

## C<sub>60</sub> and C<sub>70</sub> Solvates Studied by Raman Spectroscopy

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The formation and phase transformations of C<sub>60</sub> and C<sub>70</sub> solvates with benzene, toluene, and *n*-hexane have been studied in-solution by Raman spectroscopy for the first time. It was found that C<sub>60</sub> and C<sub>70</sub> solvates exhibit Raman spectra which are quite distinct from pure fullerenes and very similar to spectra from fullerene-sulfur compounds. Two different solvates are found for the C<sub>60</sub>–toluene system in good agreement with recent DSC studies. Upon heating, all three solvates decompose to pure fcc C<sub>60</sub> and all new peaks and shifts of peaks typical for the solvates disappear. No changes on Raman spectra of C<sub>60</sub> and C<sub>70</sub> solvates were found upon cooling to 78 K with the exception of the C<sub>70</sub>–benzene solvate which showed a broad phase transition around 263 K. Some possible explanations for the changes in Raman spectra are discussed.

### 1. Introduction

It is known that C<sub>60</sub> forms solvates with a number of different organic solvents.<sup>1</sup> Many of these solvates are unstable at room temperature and lose solvent very rapidly immediately after taking them out of solution. Nevertheless structures of many C<sub>60</sub> solvates have been successfully solved at low temperatures. These studies show that each of the solvents produces its own kind of phase with weak van der Waals bonding and different symmetries ranging from triclinic to cubic. A review on known structures of C<sub>60</sub> solvates has been given by Ceolin et al.<sup>1</sup>

An interesting property of the solvates was discovered by studying the temperature dependence of the C<sub>60</sub> solubility. Ruoff et al.<sup>2</sup> reported that this temperature dependence has a maximum near room temperature for several solvents. Smith et al.<sup>3</sup> showed that this anomalous behavior of the solubility can be explained thermodynamically. According to their model, two phases can exist in equilibrium with solution; one of them with a positive enthalpy of dissolution, another with a negative. These phases can be either both solvated with different amounts of solvent, or one of them can be pure C<sub>60</sub>. Usually at low temperature the solvate is stable in the solution but at some temperature a phase transition between the two phases occurs. The solvated crystal melts and another phase forms such as pure C<sub>60</sub> or C<sub>60</sub> with a smaller amount of solvent. This phase transition gives a change in the slope of the temperature dependence of solubility. Differential scanning calorimetric experiments made for a number of solvents<sup>4–6</sup> showed that such transitions can be seen as a maximum in the temperature dependence of the heat capacity. This model is confirmed by the results of direct observations of the phase transition C<sub>60</sub>–C<sub>60</sub>•4C<sub>6</sub>H<sub>6</sub> in benzene.<sup>7</sup> The C<sub>60</sub>•4C<sub>6</sub>H<sub>6</sub> solvate is stable in equilibrium with a saturated solution at temperatures below 313 K while the pure C<sub>60</sub> fcc phase is stable above this temperature. Crystals of the benzene solvate can be easily obtained from C<sub>60</sub> powder by spontaneous recrystallization of a C<sub>60</sub> powder in equilibrium with a solution cooled to 278–280 K. These crystals remain stable upon heating to 313 K where a phase transition to pure fcc C<sub>60</sub> occurs. The phase transition has been observed by optical microscopy and X-ray powder diffraction.<sup>7</sup>

Despite the fact that many of the solvates were synthesized a relatively long time ago, many of their properties, especially

near room temperature, have yet to be investigated. For example, IR and Raman spectroscopy studies of C<sub>60</sub>–benzene, C<sub>60</sub>–toluene, and some other solvates have been performed out of solution.<sup>8,9</sup> These data, however, probably do not originate from solvates because a significant degradation of the C<sub>60</sub>•4C<sub>6</sub>H<sub>6</sub> structure occurs within a few minutes of taking the samples out of solution.<sup>7</sup> This shows that experiments at room temperature can only be performed on samples which are covered with solution. This technique was used by He et al.<sup>10</sup> for their NMR studies of the C<sub>60</sub>–benzene solvate which confirmed the weak van der Waals nature of bonding in this compound. Also they addressed the question of a possible difference between structures of C<sub>60</sub>–benzene determined at low temperature and room temperature. The optical activity of the room-temperature solvate described by He et al.<sup>10</sup> is not compatible with a centrosymmetric low-temperature structure of C<sub>60</sub>•4C<sub>6</sub>H<sub>6</sub>. This may be investigated more generally since most of the solvate structures were determined at low temperatures and some phase transitions may exist below room temperature and below the freezing point of the solvent. Unfortunately, calorimetry data reported by several groups describe only a temperature range where the solvents exist as liquids.

Even less information is now available for the C<sub>70</sub> phases and solvates formed by crystallization from different solutions. The first remarkable difference from the C<sub>60</sub> solvates is the absence of maxima in the solubility curves of C<sub>70</sub> for studied solvents.<sup>11</sup> The second important difference is the stability of C<sub>70</sub> solvates out of solution. The C<sub>70</sub>–toluene solvate was first described by Agafonov et al.<sup>12</sup> and studied later by Takahashi<sup>13</sup> with high-resolution transmission electron microscopy and found to exhibit a orthorhombic structure with the *Amm*2 space group. Our experiments made by X-ray powder diffraction on in-solution samples showed the existence of very similar structures for benzene and hexane solvates. Large crystals of benzene solvate also were found to be stable in air for several months and decomposed only after heating to 420 K.<sup>14</sup> The dielectric properties of these crystals were studied by Sherman et al.<sup>15</sup> and showed two anomalies which suggest phase transitions at 150 K and 275 K.

It is clear that a variety of interesting phenomena such as phase transitions of C<sub>60</sub> and C<sub>70</sub> in solution and below the

freezing points of the solvents require more detailed study. In this paper we use Raman spectroscopy for studying in-solution solvates of C<sub>60</sub> and C<sub>70</sub> with benzene, toluene, and hexane. One of the main advantages with this method is a very small illumination area. Unlike calorimetry and X-ray powder diffraction which give an average information over many crystals (so far calorimetry experiments have been performed only for powder due to problems with the growth of large crystals), we are able to focus the laser beam on individual small crystals and record Raman spectra for crystals with visual differences in morphology. This may be very useful, for example, when studying the C<sub>60</sub>–toluene system where probably two different solvates exist at the same temperature.<sup>16</sup> Also in this study, Raman data obtained from the solvates are compared with spectra from sulfur-fullerenes reported by us recently<sup>17</sup> since both of these groups of compounds have a similar kind of weak van der Waals bonding. It was also found that a weak van der Waals bonding between the crown-shaped S<sub>8</sub> rings and C<sub>60</sub> or C<sub>70</sub> molecules produce certain changes in the Raman spectra of the fullerenes and it is possible that similar effects may exist in other groups of van der Waals fullerene solids. If this is true Raman spectroscopy may be a very efficient tool for studying phase transitions in many fullerene–solvent systems.

## 2. Experimental

Fullerenes from MER corporation (C<sub>60</sub>-99.9%, C<sub>70</sub>-99%) and 99.9% pure benzene, toluene, and *n*-hexane were used. Samples were prepared for direct microscopy observations and Raman spectroscopy by placing C<sub>60</sub> or C<sub>70</sub> powder between two thin glasses in a drop of solution. To prevent evaporation of the solvent the glasses were glued together by silicate glue.

C<sub>60</sub> solvates can only be formed in a certain temperature interval since a phase transition from solvate to a pure C<sub>60</sub> phase occurs at some temperature. The benzene system was studied in a previous publication and this phase transition was observed at 313 K.<sup>7</sup> Benzene–solvate crystals can be easily obtained by cooling the sample 20–30 K below this temperature. New red crystals with a triclinic morphology are then formed and they remain stable also after heating back to room temperature. The toluene system was studied by calorimetry in detail by Korobov et al. and exhibited a more complicated behavior.<sup>16</sup> The DSC curves showed two peaks at 285 and 320 K if the sample was preliminarily cooled to 260 K. This suggests that two solvates may exist in this system. Following this procedure we obtained toluene-solvates by cooling our samples to 233 K until new red transparent rhombic-shaped crystals were formed. The heating experiments with these crystals will be discussed below.

The maximum of the solubility curve of C<sub>60</sub> in hexane was reported to ~280 K by Ruoff<sup>2</sup> and later confirmed by Beck et al.<sup>18</sup> However no X-ray diffraction or calorimetry data that show the phase transition are yet available. We therefore performed experiments to define the phase transition temperature between solvate and pure C<sub>60</sub>. A sample was cooled to 278 K and after 1 h a number of new brown-red crystals was observed. Upon heating these new crystals melted at approximately 318 K, which is much higher than the reported maximum temperature of solubility.<sup>18</sup> Due to the very low solubility of C<sub>60</sub> in *n*-hexane it is reasonable to expect much slower rates of reaction in such a solution and solvate crystals may exhibit high stability at metastable conditions. At room temperature (10 K higher than solubility maximum point) we have not observed any decomposition even after several days.

As described in a previous publication, C<sub>70</sub> powder transforms to a solvate phase at room temperature by an intercalation

process without the formation of new crystals.<sup>14</sup> This process takes several hours for hexane and 10–20 min for benzene and toluene. The rate of solvate formation which was studied by X-ray powder diffraction was found to depend on the solubility of fullerene in the solvent. The solubility of C<sub>70</sub> in hexane at room temperature is approximately one hundred less (0.01 g/L) than benzene and toluene.

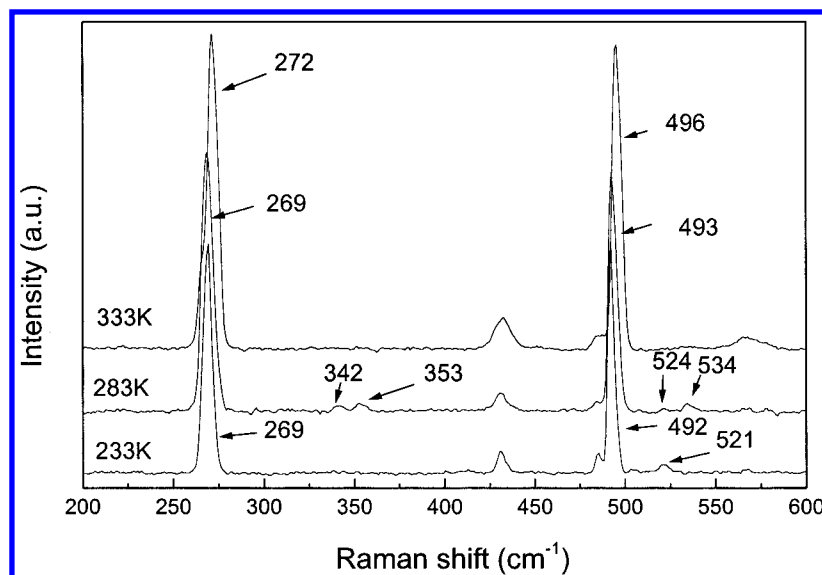
Reference C<sub>60</sub> and C<sub>70</sub> spectra were obtained by sublimation of fullerene powder which resulted in the formation of a bulk polycrystalline sample which was analyzed out of vacuum. These spectra appeared to be the same as the spectra of C<sub>60</sub> and C<sub>70</sub> taken from unsublimed microcrystals studied in air.

Raman spectra were recorded by Renishaw Raman 2000 spectrometer using a 780 nm excitation wavelength with a resolution of 2 cm<sup>-1</sup>. The temperature-dependent measurements were completed with the help of a heating/cooling stage down to 78 K. Precautions were taken to avoid laser-induced photopolymerization during the measurements. Only a low laser power (<5 W/cm<sup>2</sup>) was used for all experiments and no traces of photopolymerization were found in the recorded spectra.

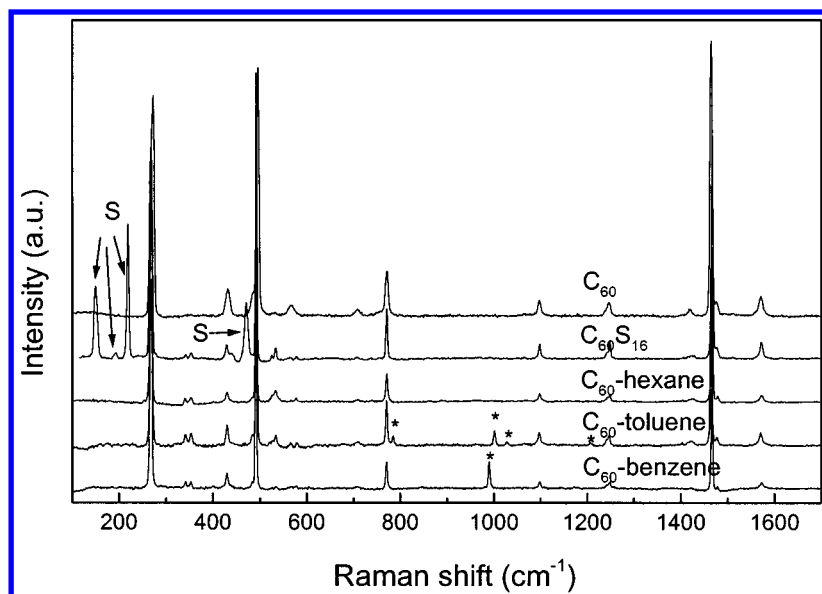
## 3. Results

**3.1. Raman Spectra of C<sub>60</sub> Solvates.** Spectra of solvates consist of two parts: peaks from C<sub>60</sub> and peaks from solvent. Since our experiments were performed on crystals immersed in a saturated solution we do not discuss peaks from the solvent because they obviously mainly originate from solution. Nevertheless, we consider peaks of C<sub>60</sub> as coming from the crystalline solvate despite the presence of some fullerene in solution. Since the solubility of C<sub>60</sub> in the solvents is rather low (1–0.01 g/L) and taking into account that the laser spot was focused on the surface of the crystals we assume that the C<sub>60</sub> peaks originated from the crystals and the contribution from C<sub>60</sub> in solution is negligible. This consideration is confirmed by analysis of obtained spectra and will be discussed below.

The most interesting phenomenon was observed in the C<sub>60</sub>–toluene system. Our experiments confirmed the existence of two different solvates (one of them metastable) in this system as suggested by Korobov et al.<sup>16</sup> Grains in the initial C<sub>60</sub> powder are black and not transparent. Raman spectra of these grains remain the same after immersion in solution. As described above, the initial C<sub>60</sub> powder grains start to dissolve and red transparent crystals of a toluene solvate starts to form when the solution-powder sample is cooled to 233 K. These new crystals showed some differences in Raman spectra compared with pure C<sub>60</sub>. Some of the initial powder grains which remain in solution were also analyzed and showed no difference compared to pure C<sub>60</sub>. In the following the crystals obtained at a temperature of 233 K will be called solvate I. Upon heating from 233 K we observed melting of relatively large crystals of solvate I around 280 K and the formation of new polycrystalline grains. If this polycrystalline sample was heated rapidly (~20–30 min) to temperatures higher than 320 K, a second transformation was observed which was detected mainly by differences in Raman spectra without a significant change in morphology of the grains. The solvate which exists in the temperature range 280–320 K we will call solvate II. This solvate appeared to be metastable. If the sample was stored at room temperature for 1 h the crystals of solvate II completely disappeared. The Raman spectra recorded at 233 K (solvate I), 283 K (solvate II) and at 333 K (pure C<sub>60</sub>) are shown in Figure 1. Typical features of spectra from solvate I compared with pure C<sub>60</sub> spectra are a new weak peak at 521 cm<sup>-1</sup> and a downshift of the C<sub>60</sub> peaks at 496 and



**Figure 1.** Raman spectra of  $C_{60}$ -toluene: 233 K, solvate I; 283 K, solvate II; 333 K, pure  $C_{60}$ .



**Figure 2.** Raman spectra of  $C_{60}$ -toluene, *n*-hexane, and benzene solvates compared with spectra of  $C_{60}S_{16}$  and pure  $C_{60}$ . Sulfur and solvent peaks are marked by S and asterisk, respectively.

272  $\text{cm}^{-1}$  to 492 and 269  $\text{cm}^{-1}$ , respectively. For solvate II the difference in spectra to compare with pure  $C_{60}$  is even stronger. Four new weak peaks detected at 342, 353, 524, and 534  $\text{cm}^{-1}$  and the  $C_{60}$  peaks at 496 and 272  $\text{cm}^{-1}$  are shifted to 493 and 269  $\text{cm}^{-1}$ , respectively. Although the resolution of our equipment is 2  $\text{cm}^{-1}$  the difference in peak position for solvate I at 492  $\text{cm}^{-1}$  and solvate II at 493  $\text{cm}^{-1}$  is reliable. A reproducible shift of 1  $\text{cm}^{-1}$  was observed in several temperature cycles around the phase transition at 280 K.

Raman spectra of  $C_{60}$  solvates with benzene and hexane appeared strikingly similar to spectra from toluene solvate II. They are shown in Figure 2 and are compared with a spectrum from pure  $C_{60}$  and spectrum from a  $C_{60}S_{16}$  compound taken from a previous publication.<sup>17</sup> In Figure 2, we can see some clear differences between spectra from pure  $C_{60}$  and spectra from solvates. It is especially remarkable that these differences are very similar for all three solvents and for  $C_{60}S_{16}$ . Most clearly the difference between pure  $C_{60}$  and the solvates can be observed in the region below 600  $\text{cm}^{-1}$  which is dominated by more radial vibrational modes of  $C_{60}$  (see Figure 3). New weak peaks at 342, 353, and 534  $\text{cm}^{-1}$  are typical for all three solvents. A

new, very weak peak at 579  $\text{cm}^{-1}$  was observed for the toluene and the benzene solvate while for hexane this peak was found at 577  $\text{cm}^{-1}$ . Also a reduced peak width and some changes in relative intensity of peaks can be seen (a reduced intensity of the peak at 566  $\text{cm}^{-1}$ ). Furthermore, a downshift of about 3  $\text{cm}^{-1}$  can be seen for the  $A_g(1)$   $C_{60}$  peak at 492  $\text{cm}^{-1}$  and the  $H_g(1)$  peak at about 269  $\text{cm}^{-1}$  (Figure 3). It is clear that the new peaks and the shifts described above can be assigned to  $C_{60}$  in its solvate phases. Nontransparent grains of unreacted  $C_{60}$  in the solution are black and spectra taken from these grains were identical to pure  $C_{60}$  spectra. In contrast, the new solvate crystals are red, transparent, and only such crystals exhibited additional lines and line shifts. Heating of these samples to temperatures above phase transition (313 K for benzene, 318 K for hexane, 280 K for toluene) led to a melting of the solvates and the formation of pure  $C_{60}$ . This process can be followed in the Raman spectra as all new peaks and peak shifts disappear and only peaks from pure fcc  $C_{60}$  can be seen above the transition temperature.

**3.2. Raman Spectra of  $C_{70}$  Solvates.** Raman spectra of pure  $C_{70}$  are more complicated compared with spectra of  $C_{60}$  due to

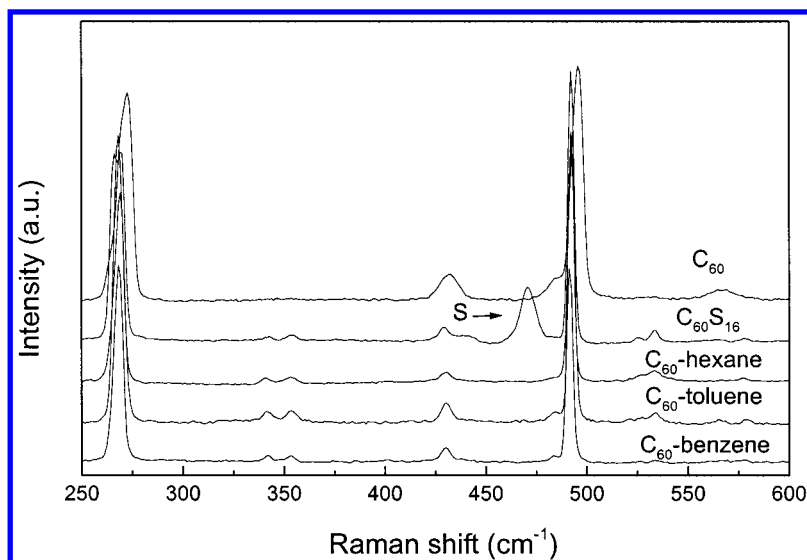


Figure 3. Fragment of Figure 2 in the range of 200–600 cm<sup>-1</sup>.

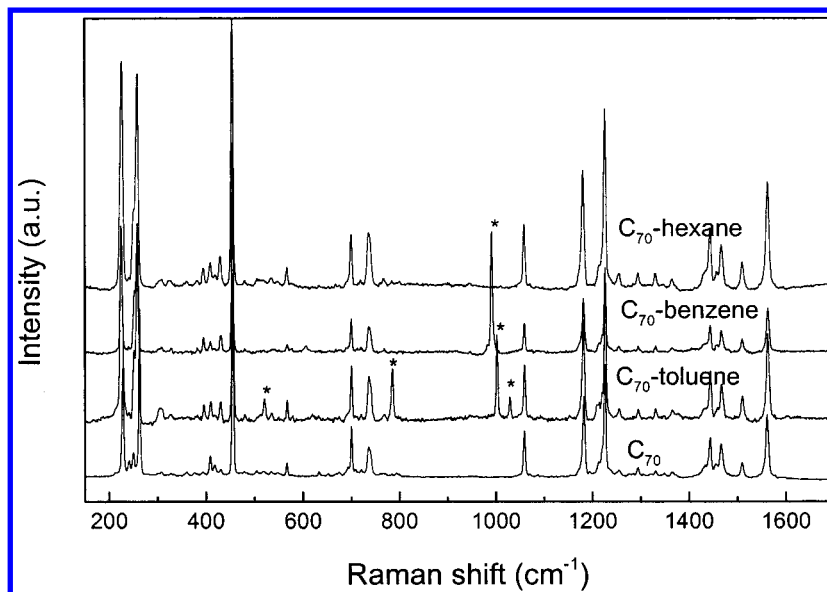


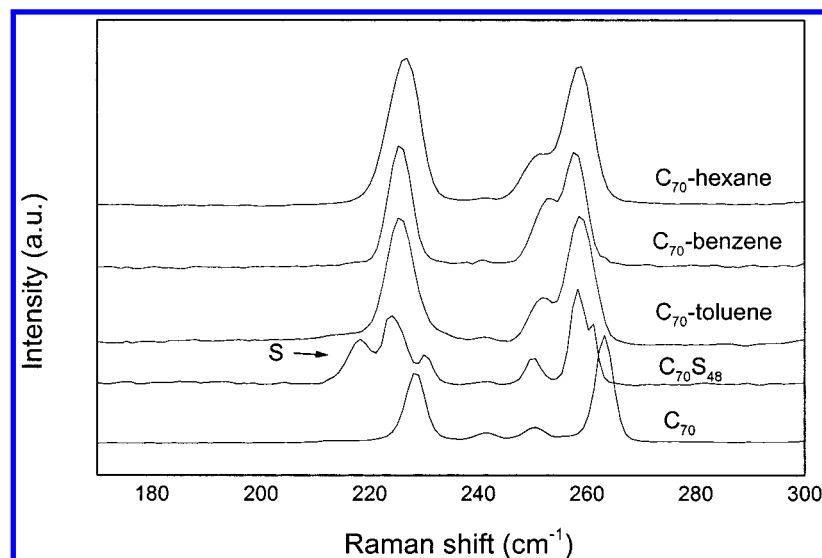
Figure 4. Raman spectra of C<sub>70</sub>-hexane, benzene, and toluene spectra compared with spectra of pure C<sub>70</sub>. Solvent peaks are marked with an asterisk.

the lower symmetry of C<sub>70</sub>. Raman spectra of C<sub>70</sub> in toluene, benzene, and *n*-hexane solutions are shown in Figure 4. As can be seen all the peaks which can be observed for a pure C<sub>70</sub> sample are present in these spectra too. Nevertheless there are some clear changes which allow us to confirm the formation of new solvate phases in solution. The main difference was observed in a region below 450 cm<sup>-1</sup>. Peaks of C<sub>70</sub> at 263 and 228 cm<sup>-1</sup> are downshifted to 258 and 225 cm<sup>-1</sup> respectively for all three solvates (Figure 5). Also three weak peaks between 400 and 450 cm<sup>-1</sup> showed some clear changes in relative intensity. Unlike C<sub>60</sub> solvates there is no sharp decrease of line width in a spectra of benzene and toluene solvates while for the *n*-hexane solvate the line width is increased.

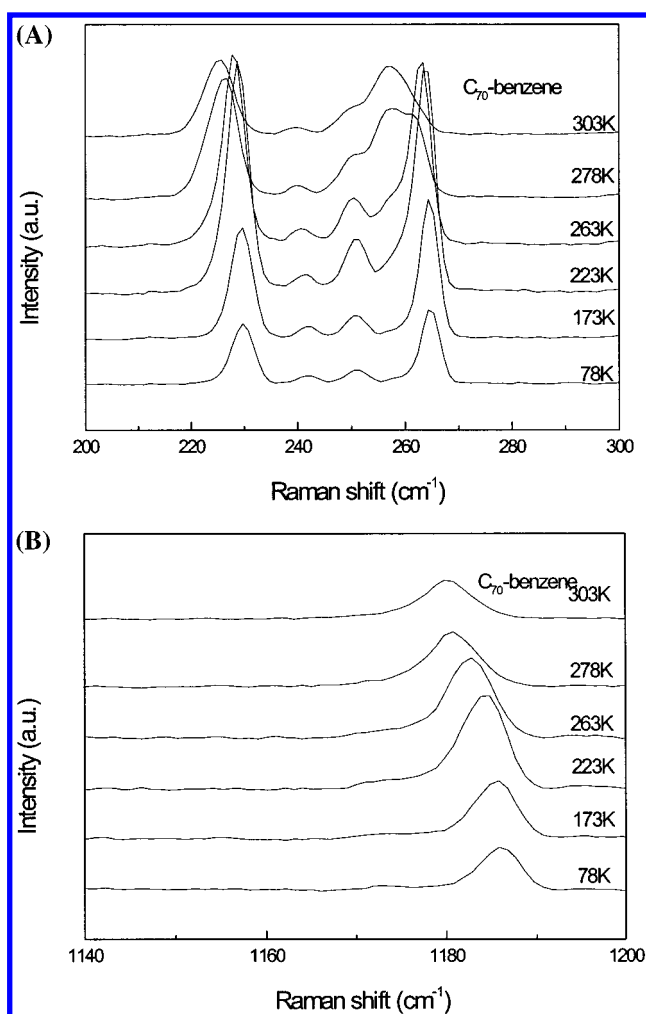
It is known that the C<sub>70</sub>-toluene solvate has a 1:1 composition and an orthorhombic structure. As shown in a recent study, C<sub>70</sub>-benzene and hexane solvates also have orthorhombic structures similar to the toluene solvate.<sup>14</sup> In our recent study of the dielectric properties of C<sub>70</sub> solvate single crystals we found two phase transitions, one at 150 K and a second at 275 K.<sup>15</sup> It was interesting to investigate the Raman spectra at these phase transitions and to find out if other C<sub>70</sub> solvates show

similar transformations. Taking into account the structural similarity of the C<sub>70</sub> solvates at room temperature we expected to find similar phase transitions for all three solvents, but unexpectedly the picture appeared to be more complicated. We found evidence for a phase transition in the C<sub>70</sub>-benzene system but not for the C<sub>70</sub>-toluene and the C<sub>70</sub>-hexane solvates. The Raman spectra of the C<sub>70</sub>-benzene solvate acquired upon cooling from room temperature to 78 K are shown in Figure 6. The clear shift of some peaks which was observed around 263 K (Figures 6 and 7) is in good agreement with our data on dielectric function temperature dependence.<sup>15</sup> No further changes were detected down to 78 K. As can be seen in Figure 7, the peaks of the room-temperature C<sub>70</sub>-benzene solvate at 258, 225, and 1180 cm<sup>-1</sup> are shifted to 264, 230, and 1186 cm<sup>-1</sup>, respectively, during the cooling. This can be seen as a much smaller overlapping with the peak at 250 cm<sup>-1</sup> which remains unshifted. The curve taken at 278 K shows both shifted and unshifted peaks which are overlapped. The low-temperature spectra are similar to the pure C<sub>70</sub> spectrum. Also three weak peaks between 400 and 450 cm<sup>-1</sup> showed some clear changes in relative intensity so that they look more similar to a pure





**Figure 5.** Raman spectra of  $C_{70}$ -hexane, benzene, and toluene spectra compared with spectra of pure  $C_{70}$  and  $C_{70}S_{48}$  in the range of 160–300  $\text{cm}^{-1}$ .



**Figure 6.** Fragments of Raman spectra of  $C_{70}$ -benzene recorded during cooling. Only the peaks which undergo shifts are shown.

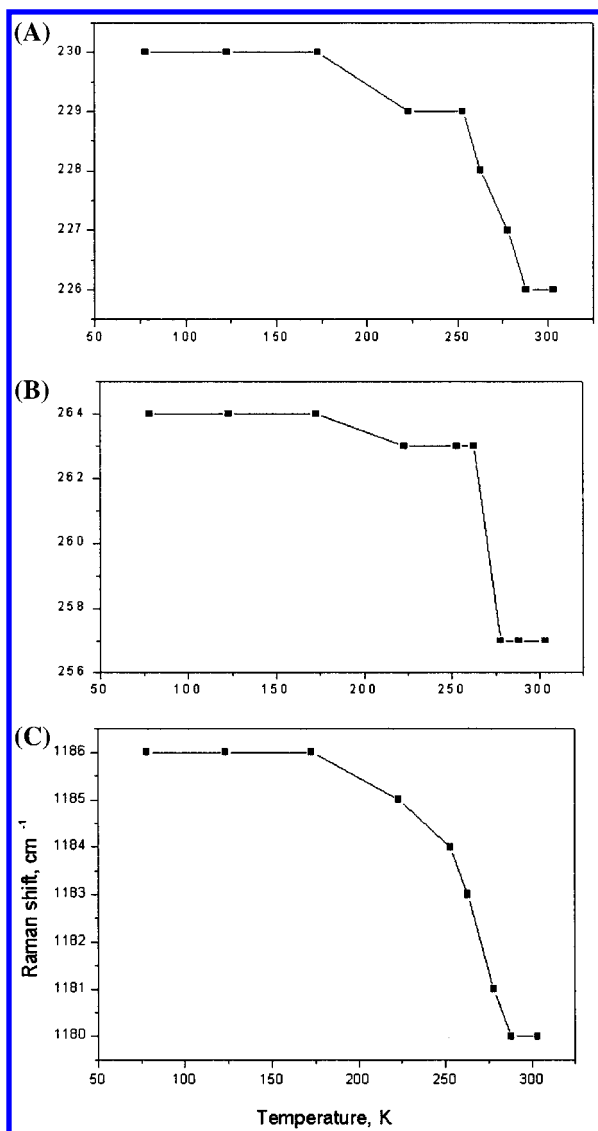
$C_{70}$  spectra. The shifts are reversible upon heating. Nevertheless some kind of irreversibility may be observed by comparing the intensities of the peaks at 258 and 250  $\text{cm}^{-1}$ . The relative intensity of the peak at 250  $\text{cm}^{-1}$  is clearly increased after the cooling-heating cycle. Finally it should be noted that the phase transition seen in Figure 6 occurs near the melting point of pure

benzene (278.5 K) and also near the orientational phase transition in pure  $C_{70}$ .

#### 4. Discussion

Our results clearly show that Raman spectra from different solvate phases as well as fullerene-sulfur compounds exhibit some common features and are different compared to spectra from pure  $C_{60}$  and  $C_{70}$ . This suggests that Raman spectroscopy can be a very efficient tool to study phase transformations in this kind of compound with weak van der Waals bonds. A good starting point for the discussion of the results is to look in more detail at the pure  $C_{60}$  spectra shown in Figures 1–3 which are in good agreement with those published in the literature.  $C_{60}$  is a highly symmetric molecule and exhibits only 46 fundamental vibrational modes. Only 10 of these modes ( $A_g$  and  $H_g$ ) are Raman-active, four  $F_{1u}$  modes are IR-active and the remaining 32 modes are silent in the isolated  $C_{60}$  molecule. It is well-known, however, that Raman spectra of fcc  $C_{60}$  can contain more than the 10 active  $A_g$  and  $H_g$  modes (see e.g. refs 19, 20). Examples of such extra peaks are splitting of  $A_g$  and  $H_g$  modes, activation of silent modes and new combination modes. The splitting and the activation of extra peaks have been explained to be due to several factors such as crystal-field effects due to hindered rotation, isotope effects caused by  $^{13}\text{C}$ , and by disordering in the solid material.<sup>9,19,20</sup>

Our  $C_{60}$  spectra in Figures 1–3 show all ten  $A_g$  and  $H_g$  peaks as well as three peaks at 485, 567, and 1478  $\text{cm}^{-1}$ . These peaks are also generally observed in Raman spectra from  $C_{60}$  and can be assigned to activated silent modes (485  $\text{cm}^{-1}$   $G_g(1)$ , 568  $\text{cm}^{-1}$   $F_{2g}(1)$ ) and combination mode (1482  $\text{cm}^{-1}$   $H_g(3)+H_g(4)$ ). However, a comparison between our  $C_{60}$  spectra and the spectra from the solvates and  $C_{60}S_{16}$  shows that the latter contain additional peaks which are not present in the pure  $C_{60}$  spectrum (see Figures 1–3). It is interesting to note that several of these new peaks (e.g. 342, 353, 524, and 534  $\text{cm}^{-1}$ ) have been observed previously in disordered  $C_{60}$  films which were claimed to be solvent-free.<sup>9</sup> The fact that the spectra from the solvate phases and  $C_{60}S_{16}$  are so similar suggests that they originate from  $C_{60}$  and that they are due to some effect caused by the weak van der Waals bonding between the fullerene and an organic solvent or an  $S_8$  ring. Several possibilities may be considered when explaining the new peaks and peak shifts in



**Figure 7.** The peak position dependence on temperature for three modes which undergo shifts during cooling.

our spectra. These are: (i) freezing of free rotational state of the C<sub>60</sub> molecule due to the presence of solvent molecules; (ii) symmetry-lowering effects arising from a disordered arrangement of C<sub>60</sub> in the solvate phases; and (iii) a shape distortion of C<sub>60</sub> caused by solvent–fullerene interactions. In the following these effects will be discussed in more detail.

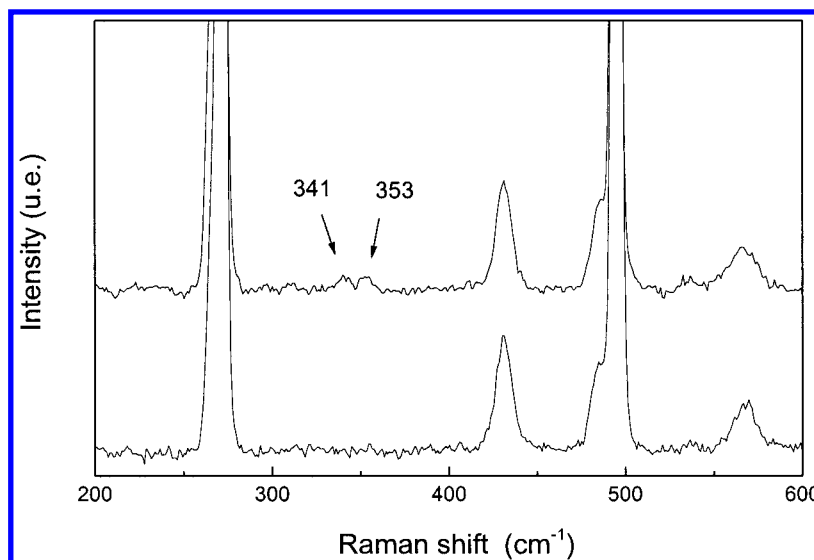
One of the most obvious explanations to the new peaks and peak shifts is that they are due to symmetry breaking caused by the presence of solvent molecules. The solvent molecules will interact with C<sub>60</sub> molecules and may hinder a free rotation of this molecule. This is similar to what can be seen in the low-temperature sc C<sub>60</sub> phase.<sup>19</sup> In the room-temperature fcc C<sub>60</sub> phase, the molecules are free to rotate but below the phase transition temperature to a simple cubic structure (261 K), two of the three degrees of rotational freedom are lost. Raman studies have showed a splitting of several modes that can be attributed to symmetry-reduction (crystal field effects). It is certainly likely that the presence of solvate molecules in the structure may cause a similar loss of rotation and subsequent change in the Raman spectra. However, it has been found that such crystal field effects mainly will lead to splitting of Raman-active modes. It is clear that our Raman spectra show no splitting of peaks (with the exception of the H<sub>g</sub>(1) mode in C<sub>60</sub>S<sub>16</sub>). Another effect of rotational freezing on Raman spectra is a sharp decrease in line

width of several modes for the sc C<sub>60</sub> phase (factors of 3–4).<sup>20</sup> Indeed we observed a significant decrease of line width for several modes but not so strong as reported for fcc-sc phase transition (factors of 1.3 and 1.9 for H<sub>g</sub>(1) and A<sub>g</sub>(1) modes, respectively).

An interesting question which has to be addressed at this point is: can the C<sub>60</sub> molecules in the solvates and C<sub>60</sub>S<sub>16</sub> rotate freely or is their rotation hindered or frozen? The structure of C<sub>60</sub>S<sub>16</sub> has been solved at room temperature up to the positions of the carbon atoms and it could be suggested that the rotation of the C<sub>60</sub> molecules is frozen in this compound.<sup>21</sup> However, the Raman spectra from C<sub>60</sub>S<sub>16</sub> only show a splitting of the H<sub>g</sub>(1) mode while up to 10 peaks have been found split in sc C<sub>60</sub>. This splitting of the H<sub>g</sub>(1) mode can be due to crystal field effects but the fact that other modes remain unsplit suggest that these effects must be much weaker than in sc C<sub>60</sub>. For the solvate phases the question is more complicated. Attempts to solve the structure of many solvates at room temperature have failed because of strong disorder. This suggest that the C<sub>60</sub> molecules in these compounds have a free rotation at room temperature. NMR studies have also confirmed that the fullerene molecules in the C<sub>60</sub>–benzene solvate have free rotation not only at room temperature but also at temperatures as low as 120 K.<sup>10</sup> This is in contradiction, however, to X-ray diffraction studies carried out at low temperatures (104 K), where the structures of the toluene and benzene solvates have been successfully solved and it has been shown that the C<sub>60</sub> molecules are frozen.<sup>22</sup> Our results show no splitting of the Raman speaks from the solvates at room temperature or when cooled to 78 K. This suggests crystal field effects are not present or that these effects are too weak to show up in the spectra. Nevertheless, the decrease of peak line width may suggest that solvates have a decreased state of rotational freedom.

As mentioned above, many of the new peaks observed in our spectra are similar to those observed by Love et al.<sup>9</sup> in pure C<sub>60</sub> films with a high degree of disorder. It is therefore possible to ascribe the new peaks in Figures 1–4 to sample imperfection in the solvates as well as the C<sub>60</sub>S<sub>16</sub> phase. Our suggestion about disorder as a reason for new weak peaks is supported by the following experiment which we performed with pure C<sub>60</sub>. It is known that C<sub>60</sub> is so plastic that crystal crushing easily introduces stacking faults and plastic deformation. Figure 8 shows spectra of initial C<sub>60</sub> powder and the same powder after moderate grinding. The new peaks on a ground sample at 341 and 353 cm<sup>-1</sup> are very similar to peaks which we observed for C<sub>60</sub> solvates and C<sub>60</sub>S<sub>16</sub>. This peaks can be attributed to combination mode H<sub>g</sub>(4)–H<sub>g</sub>(2) (343.5 cm<sup>-1</sup>) and silent F<sub>2u</sub>(1) mode (354 cm<sup>-1</sup>).<sup>19</sup> This could also explain why the spectrum from the toluene solvate I shows no additional peaks since this solvate phase is formed at much lower temperature than the other solvates and therefore may be less disordered. However, sample disorder is also expected to give rise to a broadening of the Raman peaks. A comparison of the line widths shows that the solvate phases generally exhibit more narrow peaks than the pure C<sub>60</sub> phase. This suggests that sample disorder alone cannot explain the observed changes in spectra.

Although the appearance of new weak peaks can be attributed to strong disorder of solvate structures it cannot explain observed shifts of A<sub>g</sub>(1) and H<sub>g</sub>(1) modes. Such shifts can be attributed to the interaction of solvent and fullerene which leads to a slight distortion of the fullerene cages. It is known that fullerene compounds with charge transfer exhibit significant line shifts in their Raman spectra. One of the most sensitive modes to charge transfer in C<sub>60</sub> is the A<sub>g</sub>(2) mode. For example, in the



**Figure 8.** Raman spectra of  $C_{60}$  (lower) before grinding and (upper), after moderate dry grinding.

relatively well studied charge-transfer complex TDAE- $C_{60}$  this mode is downshifted  $\sim 6\text{ cm}^{-1}$  while the  $A_g(1)$  mode is downshifted only  $2\text{ cm}^{-1}$  and the  $H_g(1)$  mode remains unshifted.<sup>23</sup> Alkali metal fullerenes show a downshift of the  $A_g(2)$  mode by  $6\text{ cm}^{-1}$  per each dopant metal atom.<sup>20</sup> But unlike the TDAE- $C_{60}$  complex the  $A_g(1)$  and the  $H_g(1)$  modes are upshifted.

Raman spectra of solvates do not show any shift of the  $A_g(2)$  mode and this can be considered as evidence for an absence of charge transfer in these compounds. Nevertheless, it can be argued that van der Waals interactions alone may be responsible for the observed downshifts of the  $A_g(1)$  and  $H_g(1)$  modes. This suggestion is in line with a stronger downshift of the  $H_g(1)$  mode in toluene solvate I compared with solvate II. According to DSC data<sup>16</sup> solvate I shows a higher decomposition enthalpy than solvate II which is a sign of stronger interaction between solvent and fullerene molecules in solvate I. However, a line shift caused by chemical interactions should have implications for the rotation of the  $C_{60}$  molecule. It is conceivable to assume that such interactions also should reduce the rotational freedom and thereby cause the effects on the Raman spectra discussed above. It is interesting to note that most of the new peaks and peak shifts in the Raman spectra from the solvates can be found in the spectral range below  $600\text{ cm}^{-1}$  where more radial modes of  $C_{60}$  dominate. It is likely that these modes are most strongly affected by the presence of solvate molecules around the  $C_{60}$  cage.

The Raman spectra of  $C_{70}$  is rather more complicated than for  $C_{60}$  because of the lower symmetry. According to molecular symmetry, 122 distinct frequencies exist for  $C_{70}$ ; 53 modes are Raman active and 31 are infrared active.<sup>24</sup> Unlike the case for  $C_{60}$  the experimental spectra of  $C_{70}$  are not yet completely understood and a full assignment of all observed frequencies is not available. The spectra of the  $C_{70}$  solvates are also quite different from the spectrum of pure  $C_{70}$ . However, in contrast to the  $C_{60}$  solvates there are no additional lines. The main difference is peak shifts of some modes. Furthermore, the  $C_{60}$  solvates typically exhibited sharper peaks than in pure  $C_{60}$ . For the  $C_{70}$  solvates the picture is slightly more complicated. Unlike the  $C_{60}$  solvates there is no sharp decrease of line width in spectra of benzene and toluene solvates while for the *n*-hexane solvate the line width is increased.

To explain the  $C_{70}$  solvate spectra it is appropriate to start with a discussion on the effect of rotational ordering. In pure  $C_{70}$  orientational ordering occurs in several steps and a full set

of phase transitions is not yet well established. Even the number of these phase transitions is still discussed but the most reliable ones are at 340 K and 280 K.<sup>24</sup> At room-temperature,  $C_{70}$  molecules are aligned along their long axes with a free rotation around them. At 280 K rotation about the *C*-axis becomes frozen. It is interesting to note that the orientational ordering phase transition which occurs in  $C_{70}$  at 280 K does not show such clear changes in the Raman spectra as observed for  $C_{60}$ . Some changes such as appearance of new peaks and splitting of some modes can be found only below 155 K.<sup>25</sup> It is clear that a freezing of the rotational freedom should produce certain effects on the Raman spectra but it is unclear why they are not observed at the point of orientational phase transition to the same extent as in  $C_{60}$ . The DSC data obtained with  $C_{70}$ -toluene solvate show an absence of phase transitions typical for pure  $C_{70}$ . Instead a broad shallow endotherm appears from 170 to 280 K.<sup>26</sup> The NMR data suggest that toluene at room temperature reduces the mobility of  $C_{70}$  without a complete freezing of rotation. The toluene molecules themselves are claimed to be in a liquidlike state which freeze only below 180 K.<sup>26</sup> This temperature is close to the melting point of toluene which suggests that similar anomalies may exist for other solvents. Unfortunately, DSC and NMR data from other solvates are not available. However, taking into account the structural similarity of all three solvates it is conceivable to assume that the benzene and hexane solvates should exhibit a similar behavior.

To our knowledge there are no reports on structures of  $C_{70}$  solvates where the position of the carbon atoms has been determined. This suggests that the rotation of  $C_{70}$  is not hindered in the solvates; but the result could also be due to poor quality of the crystals. Our own attempts to solve the structure of the  $C_{70}$ -benzene solvate have failed due to poor crystal quality. However, it is known that rotation of  $C_{70}$  is frozen at room temperature in  $C_{70}S_{48}$ .<sup>27,28</sup> It is therefore interesting to examine Raman spectra of this compound published in a previous study<sup>17</sup> and compare them with spectra from pure  $C_{70}$  and the solvates. The spectra from the solvates and  $C_{70}S_{48}$  all show a clear downshift with  $4\text{ cm}^{-1}$  of peaks at 228, 263, and  $456\text{ cm}^{-1}$  compared with pure  $C_{70}$ . However, Figure 5 shows that there is a difference between the solvate spectra and the spectra from  $C_{70}S_{48}$ . This can be seen as a splitting of the  $E'_2$  mode at  $228\text{ cm}^{-1}$  into two peaks at 224 and  $230\text{ cm}^{-1}$  in the  $C_{70}S_{48}$  spectrum. As mentioned above, the fullerene molecules in  $C_{70}S_{48}$  are frozen and it is possible that the splitting is due to this effect.

The absence of any splitting in the other spectra may then suggest that the C<sub>70</sub> has a more or less free rotation in these compounds. This suggestion is also confirmed by observation of solvates line width compared to pure C<sub>70</sub>. Similar to C<sub>60</sub> the line width has to be lower in a phase with frozen rotation. Since we do not observe a decrease in line width in C<sub>70</sub> spectra we conclude that rotation of C<sub>70</sub> molecules in the solvate is unhindered in the room-temperature phase of C<sub>70</sub>.

It is also possible that the peak shifts observed in the C<sub>70</sub> solvates can be attributed to a weak interaction between C<sub>70</sub> and solvent molecules. Similar to the C<sub>60</sub> case we suggest that the slight distortion of the C<sub>70</sub> molecule shape due to van der Waals bonding with solvent molecules may prevail in these compounds. It has been reported that solvent molecules in the C<sub>70</sub>-toluene solvate are situated closer to the equatorial belt of the C<sub>70</sub> molecule.<sup>26</sup> Such an asymmetrical surrounding could produce a slight shape distortion of the C<sub>70</sub> molecule without complete freezing of rotation. A very interesting phenomenon was also observed during a cooling of C<sub>70</sub> solvates. Only the C<sub>70</sub>-benzene solvate shows a phase transition upon cooling. The broad phase transition occurs in a temperature interval between 280 and 173 K and is clearly recognizable by upshifts of three C<sub>70</sub> peaks during cooling (see Figure 7). The temperature of this phase transition is close to the melting point of pure benzene. A possible explanation for this phase transition is a freezing of the liquidlike state of benzene molecules in the solvate at this temperature. As we mentioned above such a transition has been found by NMR in the toluene solvate. The absence of any changes in the spectra from C<sub>70</sub>-hexane and C<sub>70</sub>-toluene suggests that this kind of phase transition is absent in these compounds. Indeed, however, a very slight upshift of peak at 254 cm<sup>-1</sup> was observed around 220 K for the toluene solvate but the value of this shift was only 1 cm<sup>-1</sup>. This is below the resolution of our equipment (2 cm<sup>-1</sup>) and while it was observed repeatedly it still cannot be considered as evidence for a phase transition.

## 5. Conclusions

The results clearly show that C<sub>60</sub> and C<sub>70</sub> solvates exhibit Raman spectra which are quite distinct from the pure fullerenes. Very similar effects can also be seen in spectra from fullerene-sulfur compounds. The fact that all these compounds have weak van der Waals bonds between the fullerene and the solvent molecules (or S<sub>8</sub> ring) suggests that the effects are related to changes in the nature of the fullerene molecules. The clear difference between the spectra of solvates and C<sub>60</sub> and C<sub>70</sub> shows that Raman spectroscopy can be a very powerful technique to study phase transitions in solution. In this study, the formation and phase transformations of C<sub>60</sub> and C<sub>70</sub> solvates with benzene, toluene, and *n*-hexane were studied in-solution by Raman spectroscopy for the first time. Spectra of C<sub>60</sub> solvates exhibited clear differences compared to pure C<sub>60</sub> and the spectra appeared to be extremely similar for all three studied solvents as well as for C<sub>60</sub>S<sub>16</sub>. Two different solvates were found for C<sub>60</sub>-toluene in good agreement with recent DSC studies. Upon heating all three solvates decomposed to pure fcc C<sub>60</sub> and all new peaks and shifts of peaks typical for solvates disappeared at this point. The temperatures of the phase transitions from C<sub>60</sub>-solvent to C<sub>60</sub> are in a good agreement with previous data. No changes in Raman spectra of all three solvates were found upon cooling to 78 K. The C<sub>70</sub> solvates with toluene, benzene, and *n*-hexane also exhibited a clear difference from pure C<sub>70</sub> and striking similarity to new features observed in the C<sub>70</sub>S<sub>48</sub> compound. The benzene solvate showed a broad phase transition upon

cooling in a temperature range between 278 and 173 K with the most significant changes around 263 K.

A comparison of the different spectra show that the main effects of the solvents (and the S<sub>8</sub> rings) are peak shifts and new peaks originating from, for example, the activation of silent modes. Also there are changes in line widths of the peaks. A problem which remains to be solved is to explain the nature of these effects and how they affect the Raman spectra in detail. It is clear that various possibilities such as breaking of symmetry due to rotational ordering, sample disorder, and chemical bonding can cause the effects observed in the spectra. No simple model, however, may explain all obtained data and a combination of several factors is likely.

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