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Raman identification of C_{70} monomers and dimers

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ABSTRACT:

Fullerenes easily polymerize under high pressure by forming covalent intermolecular bonds. For C_{60} this reaction is easily monitored by Raman scattering, but for C_{70} no simple method to determine its bonding state is known. In this work C_{70} has been heated over a wide range of temperatures at a pressure of 1.6 GPa and the treated material has been studied by Raman spectroscopy, using 830 nm laser excitation to avoid photo-induced polymerization. By comparing the present data with earlier results for pure dimers, zig-zag chain polymers and pressure treated powders, characteristic fingerprint peaks can be found for the C_{70} monomer and the C_{140} dimer. The molecular stretching mode near 88 cm^{-1} is a clear fingerprint for dimers while the strong A_1' peak near 455 cm^{-1} clearly shows the presence of monomers. Several other new peaks appear in pressure-treated material and the relative intensities of many peaks change in a systematic way, but it is not clear whether these changes indicate the presence of dimers or of small oligomers in general. Simple strategies for semi-quantitative structural analysis of pressure-treated C_{70} material by Raman spectroscopy are briefly discussed.

HIGHLIGHTS:

- The presence of dimers in pressure-treated C_{70} is ascertained by Raman scattering.

- Raman fingerprints for C_{70} and C_{140} are identified.

- Practical methods for the semi-quantitative analysis of the dimer fraction are discussed.

- The dimer fraction is measured as a function of treatment temperature at 1.6 GPa.

GRAPHICAL   ABSTRACT:
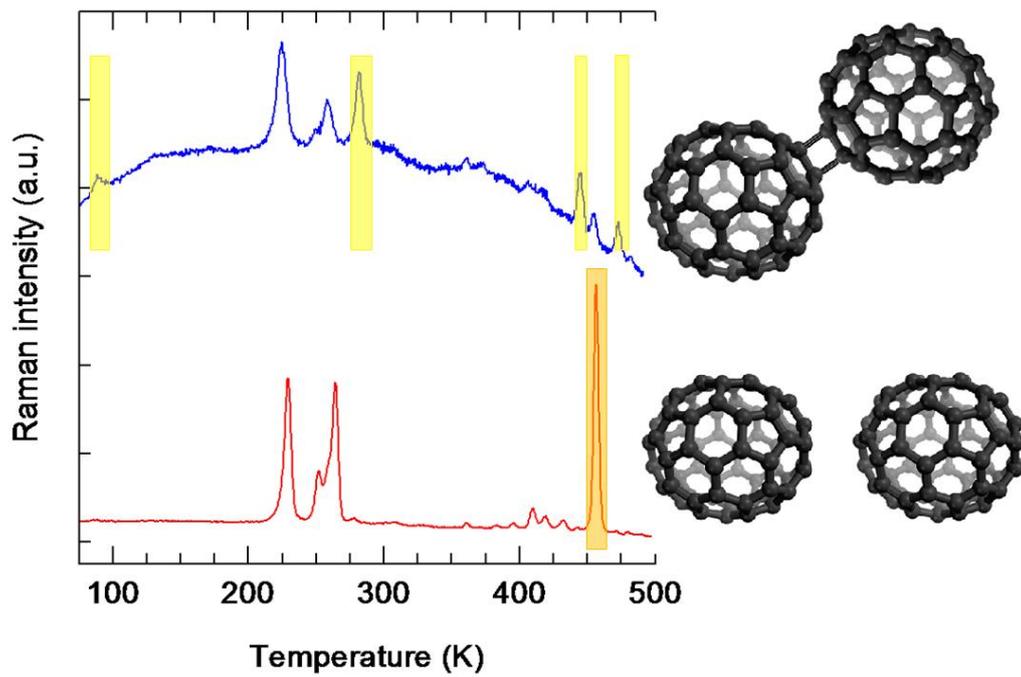
1. Introduction

Fullerene molecules in solid crystals easily form covalent bonds with their molecular neighbors when exposed to irradiation or to elevated temperatures at high pressure. The high pressure reactions of the most common fullerene, C_{60}, have been investigated in a large number of experiments reviewed, for example, in refs. [1-4]. In contrast, for the slightly larger molecule C_{70} only a relatively small number of studies have been carried out [1-3,5-6]. While C_{60} has 30 reactive double bonds, C_{70} has only ten, with five of these distributed radially around each pentagonal "polar cap". C_{70} is thus in practice much less reactive than C_{60} and the bonds formed are highly directional. At ambient conditions C_{70} usually forms a face centered cubic structure with freely rotating molecules. When pressure is applied the free rotation stops and the molecules line up with their poles in the original 111 direction of the lattice while retaining a uniaxial rotational motion. In this rhombohedral state the three-fold symmetry of the lattice is not compatible with the five-fold symmetry of the reactive bonds and it has long been believed that in this state only molecular dimers, but no long-range ordered polymers, can be formed. This assumption was recently challenged by the discovery of two long-range ordered polymeric structures formed above 7 GPa at elevated temperatures [5,6]. On the other hand, starting from the more unusual A-B stacked hexagonal close-packed structure, C_{70} can also form a long-range-ordered polymer, consisting of zig-zag molecular chains, near 2 GPa [7].

Fullerenes are interesting components for the synthesis of novel nanocarbon-based materials under mild pressure conditions. While graphene and carbon nanotubes are practically inert at low pressures, the fullerenes react easily and thus may act as a "glue" in the synthesis of such materials. Alternatively, fullerene molecules can be solvated in a matrix and if their positions and orientations are favorable, high pressure reactions can produce anisotropic or open structures with predictable structures and interesting and tunable properties. The fact that intermolecular bonding in C_{70} is strongly directional makes this molecule particularly suitable for such experiments and it is thus of some interest to investigate in detail its reaction properties under high pressure conditions.

In this work, the high pressure dimerization of C_{70} is studied up to 600 K at 1.6 GPa in an attempt to find a suitable method for semi-quantitative analysis of the bonding reaction under pressure. Recently, it was shown that the reaction diagram of C_{60} could be analyzed in a semi-quantitative way by Raman scattering, such that the relative amounts of monomers, dimers, one- and two-dimensional polymers and disordered oligomers could be deduced from the relative shift of the $A_g(2)$ "pentagonal-pinch" mode and the dimer and chain stretching modes [8]. For C_{70}, no such easy and convenient method is known and the present work should be seen primarily as an attempt to evaluate different ways to identify the relative amounts of monomers and dimers in pressure-treated material using near-infrared (NIR) Raman scattering.

2. Experimental details

A simple technique for accurately mapping reaction diagrams for high pressure reactions resulting in metastable phases was recently developed [9] and used to map the intermolecular bonding reaction in the fullerene C_{60} under pressures up to 2 GPa at temperatures up to 700 K[8]. The same basic technique was used here. In brief, the sample was deposited on a copper strip which was heated at one end. The temperature was measured at six points along the strip by putting thin, calibrated Constantan wires in contact with the copper and pressure was applied in a large piston-cylinder vessel, using Teflon and a small amount of talc powder as quasi-hydrostatic pressure-transmitting media. For the present experiment, 99.5 % pure C_{70} obtained from BuckyUSA, Houston, TX, was dried for more than 24 h at 200°C under dynamic vacuum (created by a turbomolecular pump) and the dried material was deposited on the copper strip in a glove-box under Ar gas with water and oxygen levels below 1 ppm. The pressure in the cell was increased to 1.6 GPa after which the hot end temperature was increased at an approximate rate of 20 K/min and held at the maximum temperature for 2 h. The power was then switched off, resulting in a rapid temperature quench to near room temperature, before the pressure was slowly released to atmospheric pressure.

The pressure cell was opened and the sample removed under red darkroom light to avoid additional photopolymerization. During the pressure treatment the sample was compressed to form thin solid plates. The surfaces facing the Cu strip were analyzed using Raman scattering, using a NIR laser (wavelength 830 nm) to avoid photopolymerization. Treatment temperatures were deduced from positions using the known temperatures at the thermocouple positions. The Raman spectra obtained were analyzed in detail using PeakFit™ software [10].

3. Experimental results and discussion

Figure 1 shows the Raman spectrum of dried, pristine C_{70} when excited by an 830 nm NIR laser. Because the detector used suffers from a gradually decreasing sensitivity for Raman shifts exceeding about 500 cm^{-1} the spectrum shown has been corrected using an exponential decay function. A comparison between Figure 1 and the Raman spectra of similar materials given by Lebedkin *et al*. [11] and Soldatov *et al*. [7] using 1064 nm excitation shows that the three spectra are in excellent agreement regarding both frequency shifts and relative amplitudes. For all stable fullerenes, more than one isotope of carbon is present in most molecules, breaking the molecular symmetry [12]. Although C_{70} formally has only 53 Raman allowed lines, a careful study will thus show many more peaks in the spectrum, many of these quite weak but clearly rising above the noise.
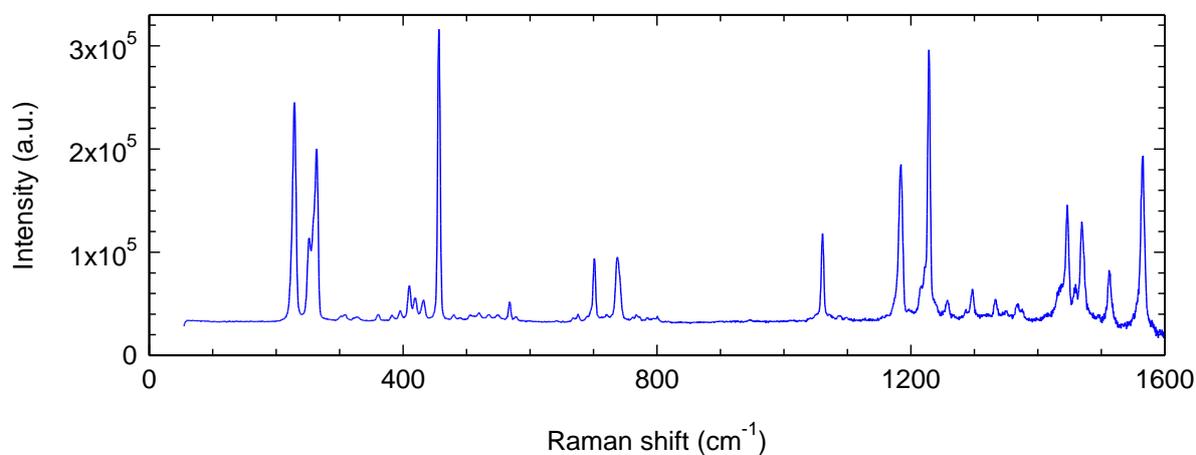

Figure 1. Raman spectrum of pristine C_{70} before pressure treatment. The intensities have been approximately corrected for the drop in detector sensitivity with increasing Raman shift.

The dimer C_{140} has previously been synthesized in several experiments. Lebedkin *et al*. [11] produced C_{140} in high yield at a pressure of 1 GPa at a temperature near 473 K and purified the dimer by liquid chromatography. The zig-zag chain polymer of C_{70} was later produced from hexagonal close-packed C_{70} at 2 GPa and 573 K by Soldatov *et al*. [7]. Good Raman spectra, measured using 1064 nm NIR excitation, are available for both materials and the spectra obtained in this work were analyzed and compared to the spectra of both these phases.

In the present investigation the C_{70} sample was treated at 1.6 GPa, intermediate between the pressures used by Soldatov *et al*.[7] and Lebedkin *et al*.[11], and the total temperature range studied was about 360 to 600 K. The reaction time at elevated temperature was chosen as 2 h to ensure that the dimerization reaction had been completed. For the present sample, a total of 43 Raman spectra were measured using NIR laser excitation and Figure 2 shows eight of these. In the range from 370 to about 500 K there was a clear evolution of the spectra with
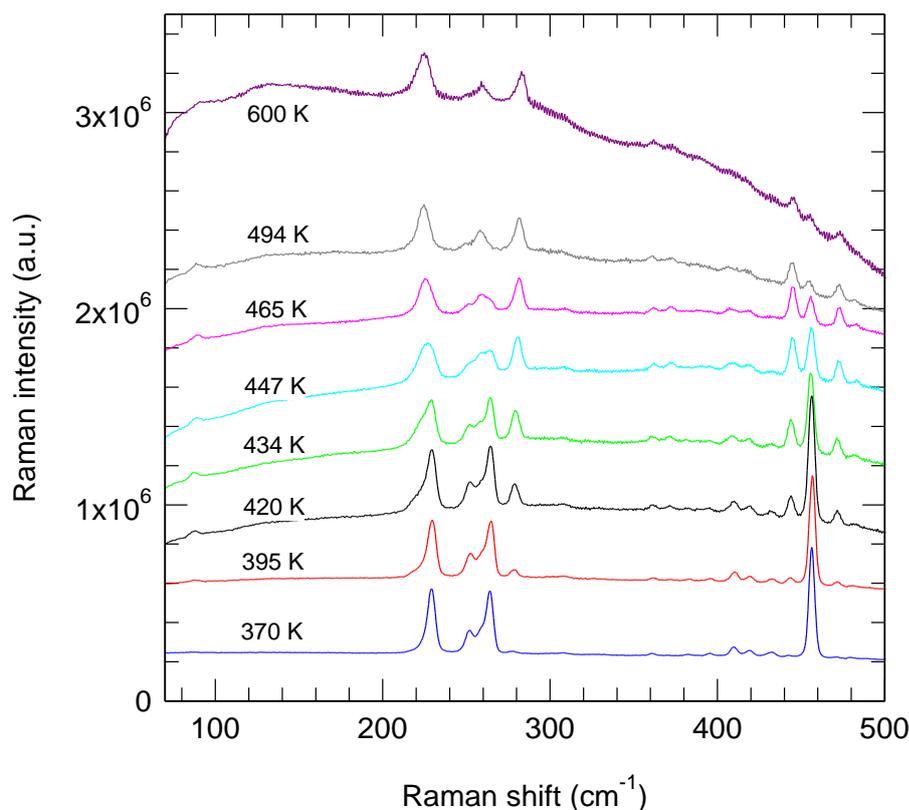

Figure 2. Raman spectra for C_{70} treated for 2 h at 1.6 GPa, at the temperatures indicated.

increasing treatment temperature and spectra are shown for seven different treatment temperatures in this range. Above 500 K little further change was observed, and only the final spectrum obtained for material treated at close to 600 K is shown. Most spectra were measured over the range $50 - 1600$ cm^{-1}. However, with increasing treatment temperature the quality of the spectra deteriorated due to an increasing background level. Because the sensitivity of the detector also decreased at high wavenumbers the spectra shown have been limited to the range below 500 cm^{-1}. This range includes most of the Raman lines useful for the identification of dimers and the expansion of the scale also facilitates the discussion of the spectra. Note that the intensities of the spectra shown have been approximately normalized using the product of the laser intensity used and the exposure time, and the spectra have been shifted vertically by arbitrary amounts to allow easy comparison. No background correction has been applied. The peaks were analyzed by fitting Voigt functions to the data, and the areas of the fitted peaks will be referred to in the following as the "intensities" of the peaks.

A comparison between Figures 1 and 2 shows that material treated at 370 K has a Raman spectrum essentially identical to that of the pristine material, but with increasing treatment temperature the intensities of the different lines change and several new lines appear. For most of the Raman lines observed for pristine C_{70} there is a slow decrease in intensity with increasing treatment temperature.

The most important of the new modes observed is the low-frequency dimer stretching mode at 88 cm^{-1}. For individual C_{70} molecules no Raman modes exist in this frequency range and this mode can thus be positively identified and used as a fingerprint for the existence of dimers in the sample. The same mode was observed at 89 cm^{-1} by Lebedkin *et al*.[11], in excellent agreement with the present result. This mode is not observed in pristine C_{70} and for material treated at 370 K it is too weak to be observed on the scale of the figure. However, as shown in Figure 3 the intensity grows rapidly with increasing treatment temperature until it saturates near 500 K. Above this temperature the intensity appears to be approximately constant, or even to decrease slightly with increasing treatment temperature. Lebedkin *et al*. also observe
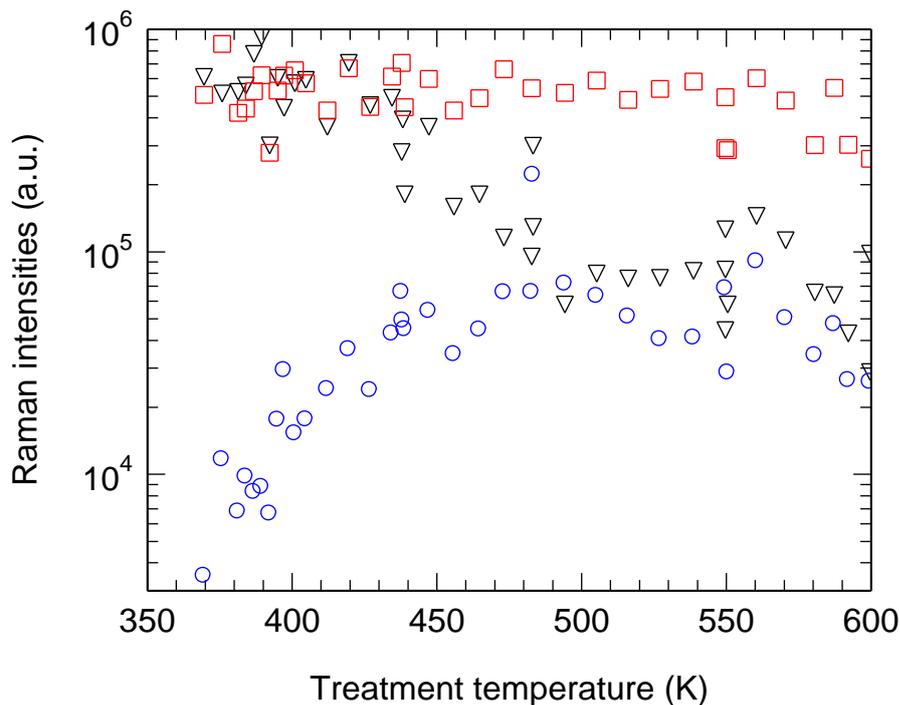
Figure 3. Intensities of the Raman lines observed near 88 cm^{-1} (blue circles), 225 cm^{-1} (red squares) and 456 cm^{-1} (black triangles) as functions of treatment temperature. The intensities have been normalized by laser intensities and exposure times used.

some weak, related modes between 118 and 130 cm^{-1}. However, no such modes could be identified in the present study although some spectra showed a low, broad "hump" structure centered on 124 cm^{-1}. For the zig-zag chain polymer the stretching mode was identified at 105 cm^{-1} with a weaker satellite near 120 cm^{-1}[7]. Neither of these lines was observed in any of the spectra from the present sample, which confirms that the chain structure can only be produced from hexagonal close-packed C_{70}. Although a small volume fraction of this lattice structure could exist as stacking faults in the starting material used here, the amount is clearly too small to be observed.

A second new peak appears near 280 cm^{-1} and shows an interesting evolution with treatment temperature. At low temperatures it is clearly centered at 278 cm^{-1}, but near 400 K a shoulder appears on the high energy side near 283 cm^{-1} and rapidly outgrows the initial peak. Although in principle this line could be fitted with a single peak, shifting its position with treatment

temperature, the fit is almost always better if two peaks are fitted. When the intensities of the two subpeaks are plotted as functions of the dimer stretching mode peak it is clear that neither of the two intensities shows a direct proportionality to that of the stretching mode, but for temperatures up to about 500 K the total joint area of the two peaks showed a very good linear relationship to the intensity of the stretching mode. This peak has also been observed in earlier experiments [7,11,13] and a comparison with available data shows that the peak has very similar relative intensities for both pure dimers and for zig-zag chains. It thus cannot be positively identified it as a "dimer" peak but probably shows the presence of both dimers and other small oligomers or polymers. Since it cannot identify the structural units present, this line should thus be treated with some care.

Pristine C_{70} has a very strong A_1' [14-16] Raman line at 456 cm^{-1}. When the treatment temperature increases the intensity of this line decreases rapidly (figure 3) and above 500 K only a weak residual line remains. While the intensity of this line decreases, two new satellite peaks appear at about 445 and 473 cm^{-1} and rapidly grow in intensity. Again, these two peaks appear for both dimers and zig-zag chains but with different relative intensities. For pure dimers [11] the peak at 445 cm^{-1} has a higher intensity, in agreement with the present results, while for the chain structure [7] the relative intensities show an opposite tendency. For both dimers and chains the original line at 456 cm^{-1} is absent [7,11]. It is thus clear that this line is characteristic for the C_{70} monomer and that the two new nearby modes indicate the presence of dimers and, if present, other oligomers.

While the intensities of most lines in the Raman spectrum decrease with increasing treatment temperature, the line near 225 cm^{-1} shows a total intensity which is almost independent of temperature. This is shown in Figure 3, where the intensity of this line is compared to those of the lines at 88 and 456 cm^{-1} discussed above. For pristine C_{70}, the line at 225 cm^{-1} must be fitted by two sub-lines, near 224 and 229 cm^{-1}. With increasing treatment temperature the relative intensities of these sub-lines change and an additional sub-line appears near 220 cm^{-1} such that the center of the line shifts to lower energy. These observations agree well with

earlier observations for dimers [11] and chains [7]. Although the intensities of the sub-lines change significantly the total intensity of the line complex changes little below 570 K. Above this temperature there is a general drop in intensity for all lines, possibly indicating the beginning of molecular breakdown into amorphous carbon. The complex line near 225 cm^{-1} is the only strong peak in the spectrum which is found to have a practically constant intensity and it is thus quite useful for normalization of the spectra. It should be noted that although this line is quite strong when excited by NIR lasers it is usually weak when excited by visible light.

Finally, the intensity of the complex peak centered near 260 cm^{-1} decreases strongly with increasing treatment temperature. This line must be fitted by three sub-lines, near 252, 259 and 264 cm^{-1}, respectively. While the line near 259 cm^{-1} shows only a weak decrease, and in fact is almost constant over most of the temperature range studied, the two others show a much stronger decrease. The line near 264 cm^{-1} decreases in intensity by about an order of magnitude in the range studied here and might possibly be an indicator for the presence of monomers. Relative to the "normalization" peak near 225 cm^{-1} the total intensity of this peak complex decreases by more than 60% at the highest temperatures. Although the resolution of the spectra given by Lebedkin *et al.* [11] is not very high they give a position of 256 cm^{-1} for this peak for pure dimers, in reasonable agreement with the present result. For chains, the main peak shifts even further down to 249 cm^{-1} [7].

From the results above it can be concluded that two lines are very clear fingerprints for the molecular state, a "monomer" line at 456 cm^{-1} and the dimer stretching mode at 88 cm^{-1}. In addition, three further lines at about 280, 445 and 473 cm^{-1} indicate the presence of dimers. However, these lines may also indicate the presence of other ordered or disordered oligomers or polymers and should be treated with some caution. The sub-line at 264 cm^{-1} mentioned above could possibly also be used as an indicator for the presence of monomers, but because of the difficulty to accurately fit the areas of such sub-peaks it was not seriously considered as a reliable fingerprint. Several peaks at higher Raman shifts could also potentially be used to

identify the presence of dimers. For example, weak new lines are observed to appear near 722, 732 and 1195 cm^{-1}, but the signal-to-noise ratio in this frequency range is too low to give reliable values for their relative intensity and the last two are very close to neighboring peaks and thus suffer from the same problem as the 264 cm^{-1} sub-line. For both dimers [11] and zig-zag chains [7] a new line has also been reported near 968 cm^{-1}, and the strong line at 1564 cm^{-1} is reported to split into two, but neither of these features is observed here. It is possible that these two features depend strongly on excitation energy since neither feature has been observed in other experiments using visible light excitation [13,17,18].

For C_{60}, the relative intensities of dimer and chain stretching modes and the relative intensities of the original and four frequency-shifted components of the "pentagonal pinch" $A_g(2)$ mode can be used to estimate in a semi-quantitative way the relative fractions of monomers, dimers, ordered orthorhombic (one-dimensional chain) and tetragonal (two-dimensional plane) polymers and disordered oligomers as functions of treatment pressure and temperature [8]. The situation for C_{70} is less complicated in the sense that we only expect to find monomers and dimers at 1.6 GPa, but at the same time more difficult because we have no simple way to estimate the relative fraction of monomers and dimers from the shift of a single line.

In an attempt to estimate the relative fractions of monomers and dimers as functions of treatment temperature, the following procedure was used. First, all relevant intensities were divided by the intensity of the 225 cm^{-1} "normalization" line. The resulting normalized intensities for the 456 cm^{-1} "monomer" line were plotted as a function of the normalized intensity of the dimer stretching line, as shown in Figure 4, using data in the range 370 to 500 K. As long as only dimers are produced in the reaction and a negligible amount of material is lost by molecular breakdown into amorphous carbon, there should be a linear relationship between these two intensities. Although the scatter is relatively large, a straight line can indeed be fitted to the data showing that the normalized intensity of the dimer stretching line should be 0.14 when the intensity for the monomer line is extrapolated to zero, i.e., if the sample could be completely converted into dimers, C_{140}.
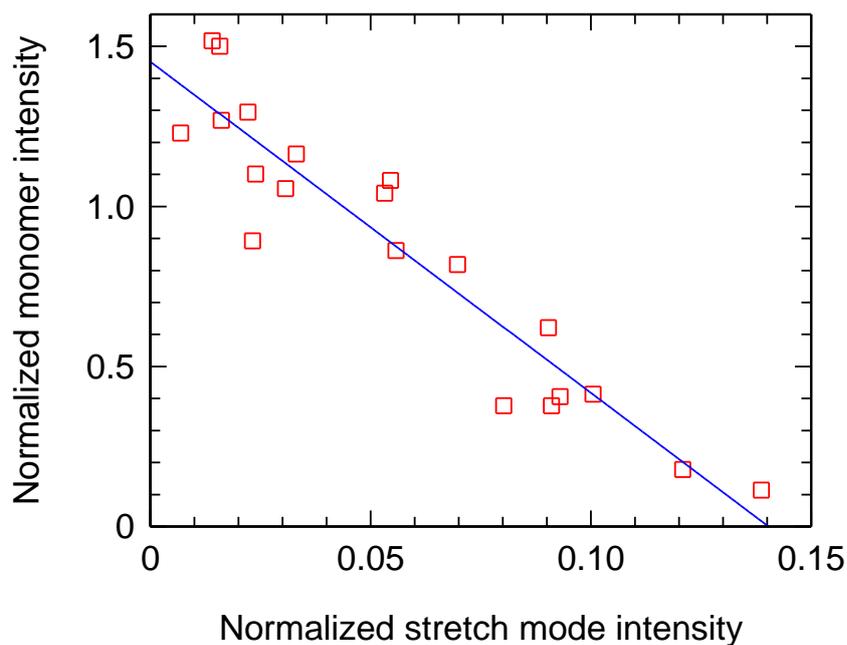
Figure 4. The normalized intensity of the "monomer" mode at 455 cm^{-1} re-plotted as a function of the normalized intensity of the dimer stretch mode at 88 cm^{-1} for treatment temperatures up to 500 K.
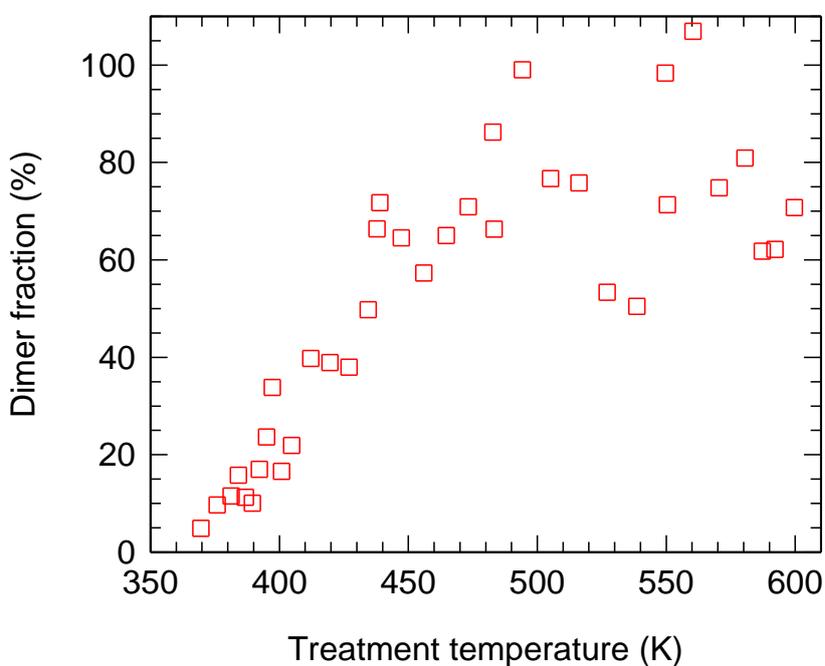

Figure 5. The relative fraction of C_{70} dimers, estimated from the normalized intensity of the dimer stretching mode, as a function of treatment temperature at 1.6 GPa.

The relative fraction of dimers in the sample can now be estimated from the normalized intensity of the dimer stretching mode by simply dividing the normalized intensities by 0.14. The results are shown in Figure 5, where the estimated dimer fraction is plotted as a function of treatment temperature. The dimer fraction increases almost linearly with increasing treatment temperature until it reaches about 80% near 500 K. Above this temperature the scatter in the data is quite large, but the average level is constant or possibly decreases slightly with increasing temperature. The saturation level is surprisingly high considering that dimerization is a random process, but is actually identical to the maximum dimer fraction deduced earlier for C_{60} [8]. The creation and breakdown of dimers at elevated temperature should be an equilibrium reaction, and the long reaction time used might help to maximize the dimer fraction by approaching an ordered, crystalline dimer phase as predicted theoretically for C_{120} [19].

When the starting material is fcc C_{70} and the pressure is below about 5 GPa [3, 5,6], only dimers and monomers are expected to be present after the reaction. It is thus possible to repeat the same calculation for the present sample using instead the normalized intensities for the less well defined "dimer" lines near 280, 445 and 473 cm^{-1}. This procedure yields results practically identical to those shown in Figure 5, except that the scatter is somewhat lower at the highest temperatures because of the higher intensities (better signal-to-noise ratios) of these lines. To further improve the accuracy and reduce the scatter in the data the dimer fraction could thus be calculated as an average over the results found using different Raman lines. A further way to reduce the scatter in the data might be to assume that only monomers and dimers are present and require that the total amount must add up to 100 percent. The use of normalized intensities in the procedure implies that any amorphous carbon formed by molecular breakdown is implicitly corrected for such that we only retain the signals from the fullerene fraction. Another advantage is that any difference in Raman cross section between dimers and monomers is implicitly taken into account in the fitting in Figure 4, and the numerical accuracy is thus in principle higher with this method than when using the relative intensities of the pentagonal pinch mode for C_{60} [8]. Finally, it should always be kept in mind

that Raman scattering is basically sensitive only to the near-surface part of a sample and that the bulk structure and composition could, in principle, be slightly different.

The procedure outlined above should give reasonably accurate quantitative data for the relative fractions of dimers and monomers in solid C_{70}, provided that the starting material has the fcc structure and that the pressure is below 5 GPa. At higher pressures other phases may be created [3,5,6] and it is then essential that "safe" fingerprint lines (such as the dimer stretch mode) are available to identify the phases present. However, for the phases formed at high pressures detailed Raman spectra are still lacking.

4. Conclusions

The results presented above show that treatment of C_{70} at elevated temperatures for 2 h at a pressure of 1.6 GPa results in the conversion of a large fraction of the original material into dimers, C_{140}. The presence of these dimers is clearly proved by the observation of a sharp dimer stretching mode at 88 cm^{-1} in the Raman spectra and, as expected, no other structural phases of C_{70} were observed. The careful handling of all material under darkroom light and the use of an 830 nm NIR laser for excitation ensures that the dimers observed were created by the high pressure treatment at elevated temperature and not by photo-induced dimerization. Raman spectra for the starting material were in excellent agreement with earlier Raman spectra obtained using NIR excitation, and the evolution of the Raman spectra with increasing treatment temperature was also in very good agreement with literature data for both dimers and high-pressure-treated material. However, some lines previously observed for dimers in the range above 900 cm^{-1} are not observed in the present investigation and the intensities of these lines may depend strongly on excitation frequency. Both literature data and the present results show that the A1′ line of pristine C_{70} at 456 cm^{-1} is characteristic for C_{70} monomers only, and the intensities of this line and the dimer stretching line were used to estimate the fraction of dimers in the pressure-treated material. The maximum dimer fraction was found to be about 80%, very close to the maximum dimer fraction observed in a recent investigation of

the intermolecular bonding reaction in C_{60} [8]. Several other new lines were also found to depend linearly on dimer concentration. Because the intensities of these lines are higher than that of the dimer stretching line it might be possible to estimate the dimer fraction with a better signal-to-noise ratio from one of these, or by calculating an average value using both these lines and the dimer stretching mode. The procedure used here implicitly takes into account the actual Raman cross-sections for different modes, laser frequencies and material structures and the method is thus inherently quite accurate. However, it should be remembered that all new lines observed here for the pressure-treated material, except the dimer stretching line, may also exist in other oligomers or polymers of C_{70} and they should thus not be used in the analysis unless dimers are the only reaction product expected.

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