Spectra of optical phonons and low-energy electronic transitions in C_{60}/TMPD and C_{60}/TPA single crystals

A. V. Bazhenov,[a] M. Yu. Maksimuk,[a] T. N. Fursova,[a] A. P. Moravsky,[b] and V. A. Nadtochenko[b]*

[a]Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation
[b]Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 (096) 515 3588

Single crystals of C_{60}/TMPD and C_{60}/TPA have been grown from a chlorobenzene solution. Optical transmission spectra of single crystals of fullerene complexes with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and triphenylamine (TPA) are studied in the spectral range from 600 to 16000 cm^{-1}. Splitting of the intramolecular vibration of C_{60} is observed at 1428 cm^{-1}, which is likely caused by freezing of the rotation of the C_{60} molecules due to their interaction with amines. Single crystals of C_{60}/TMPD differ from those of C_{60}/TPA by a decrease in the vibration frequency at 1428 cm^{-1}, vibrations of the C—C bonds of the TMPD molecule, and the redistribution of the forces of the oscillators of the vibrations of the C—N bonds. These peculiarities are interpreted to be the result of partial electron transfer from TMPD to C_{60} in the C_{60}/TMPD single crystals. The electron transfer in the C_{60}/TPA system is less pronounced.

Key words: fullerene C_{60}, single crystals, fullerene complexes; electron transfer, optical transmission spectra, electronic transitions, charge-transfer complexes.

A molecule of C_{60} possesses electron-accepting properties,[1,2] which determines its ability to form donor-acceptor complexes with donors[3] and act as an electron acceptor in dark and photochemical redox processes.[4—7] The chemical and photochemical redox properties of C_{60} in solutions have been studied rather completely. The photoexcited states of charge-transfer complexes (CTC) are radical ion pairs in which the rate of charge recombination depends on the value of the free energy of charge recombination in the pair and on the physicochemical properties of the solvent.[7] In the case of intermolecular electron transfer, free radical ions are formed between the photoexcited triplet C_{60} molecule and electron donors in solutions.[4—6] The properties of CTC between C_{60} and ternary amines in crystals have been poorly studied. However, it is known that ternary amines with low oxidation potentials form radical ion salts with C_{60} and exhibit ferromagnetic properties, as shown in the case of tetrakisdiethylamine.[8] In the present work, we report on the preparation of single crystals of C_{60} with two ternary amines, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and triphenylamine (TPA), whose oxidation potentials differ substantially and are equal to 0.12 eV for TMPD and 1.12 eV for TPA relative to SCE.[9]

Experimental

Single crystals were obtained from a solution of C_{60} in chlorobenzene with the corresponding amine by slow evaporation of the solvent. In the initial solutions, the concentrations of fullerene and amine were 0.001 mol L^{-1} and 1 mol L^{-1}, respectively. Crystals of complexes were washed from residues of the amine with acetone. Crystals C_{60} (C_{60}/CB) were also obtained from chlorobenzene (CB) without amine additives for comparison. Single crystals C_{60}/TMPD, C_{60}/TPA, and C_{60}/CB with sizes up to 0.5×0.5×0.5 mm^3 were used for analysis. Amines were purified by sublimation and recrystallization, and solvents were purified by the standard procedures.[10] No decomposition of the crystals was observed when they were kept in air at room temperature.

Optical transmission spectra were recorded at room temperature on an IR microscope of a Fourier spectrometer in the range from 600 to 9500 cm^{-1}. Spectra in the range from 10500 to 16000 cm^{-1} were recorded by a prism low-resolution spectrograph equipped with a microscope. Spectra of optical phonons in the range from 600 to 4500 cm^{-1} were recorded with a resolution of 0.3 cm^{-1}.

Results and Discussion

IR spectra of chlorobenzene, TPA, and TMPD in C_{60}/CB, C_{60}/TPA, and C_{60}/TMPD crystals. All three types of single crystals were grown from solutions in chlorobenzene. Therefore, it seemed important to recognize whether chlorobenzene is present in them as an admixture. The line at ~700 cm^{-1} caused by the vibrations of the C—Cl bond is present in the spectra of the optical density of chlorobenzene and of the C_{60}/CB single crystal (Fig. 1, *a*). According to the data obtained previously,[11] the line at 702 cm^{-1} corresponds to this vibration. However, it cannot be excluded that the line

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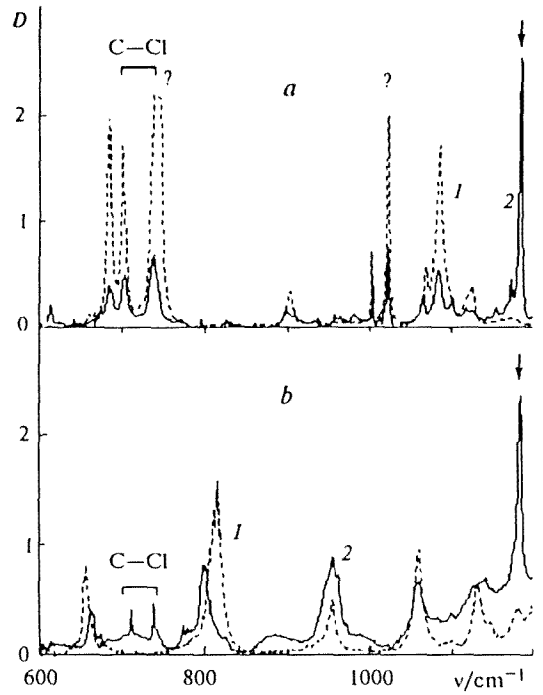

Fig. 1. Spectra of optical density including stretching vibrations of the C—Cl bond (~700 cm^{-1}) of chlorobenzene molecules: *a*, chlorobenzene (*1*) and C_{60}/CB single crystal (*2*); *b*, TMPD (*1*) and the C_{60}/TMPD single crystal (*2*). Spectra of C_{60}/CB and C_{60}/TMPD crystals are reduced to equal values of the integral of the absorption line of C_{60} at 1183 cm^{-1} (indicated by arrow). T = 300 K. In all figures, the sign "?" indicates lines with strong absorption, whose forms were not recorded correctly.

at 737 cm^{-1}, which was not mentioned in Ref. 11, is also assigned to the vibrations of the C—Cl bond. This line is absent in the spectra of TMPD and TPA. Taking into account the widths of the C_{60}/CB single crystals used and of a droplet of chlorobenzene, the approximate ratio of chlorobenzene and C_{60} in the crystal can be estimated as 1 : 20.

No lines corresponding to stretching vibrations of the C—Cl bond (702 or 737 cm^{-1}) are observed in the transmission spectrum of TMPD (see Fig. 1, *b*, spectrum *1*). However, the similar lines at 711 and 739 cm^{-1} are present in the spectrum of the C_{60}/TMPD single crystal (see Fig. 1, *b*, spectrum *2*). If it is assumed that they are caused by chlorobenzene, it follows from the comparison of the integral intensities of these lines in the spectra of C_{60}/CB and C_{60}/TMPD that the concentration of chlorobenzene in C_{60}/TMPD is at least sixfold lower than that in C_{60}/CB. Thus, the content of the chlorobenzene admixture in the C_{60}/TMPD single crystal is lower than 1 molecule per 100 molecules of C_{60}. The analogous conclusion can be drawn for the C_{60}/TPA crystals.

The spectra of all crystals studied contain characteristic pairs of lines at ~1500 cm^{-1} (Fig. 2), which are also observed in the spectra of chlorobenzene, TPA, and

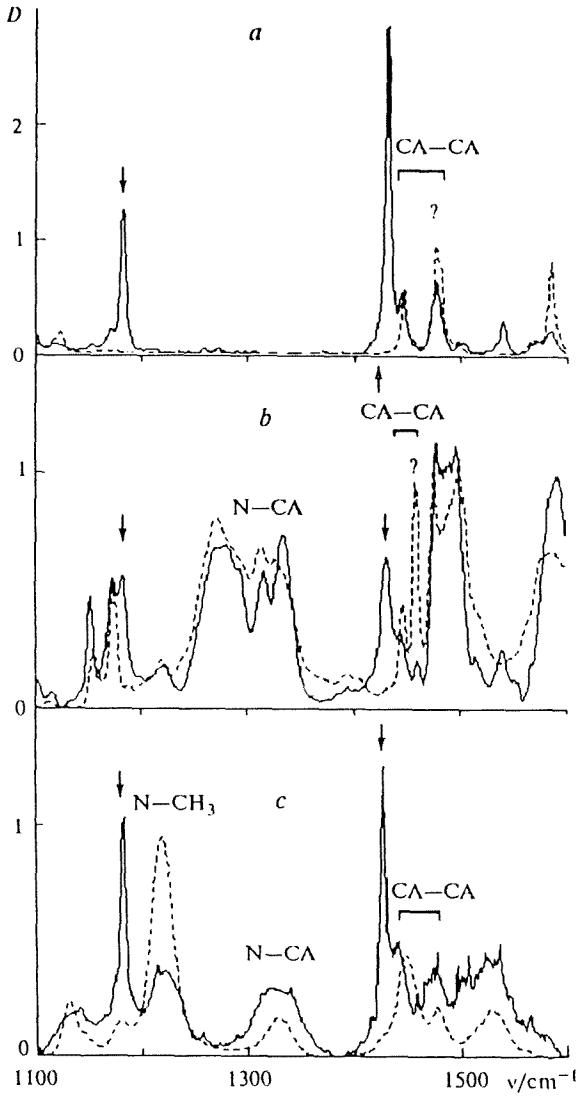

Fig. 2. Spectra of optical density of the C_{60}/CB (*a*), C_{60}/TPA (*b*), and C_{60} TMPD (*c*) single crystals (solid lines) in the spectral range including intramolecular vibrations of C_{60} at 1183 and 1428 cm^{-1} (indicated by arrows) and stretching vibrations of the C—C bonds of the benzene ring at ~1500 cm^{-1}. Dotted lines show spectra of CB, TPA, and TMPD, respectively. Spectra of TPA and TMPD are normalized in such a way that the maximum number of their lines coincides in intensity with their analogs in crystals. T = 300 K.

TMPD (dotted lines). They are caused by stretching vibrations of the C—C bonds of the benzene ring[11] and are slightly different in the spectra of C_{60}/CB and C_{60}/TPA crystals from those in the spectra of free chlorobenzene and TPA (see Fig. 2, *a*, *b*). However, in the case of C_{60}/TMPD (see Fig. 2, *c*), the line of TMPD at 1450 cm^{-1} is considerably shifted to the low-energy region to 1439 cm^{-1}, while the line of TMPD at 1476 cm^{-1} is broadened toward the long-wave region with the mass center at 1472 cm^{-1}.

The vibrational modes of ~1300 cm^{-1} of TPA molecules (see Fig. 2, *b*) and of 1330 cm^{-1} of TMPD molecules (see Fig. 2, *c*) are caused by stretching vibrations of the C—N bonds (see Ref. 12). In the spectrum of TMPD, the line at 1330 cm^{-1} likely corresponds to the vibration of the N—Ph bond, while the low-frequency mode at 1220 cm^{-1} is determined by the vibration of the longer N—CH_3 bond. In the C_{60}/TPA crystals, the parameters of the vibrational modes are close to those of free TPA. In C_{60}/TMPD, the absorption line of the 1330 cm^{-1} mode is broader than that of TMPD, and, which is more significant, considerable redistribution of the intensities of the lines determined by the vibrations of the C—N bonds is observed. The intensity of the line caused by the N—Ph bond is considerably higher in crystals, while its width is greater, and the line determined by the vibration of the N—CH_3 bonds is less intense.

Thus, in the C_{60}/CB and C_{60}/TPA single crystals, the structure of the CB and TPA molecules is slightly different than in the free states. In contrast, in the C_{60}/TMPD single crystals, the intermolecular interaction of C_{60} with TMPD results in substantial perturbation of the donor structure, which is manifested in a noticeable change in the vibrations of the C—N and C—C bonds of the TMPD molecules.

Phonon and electronic spectra of C_{60} in C_{60}/CB, C_{60}/TPA, and C_{60}/TMPD crystals. A comparison of the spectra of the crystals in the vicinity of the intramolecular vibrations of C_{60} at 1183 and 1428 cm^{-1} with the spectra of pure films of C_{60} (Fig. 3) shows that the frequency of the 1183 cm^{-1} mode is almost the same as that in pure fullerite and is only slightly broadened. The half-width of the transmission line for pure C_{60} is 4 cm^{-1} and is 5 cm^{-1} in single crystals. The line at 1170 cm^{-1} in spectrum *3* is caused by the vibration of TPA. More complicated peculiarities are observed in the structure of the line at 1428 cm^{-1}. Its splitting in the C_{60}/TPA single crystal is pronounced for the line with frequencies at 1428 and 1433 cm^{-1}, and there is a weakly resolved shoulder at 1425 cm^{-1} (see Fig. 3, spectrum *3*). An example of the splitting of this line into components in the approximation of Lorentz oscillators is also presented in Fig. 3.

In the C_{60}/CB single crystal (see Fig. 3, spectrum *1*), the line at 1428 cm^{-1} has the same energy position as that in C_{60}/TPA. A similar shoulder is observed at 1425 cm^{-1}, but no splitting is observed, probably because the transmission drops almost to zero at ~1430 cm^{-1} in the C_{60}/CB single crystals.

Unlike the spectra of C_{60}/CB and C_{60}/TPA crystals, the intramolecular 1428 cm^{-1} mode in the C_{60}/TMPD single crystal is shifted toward low energies relative to the spectrum of pure C_{60}. This mode is split into three vibrations with frequencies of 1422, 1425, and 1427 cm^{-1} (see Fig. 3, spectrum *2*), which cannot be explained by the peculiarities of the spectra of TPA, TMPD, and CB, which exhibit no lines in this region.

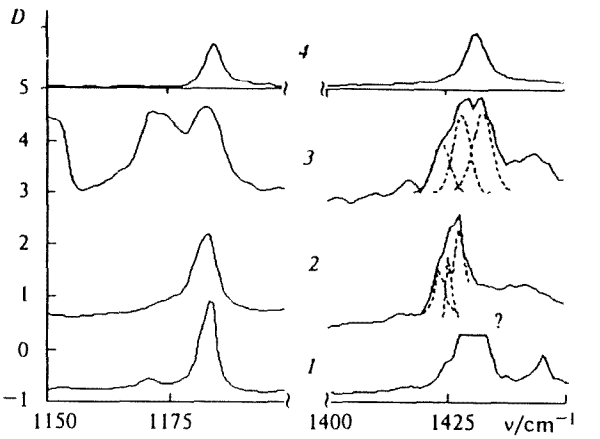

Fig. 3. Spectra of optical density of the C_{60}/CB (*1*), C_{60}/TMPD (*2*), and C_{60}/TPA (*3*) crystals in the range of intramolecular vibrations of C_{60} at 1183 and 1428 cm^{-1}; *4*, spectrum of the pure C_{60} film (sapphire substrate) obtained by vacuum sublimation. Dotted lines show the splitting of the mode of C_{60} (1428 cm^{-1}) in these crystals into components in the approximation of Lorentz oscillators. T = 300 K.

In addition, in the spectral range of electronic transitions for C_{60}/TMPD, unlike for the two other crystals, absorption of 1.2 eV with a weakly pronounced singularity near 0.9 eV is observed. In the C_{60}/TPA crystals, the absorption edge is blurred toward the long-wave region, unlike the spectrum of C_{60}/CB.

It is known that in pure fullerite the 1428 cm^{-1} mode is triply degenerate.[13] If TPA and TMPD molecules are arranged randomly in the crystal, a heterogeneous broadening of this line or its asymmetric structureless shape would be expected. Therefore, the observed splitting of this line into three components in the C_{60}/TPA and C_{60}/TMPD single crystals can be related to the presence of C_{60} complexes with amine, along with the C_{60}/CB, and C_{60} molecules, in the crystal. However, this explanation seems improbable for the following reasons. First, the X-ray diffraction measurements show that the C_{60}/TPA and C_{60}/TMPD single crystals have hexagonal and tetragonal symmetry, respectively, with no admixture of the cubic symmetry typical of pure fullerite.[14] Second, the composition of 1 : 1 has been established for the C_{60}/TMPD crystals.[14] For the C_{60}/TPA crystals, analysis of the optical absorption spectra of C_{60}/TPA crystals dissolved in toluene gives the ratio between C_{60} and TPA as 1 : 1. Finally, the content of chlorobenzene in the crystals is estimated as CB : C_{60} < 1 : 100 in this work. At the same time, the intensities of the three components of the split mode of 1428 cm^{-1} are close, as seen from spectra *2* and *3* in Fig. 3.

Another possible reason for the splitting of the band at 1428 cm^{-1} is a lower symmetry of the Bravais lattice of the C_{60}/TPA and C_{60}/TMPD single crystals. However, in the case of hexagonal and tetragonal symmetry, the C_{60} mode (1428 cm^{-1}) can be split into only two

lines. In addition, in this case, the splitting of the C_{60} mode (1183 cm^{-1}) with the same symmetry in fullerite as the 1428 cm^{-1} mode can be expected. This is not observed in the experiment. Thus, the symmetry of the Bravais lattice of the crystal plays a secondary role in our case.

A more probable explanation for the nature of the splitting of the C_{60} mode (1428 cm^{-1}) with retention of the structure of the 1183 cm^{-1} mode is the partial freezing of the rotation of the C_{60} molecules in the crystals studied at T = 300 K, which is similar to the known orientation phase transition in fullerite at T = 250 K. A study of the temperature dependence of the spectra of intramolecular vibrations of fullerite made it possible to establish[13] that at T < 250 K the 1428 cm^{-1} mode is split into three lines, whose structures are similar to those of the lines observed previously. The 1183 cm^{-1} mode remains unsplit to T = 10 K. This effect was explained by the change in the local crystal field that acts upon these two modes in different ways. In pure C_{60}, the almost free rotation of molecules at high temperatures changes their mutual orientation like this when the electron-rich bond between two hexagons (6—6 bond) of one molecule is turned to the electron-depleted pentagon of the adjacent molecule. In the author's opinion,[13] this change in the local crystal field is sufficient for the splitting of the 1428 cm^{-1} mode determined by the change in the length of the 6—6 bond while the distance to the pentagon of the adjacent molecule remains fixed. The parameters of the vibration at 1183 cm^{-1}, which is determined by the tangential movement of the 6—6 bond of unchanged length relative to the pentagon, change slightly.

In our case, freezing the rotation of C_{60} molecules is the result of their interaction with amines and leads to a lower degree of symmetry of the C_{60} molecules than of pure fullerite at T > 250 K.

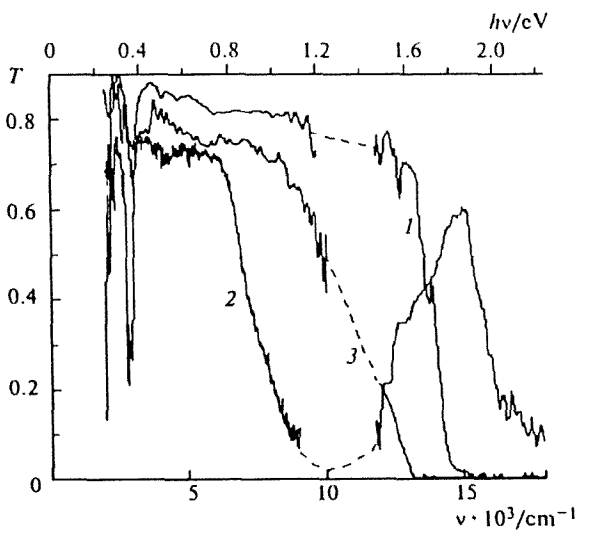

Fig. 4. Transmission spectra of the C_{60}/CB (*1*), C_{60}/TMPD (*2*), and C_{60}/TPA (*3*) single crystals including regions of electronic transitions. T = 300 K.

A specific feature of C_{60}/TMPD single crystals is the existence of electronic transitions with energy from 0.8 to 1.8 eV, which has also been observed in the spectrum of C_{60} doped with alkaline metals.[15,16] However, we believe that the main portion of this absorption is determined by the charge-transfer band from TMPD to C_{60} (in solution ~1.7 eV).[7] Hence, the fact that the low-energy absorption edge in the C_{60}/TPA single crystals is more blurred than that in the spectrum of C_{60}/CB is likely due to the long-wave wing of the charge-transfer band from TPA to C_{60}, which corresponds to the absorption line of ~2.2 eV in solution.[7] It is likely that the weakly pronounced singularity near 0.9 eV in the transmission spectrum of the C_{60}/TMPD single crystal is the transition between the excited states of the charged C_{60} molecules observed previously.[17]

According to the Malliken theory of a donor-acceptor bond, the wave function of the donor-acceptor complexes of C_{60} with amines can be presented as

$$\psi_0 = \psi_{C_{60}/Am} + \lambda\psi_{C_{60}^-/Am^+} \quad (1)$$

$$\psi_1 = \lambda\psi_{C_{60}/Am} - \psi_{C_{60}^-/Am^+},$$

where ψ_0 and ψ_1 are the wave functions of the ground state and the charge-transfer state of the donor-acceptor complex, and

$$\lambda \approx V/\Delta G, \quad (2)$$

where V is the integral of the interelectronic interaction between the $\psi_{C_{60}^-/Am^+}$ and $\psi_{C_{60}/Am}$ states, ΔG is the value of the energy gap between $\psi_{C_{60}^-/Am^+}$ and $\psi_{C_{60}/Am}$. The formation of a weak charge-transfer complex is assumed: $\lambda \ll 1$, $V \ll \Delta G$.[18]

In a solution of chlorobenzene, the ΔG value can be estimated from the values of the redox potentials $E_{1/2}(C_{60}^-/C_{60})$ and $E_{1/2}(Am/Am^+)$ according to the expression

$$\Delta G = |E_{1/2}(C_{60}^-/C_{60}) - E_{1/2}(Am/Am^+) - \Delta|,$$

$$\Delta = 0.38 - 0.75[2(\varepsilon_s - 1)/(2\varepsilon_s + 1) - (\varepsilon_0 - 1)/(2\varepsilon_0 + 1)] \text{ (eV)},$$

where Δ is the correction caused by the Coulomb interaction in the C_{60}^-/Am^+ radical ion pair in the given solvent. In the case of chlorobenzene, the Δ value is close to 0.1 eV.[7] The values of ΔG thus estimated for the systems with TMPD and TPA in clorobenzene are 0.73 and 1.73 eV, respectively.[7] Thus, the dark electron transfer in solution to form free radical ions C_{60}^- and Am^+ is thermodynamically impossible. The estimation of the value of V obtained on the basis of the measurement of the oscillator force of the charge-transfer band shows that V ranges from 500 to 1000 cm^{-1}.[7] According to Eqs. (1) and (2), the value of the charge transferred to C_{60} should be $(V/\Delta G)^2$ charge units.

The energy gap can decrease substantially in a crystal. For example, it is known that the lowest electronic

transition allowed in the dipole approximation has an energy of 3.75 eV for C_{60} in benzene.[19] In the crystal, the maximum of this absorption lies at 3.5 eV, and the red boundary is near 3.0 eV.[20] In this case, the crystal shift of the transition corresponding to the transfer of an electron from TMPD to C_{60} is ~0.5 eV. At room temperature, this shift is insufficient for the thermal excitation of an electron from TPA to C_{60} in the C_{60}/TPA crystal. However, in C_{60}/TMPD, ΔG can be ~0.2 eV. Therefore, in addition to the transfer mechanism considered in the Malliken theory, the thermal excitation of an electron from TMPD to C_{60} is also possible.

The value of the charge transferred from TMPD to C_{60} can be estimated from the empirical correlation dependence between the spectral shift of the intramolecular vibration at 1428 cm^{-1} and the charge transferred from a donor. It is known that the transition to fulleride caused by doping of fullerite with alkaline metals is accompanied by a decrease in the frequency of a given mode by a value close to 20 cm^{-1} per electron transferred to C_{60}.[21] In our case, this mode weakens by at least 1 cm^{-1} in the C_{60}/TMPD crystal. Using the dependence,[21] we find that at room temperature not less than 0.05 electrons are transferred per C_{60} molecule. Of course, this value is a rough estimation, because it does not take into account the difference in crystalline structures of C_{60}/TMPD and fullerite doped with alkaline metals. The value of the transferred charge in the C_{60}/TMPD crystal is higher than the estimation for the same complex in solution, where $(V/\Delta G)^2$ is 0.008 to 0.02 electrons per C_{60} molecule. It is likely that the weakly pronounced charge transfer in the C_{60}/TPA system is caused first of all by a greater energy gap ΔG than that in TMPD. The charge transfer from TMPD to C_{60} results in the distortion of the bonds in TMPD and the corresponding changes in the vibrational frequencies of TMPD in the C_{60}/TMPD crystal.

It is also noteworthy that a smooth shift of the 1428 cm^{-1} mode toward low energies is not observed when C_{60} is doped with alkaline metals. When the metal concentration in fullerite increases, the line of the 1428 cm^{-1} mode decreases in intensity, but does not change its spectral position, and the intensity of the 1360 cm^{-1} mode corresponding to the K_3C_{60} phase, or the 1408 cm^{-1} mode of the RbC_{60} phase increases.[21] This is the result of the known phase stratification of doped C_{60}. No phase stratification was observed in C_{60}/TMPD crystals.

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