure 3.   IR spectrum of the compound **I** in the region of ν(OH) vibrations recorded in saturated CS_2 solution, at room temperature. In the insert, a concentration dependence of the integral intensity of the stretching vibrations of H-bonded OH groups of the compound **I**, recorded in CS_2 solution is shown. The solid lines are a guide to the eye.

stretching vibration of the free OH groups but the component bands ν_1(OH) and ν_2(OH) can be attributed to vibrations of hydrogen-bonded OH groups of the compounds containing hydroxymethyl groups. Similarly, the bands near 3200 and 3300 cm^{-1} in the solid are also assigned to H-bonded OH groups of the compounds under consideration. Their intensity changes monotonically with the solution concentration (insert in Fig. 3) testifying to an invariability of the association model in the whole concentration range. The absence of the band near 3600 cm^{-1} in the solids suggests that the compounds **I** – **IV** are completely aggregated in this phase. At present, we can conclude, that the **I** – **IV** TTF-derived donor molecules form aggregates with several types of H-bonds both in solution and in the solid. Based on the IR data itself, we are not able to suggest a molecular structure of these aggregates.

For the detailed assignment of the component bands, we take into account that the decrease in OH-group valence frequency is the larger the more considerable is the weakening of the OH-bond. The formation of the hydrogen bridge weakens these bonds obviously more considerably in the case of proton-donor groups than in that of proton-acceptor ones [18–20]. Thus we suggest that the band ν_1(OH) could be assigned to stretching vibration of proton-donor group, whereas the band ν_2(OH) – to proton-acceptor one.

For the better understanding of the processes of aggregation in the set of donor molecules containing OH groups, we have performed molecular modelling of the studied molecules using molecular mechanics method supplied with the HyperChem package. The calculations show that the molecules with two hydroxylic groups (the simplest one is compound **I**) can create intramolecular and intermolecular hydrogen bonds (OH$\cdots$OH). A great variety of multimers (dimers, trimers *etc*.) are created with many hydrogen bonds in each formed entities (up to three hydrogen bonds per molecule) some of them are shown in Fig. 4. The intermolecular hydrogen bonds energy corresponding to one molecule is in the range between -1.4 and -1.6 kcal/mol. The intramolecular hydrogen bonds have a similar energy values. The modelling performed for the compounds, where the hydroxymethyl groups are substituted by the methoxycarbonyl groups (compounds **V** – **VIII**) or by protons, have been also performed for comparison. These evaluations agree with our observation from the IR investigation.

The modelling was also performed for adduct **IX**, where the donor **I** was linked to C_{60} molecule (Fig. 5). The calculations show that a long and flat substituent derived from the donor **I** is not linked to the spherical fullerene molecule radially but forms an obtuse angle. On the other hand, an orientation of the adduct molecules in the solid is random.
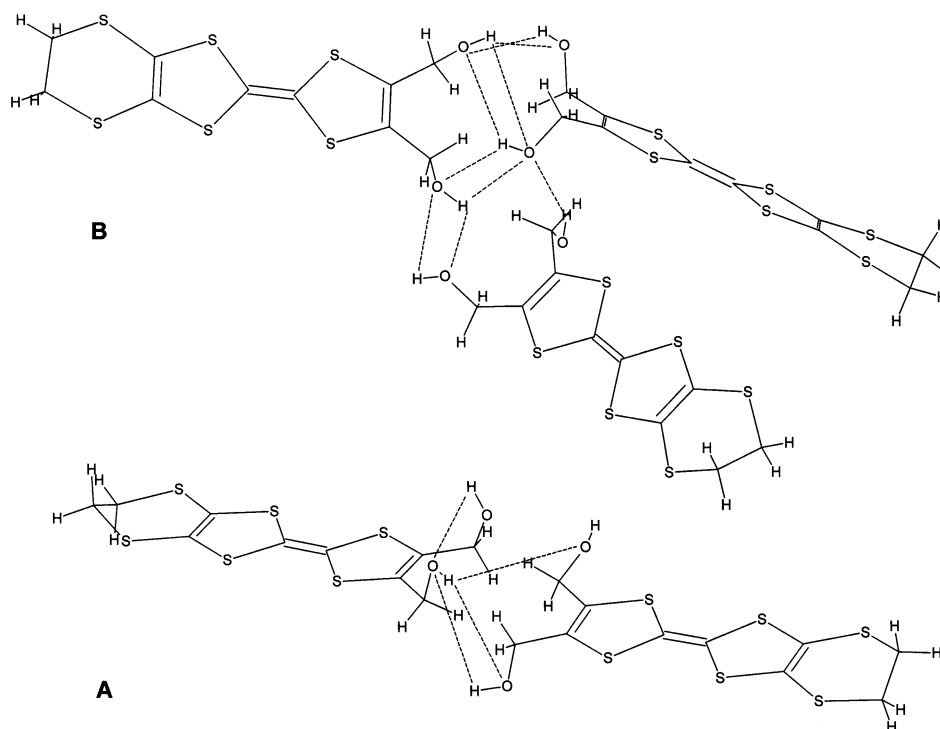

Figure 4. Modelling of possible multimers (dimers, A and trimers, B) of TTF-derived donor **I** bonded with intra- and/or intermolecular hydrogen bonds.
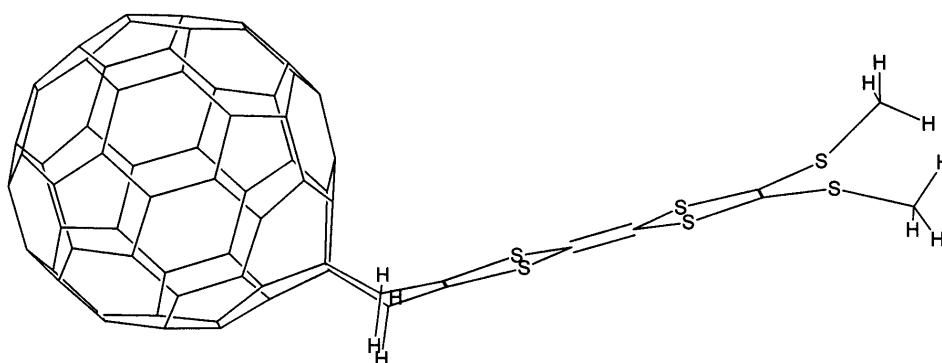
Figure 5. Modelling of the adduct **IX**, where the donor **I** is linked to C_{60} molecule.

Raman scattering studies of all TTF-derived donors and their adducts to C_{60} were also performed. Typical spectra of both TTF-derived donors with hydroxymethyl (**I – IV**) and methoxycarbonyl (**V – VIII**) groups are shown in Fig. 6. An appearance of the both types is completely different. The spectra of the TTF-derived donors with hydroxymethyl groups (**I** in Fig. 6) show strong scattering of the light with wavenumbers below 3000 cm^{-1}, which is rather frequency independent between 500 and 1500 cm^{-1}. For higher wavenumbers several very broad and weak maxima appear. The maxima may be related to the after-effects of the huge background scattering. The Raman spectra of donors with methoxycarbonyl groups (**V** in Fig. 6) are completely different. They show distinct structure with numerous narrow lines, which could be assigned to normal Raman-active vibrations of the molecules **V – VIII**. For example, the lines between 2800 and 3000 cm^{-1} are attributed to vibrations of the CH bonds probably coupled to the C–C vibrations of TTF frame, the line at about 1740 cm^{-1} – to the CO stretching, the lines between 1500 and 1640 cm^{-1} – to the C=C vibrations of the TTF skeleton and the lines between 670 and 700 cm^{-1} – to the S-CH$_3$ vibrations.

Raman spectra of various polyadducts of TTF-derived donors **I – VIII** linked to C_{60} are nearly the same for all studied adducts. Typical Raman spectrum for this group of materials is shown also in Fig. 6, where that of adduct **IX** is presented. These spectra strongly resemble that of the TTF-derived donors with hydroxymethyl groups (**I** in Fig. 6). The spectrum of the adduct shows strong scattering of the light with wavenumbers below 3200 cm^{-1}, which is nearly frequency independent between 1000 and nearly 3000 cm^{-1}; in addition, several broad but weak maxima are observed in this region. These maxima perfectly correspond to those mentioned above, and observed for TTF-derived donors with hydroxymethyl groups.
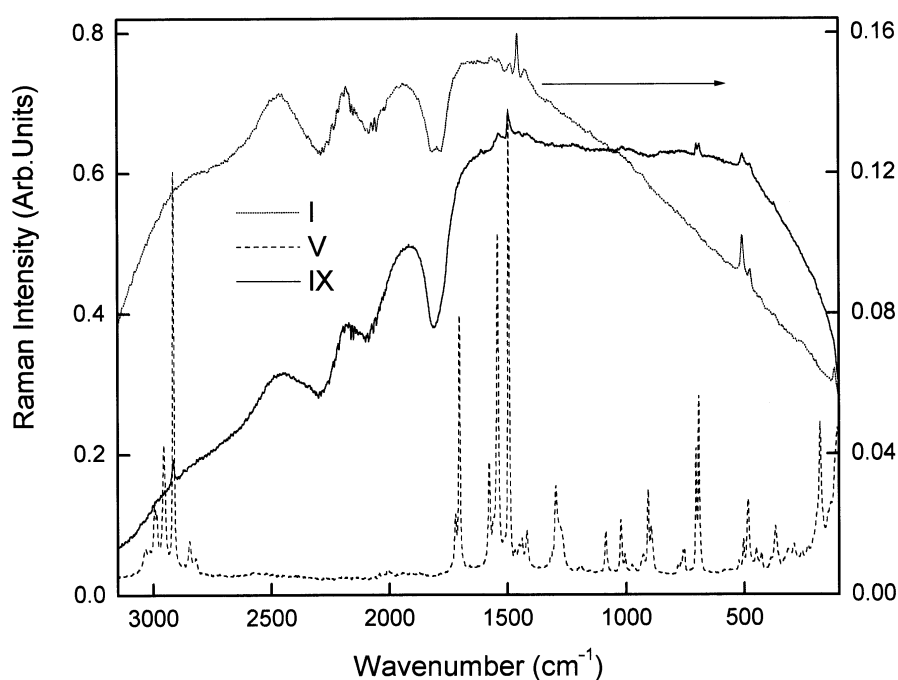
Figure 6. Raman spectra of the donors **I** and **V** and adduct **IX** recorded in KBr pellets, at room temperature.

At present, it is impossible to give an explanation of differences between Raman spectra of compounds **I** – **IV** and that of **V** – **VIII** as well as of similarities between **I** – **IV** and **IX** – **XI**. It seems that in spite of the spectral similarities, the origin of broad and strong light scattering in the last-mentioned groups of compounds is rather different. The donors **I** – **IV** form various H-bonded multimers, the material is heterogeneous and shows grainy structure. These species are able to scatter the light and as a result a broad band of background appears in the Raman spectra. The donors **V** – **VIII** do not show aggregation and are randomly distributed in the solid. Thus the sample is homogeneous in the light wavelength scale and a normal Raman scattering on the intramolecular vibrations occurs. The formation of C_{60} adducts, *e.g.* **IX** – **XI** causes a charge transfer from the donor moiety to the acceptor one. It leads to delocalization of the electrons, in particular on the C_{60} sphere. These delocalized charges can probably scatter the light similarly as free electrons in conductors.

In conclusion, for the first time we have performed the spectral (IR and Raman) studies of two groups of TTF-derived donors and the systems having C_{60} linked to them. Based on the analysis of the stretching vibration range of free and H-bonded OH groups it was shown that the TTF-derived donors containing hydroxymethyl groups are associated both in solid and in solutions. The aggregates of various forms

and dimensions have been detected by IR spectroscopy as well as by molecular modelling using molecular mechanics method. On the other side, the donors with methoxycarbonyl groups do not form aggregates. A modelling of C_{60} adducts with TTFs revealed their reciprocal spatial orientations.

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