

Research paper

Raman study of the temperature-induced decomposition of the fullerene dimers C₁₂₀K.P. Meletov^a, J. Arvanitidis^{b,*}, D. Christoflos^c, G.A. Kourouklis^c, V.A. Davydov^d^a Institute of Solid State Physics of RAS, Chernogolovka, Moscow Region 142432, Russia^b Physics Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece^c Chemical Engineering Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece^d Institute of High Pressure Physics of RAS, Troitsk, Moscow Region 42092, Russia

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ABSTRACT

Raman spectra of the C₁₂₀ crystalline fullerene dimers, synthesized by high-pressure/high-temperature (HPHT) treatment of the C₆₀ fullerite, were measured at ambient and elevated temperatures ($T > 130$ °C) in order to study the kinetics of their thermal decomposition. Measurements exhibit an intensity decrease of the dimer-related pentagon pinch (PP) mode and an increase of the monomer's one. The relative intensity of the dimer's PP mode decreases exponentially with the thermal treatment time and becomes faster at elevated temperatures. The activation energy E_A of the dimer decomposition, obtained from the Arrhenius dependence of the exponential decay time constant on temperature, is (1.71 ± 0.06) eV.

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1. Introduction

Fullerene polymers are stable at ambient conditions but decompose at elevated temperatures reverting to the monomeric state [1,2]. The traditional studies of the C₆₀ polymers by differential scanning calorimetry (DSC) show that heating at temperatures from 160 °C to 280 °C results in fast destruction of the intermolecular C–C bonds in all known polymeric structures [3,4]. Raman scattering, infrared (IR) absorption and thermal expansion measurements have been used to study the kinetics of the polymer decomposition at elevated temperatures [1,5–9]. In addition, the experimental studies were supported by a number of theoretical calculations of the structure, energetics and vibrational properties of the fullerene oligomers (C₆₀)_N [10–13].

The fullerene C₆₀ polymerizes due to the existence of 30 unsaturated double C=C bonds in the molecular cage. The photo-polymerization of C₆₀ under intense light illumination is due to the creation of covalent bonds among adjacent fullerene molecules via the so-called [2 + 2] cyclo-addition mechanism [14]. Contrary to the photo-polymerization that takes place in surfaces of bulk samples, owing to the small light penetration depth, the HPHT treatment of C₆₀ under various conditions results in the formation of crystalline linear and planar polymeric networks [2,15]. The IR and Raman spectra of the crystalline polymers have been studied

in detail with respect to their crystal structure for samples prepared under carefully controlled conditions of the HPHT treatment [16]. The lowering of the C₆₀ molecular symmetry in fullerene polymers leads to distinct changes in their Raman and IR spectra, related to the splitting of the bands, as well as to their softening due to the decrease of the mean intramolecular bond strength [17]. The spectroscopic identification of the C₆₀ polymers is mainly based on the behavior of the A_g(2) pentagon pinch (PP) mode of the C₆₀ cage, corresponding to the in-phase stretching vibration that involves tangential displacements of carbon atoms with a contraction of the pentagonal rings and an expansion of the hexagonal ones. The PP-mode downshifts in all polymers of C₆₀ due to the decrease of the mean intramolecular bond strength. Its softening depends on the number of the sp³-like coordinated carbon atoms per C₆₀ molecular cage that arise due to intermolecular covalent bond formation. Namely, in the case of C₁₂₀ dimers, this mode downshifts to 1463 cm^{−1} starting from the 1468 cm^{−1} of the fcc crystalline C₆₀ monomer.

The studies of the stability and decomposition kinetics of the crystalline polymers of C₆₀ at elevated temperatures, performed by the use of various experimental methods, show similar results for all polymeric structures except from C₁₂₀ fullerene dimers [3,4,9]. More specifically, the decomposition temperature of dimers synthesized by a solid-state mechanochemical reaction of C₆₀ with potassium cyanide [3,9] differs from that of those synthesized by the high pressure technique that uses as a starting material an organic compound, ET₂C₆₀ (ET – bis(ethylenedithio)

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tetrathianofulvalene) [4,18]. In view of this, further experiments are required to verify the C_{120} decomposition temperature and the related enthalpy value, also reported previously [4].

In this work, we report the results of the decomposition kinetics during thermal treatment of the HPHT crystalline dimers of C_{60} , synthesized in a way similar to that of the HPHT linear and planar polymers [19,20], by means of Raman spectroscopy. The relative intensity of the PP mode of the dimer decreases exponentially with the treatment time and the exponential decay time constant drops with the treatment temperature. At high temperature the destruction of the intermolecular bonds becomes very fast and the dimer decomposition is completed within 25 min at $\sim 170^\circ\text{C}$. From the corresponding Arrhenius plot, a value of $(1.71 \pm 0.06)\text{ eV}$ is deduced for the activation energy.

2. Experimental

The samples of the dimerized state of C_{60} (DS) were prepared by high pressure/high temperature induced polymerization of twice sublimated fine-crystalline C_{60} fullerite powder (99.98 mass% C_{60}) produced by Term USA. The sample synthesis was carried out under conditions of quasi-hydrostatic compression in a high pressure “Maksim” apparatus (piston-cylinder type). The DS samples were prepared at 1.5 GPa, 150°C and 1000 s isothermal holding time. The dimerized high-pressure state was retained at ambient conditions after quenching down to room temperature before pressure release, as suggested by X-ray diffraction (XRD), IR and Raman spectroscopy, and adiabatic vacuum calorimetry characterization. According to IR and calorimetric measurements, the DS samples are a mixture of dimeric (80%) and monomeric (20%) C_{60} molecules. This is further confirmed by our preliminary Raman measurements, where no inclusions of other polymeric forms of C_{60} were detected. The high temperature treatment (HTT) of the C_{60} dimers was performed for 30–400 min at various temperatures up to $\sim 177^\circ\text{C}$ using a high temperature cell with a quartz window. The cell was equipped with a temperature controller unit that maintains temperatures up to 400°C with an accuracy of $\pm 2^\circ\text{C}$ [8,21]. The heating and cooling rates in the temperature range of interest in our experiments are ~ 15 and $\sim 10^\circ\text{C}/\text{min}$, respectively. Raman measurements were conducted in the back-scattering geometry using a LabRam HR or a T64000 (HORIBA) spectrometer. A laser beam at 785 nm was used for excitation, focused on the sample by means of an Olympus $50\times$ long working distance objective at a power below $80\text{ }\mu\text{W}$, in order to prevent laser induced sample heating [22].

3. Results and discussion

Raman spectra of pristine and DS C_{60} , measured at room temperature in the low and high energy regions where the C_{60} related $H_g(1)$, $H_g(2)$, $A_g(1)$, $H_g(7)$ and $A_g(2)$ modes are observed, are shown in Fig. 1. The spectra reveal distinct changes between the DS and the fcc C_{60} monomer state related to the splitting of the degenerate H_g modes and the appearance of new peaks near the non-degenerate $A_g(1)$ and $A_g(2)$ modes. The additional band at 1463 cm^{-1} in the DS sample, near the $A_g(2)$ mode of the C_{60} monomer at 1468 cm^{-1} , is related to the fullerene dimers C_{120} . The dimers content can be inferred by the ratio of the spectral intensity of this band to the total spectral intensity in the frequency region of the PP-mode (dimer fractional intensity). The deduced dimers content in the DS samples is about 80%, although content values ranging between 55% and 90% can be occasionally found. These values correctly quantify the content of dimers in the DS samples as long as the Raman scattering cross-section of the PP-mode does not change significantly due to the creation of the $[2+2]$

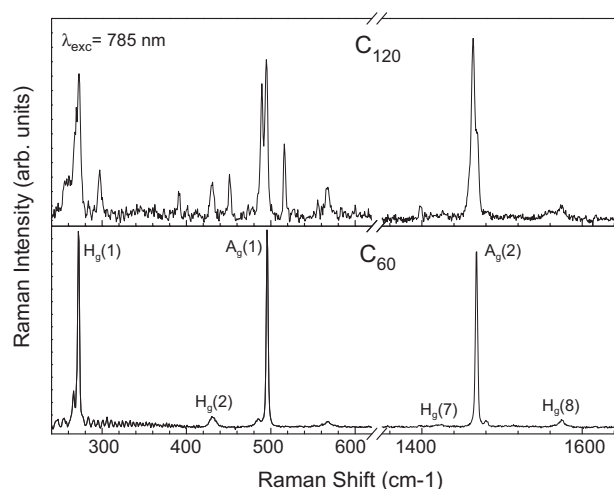


Fig. 1. Raman spectra of the HPHT synthesized dimers (top panel) and pristine C_{60} (bottom panel) measured at room temperature in the frequency region of the $H_g(1)$, $H_g(2)$, $A_g(1)$, $H_g(7)$, $A_g(2)$ and $H_g(8)$ modes, excited at 785 nm with a laser power of $80\text{ }\mu\text{W}$.

cyclo-addition bonds. In any case, the activation energy deduced from the Arrhenius plot (*vide infra*) will not be affected by an alteration in the Raman cross-section upon dimerization.

At ambient conditions, the DS samples are sensitive to light illumination similarly to the pristine C_{60} . Therefore, the laser irradiation during long acquisition Raman experiments may cause further photopolymerization of the DS samples. To examine this possibility we have studied the effect of laser irradiation time on the Raman spectra of the DS samples in the PP-mode frequency region for two laser wavelengths, 515 and 785 nm and the time evolution of the Raman spectra is presented in Fig. 2. The spectra measured with $\lambda_{\text{exc}} = 515\text{ nm}$ at a laser power of $45\text{ }\mu\text{W}$ exhibit initially the typical Raman profile of the DS, however it quickly evolves to that of the photo transformed C_{60} fullerite [23]. On the other hand, the Raman spectra of DS recorded with $\lambda_{\text{exc}} = 785\text{ nm}$ at a laser power of $80\text{ }\mu\text{W}$ do not show any changes, within the accuracy of measurements, for irradiation time as long as 200 min. The different evolution of the DS spectrum upon laser irradiation with the two wavelengths is better illustrated in the top right panel of Fig. 2 which shows the fractional intensity of the PP-mode for the C_{60} monomer with respect to the laser irradiation time.

The kinetics of the DS decomposition upon thermal treatment was studied in a series of Raman experiments in the temperature range from 130 to 177°C . The Raman spectra at various temperatures were measured during HTT up to ~ 500 min, using a new fresh DS sample for each temperature. The spectra were recorded in the frequency region of the PP-mode consecutively with appropriate fixed acquisition time for each temperature using $\lambda_{\text{exc}} = 785\text{ nm}$ and a power of $80\text{ }\mu\text{W}$. Increase of the treatment temperature results in faster destruction of the intermolecular bonds and the total treatment time decreases. Fig. 3 depicts the evolution of the DS sample structure upon 97 min of HTT at 155°C as evidenced in the consecutively recorded Raman spectra in the PP-mode region (inset). In the lower spectrum, recorded at ambient conditions, the PP-mode component of dimers is dominant, indicating a dimer content of nearly 80%. The subsequent spectra recorded at 155°C exhibit an intensity increase of the monomer component at the expense of the dimer one. Eventually, in the Raman spectrum recorded after 97 min of the HTT situation is reversed: the dominant PP-mode component is now that of the monomer and the dimer component becomes negligible. Open circles in Fig. 3 represent the fractional intensity of the dimer

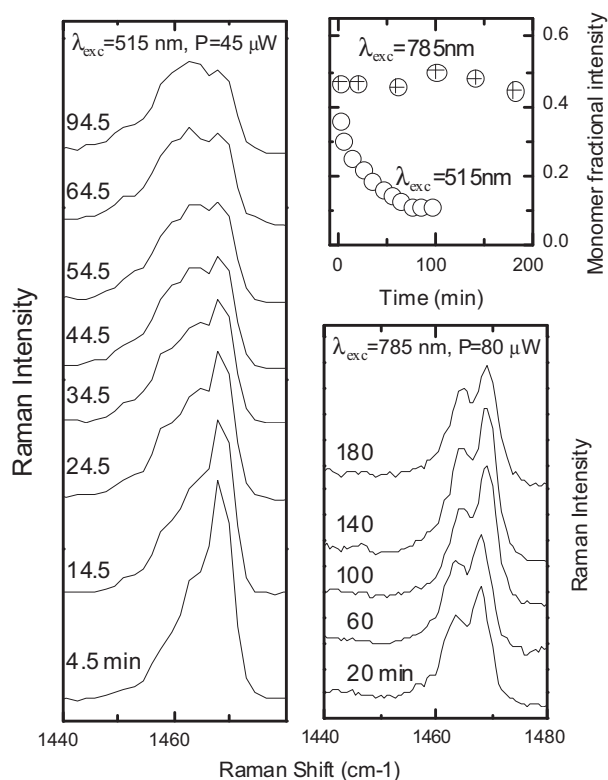


Fig. 2. The time evolution of the Raman spectra of the DS samples measured under various conditions. Left panel: Raman spectra irradiated with $\lambda_{\text{exc}} = 515$ nm and laser power $45 \mu\text{W}$. Right bottom panel: Raman spectra irradiated with $\lambda_{\text{exc}} = 785$ nm and laser power $80 \mu\text{W}$. Top right panel: variation of the fractional intensity of the C_{60} monomers in the DS samples as a function of the laser irradiation time for 515 and 785 nm excitation.

PP-mode component as a function of the thermal treatment time, whereas the dotted line is the fit of the experimental data by an exponential decay function:

$$D(t) = D_0 \times \exp(-t/\tau) \quad (1)$$

where $D(t)$ is the time-dependent content of dimers under temperature treatment, D_0 is the content of dimers in the initial DS samples, and τ is the exponential decay time constant. The dimer decomposition time constant at 155°C is $\tau = 2460$ s.

Fig. 4 illustrates the kinetics of the DS decomposition at various treatment temperatures. Circles represent the experimental data while dotted lines are the fits of these data by the exponential decay function in Eq. (1). The decomposition of DS at 135°C is relatively slow and the content of dimers decreases by a factor of two in 280 min of thermal treatment while the exponential decay time constant is $\tau = 25,140$ s. The decomposition becomes faster for higher treatment temperatures with the time constant decreasing to 7860 s for 145°C and further dropping to 414 s for 177°C . The decrease of the decay time constant with the increase of the treatment temperature indicates the activation-type behavior of the dimer decomposition that is typical for chemical reactions, similarly to other fullerene polymers. We can estimate the activation energy of the dimer decomposition reaction taking into account the Raman data regarding the dependence of the exponential decay time constant on the treatment temperature. This dependence can be described by the Arrhenius equation:

$$\tau(T) = A \times \exp(E_A/k_B T) \quad (2)$$

where E_A is the activation energy (energy barrier between the DS and the monomeric state), k_B is the Boltzmann constant, T is the

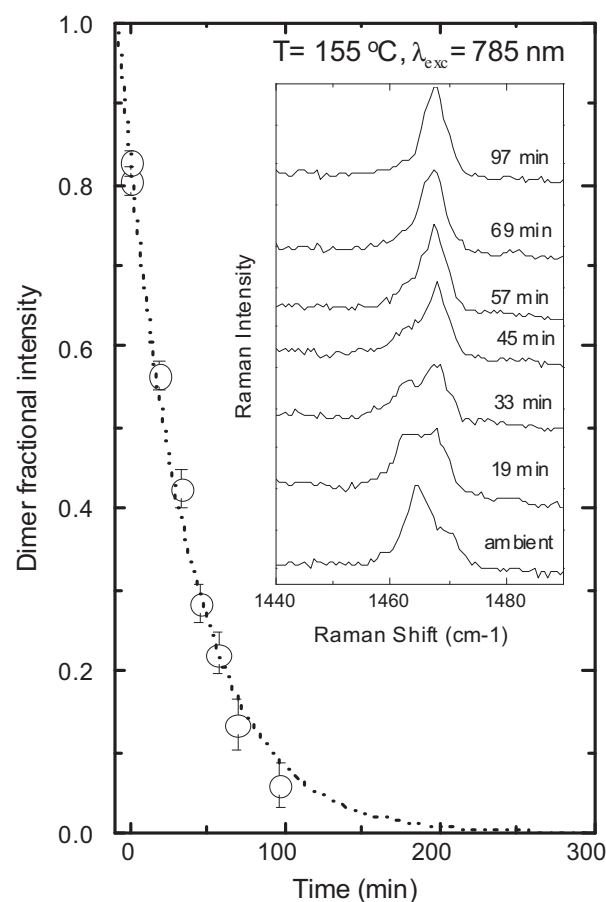


Fig. 3. The fractional intensity of the dimers in the DS sample as a function of the thermal treatment time at 155°C (circles) and the fit of the experimental data by an exponential decay function (dotted line). Inset: evolution of the Raman spectra in the region of the PP-mode during the HTT at 155°C .

treatment temperature and τ the exponential decay time constant. The constant A , related to the characteristic phonon frequency, is measured in time units [9]. The corresponding Arrhenius plot is also included in Fig. 4 as inset. The experimental data exhibit a good linear dependence in logarithmic scale, yielding an activation energy of $E_A = 1.71 \pm 0.06$ eV/molecule. This value is very close to 1.75 ± 0.05 eV/molecule obtained from the XRD thermal expansion measurements of powdered dimer samples synthesized by a solid-state mechanochemical reaction of C_{60} with potassium cyanide [9]. The activation energy of the dimer decomposition is close to the activation energies of the 1D and 2D polymers decomposition, $E_A = (1.9 \pm 0.1)$ eV/molecule, obtained earlier by thermal expansion measurements of these materials [9]. In addition, the activation energy of the 2D rhombohedral [2D-R] polymer decomposition $E_A = (1.76 \pm 0.07)$ eV/molecule obtained in Raman measurements is almost the same as that of the dimer decomposition [8]. Note that the theoretically predicted dimer dissociation energy barrier calculated by a density-functional based non-orthogonal tight-binding [DF-TB] method yields values between 1.6 and 1.9 eV for two different paths of the [2 + 2] cyclo-addition bond dissociation [13]. Similar calculations performed using the tight-binding carbon-carbon potential for the 2D-R polymer yields a dissociation energy barrier of 1.6 eV/molecule [24]. Another theoretical calculation of the dissociation energy barrier for the 2D-R polymer yields a value of 1.7 eV/molecule [25]. Thus, the activation energy of the dimer decomposition obtained in the present work and those experimentally obtained earlier for the dimers (XRD)

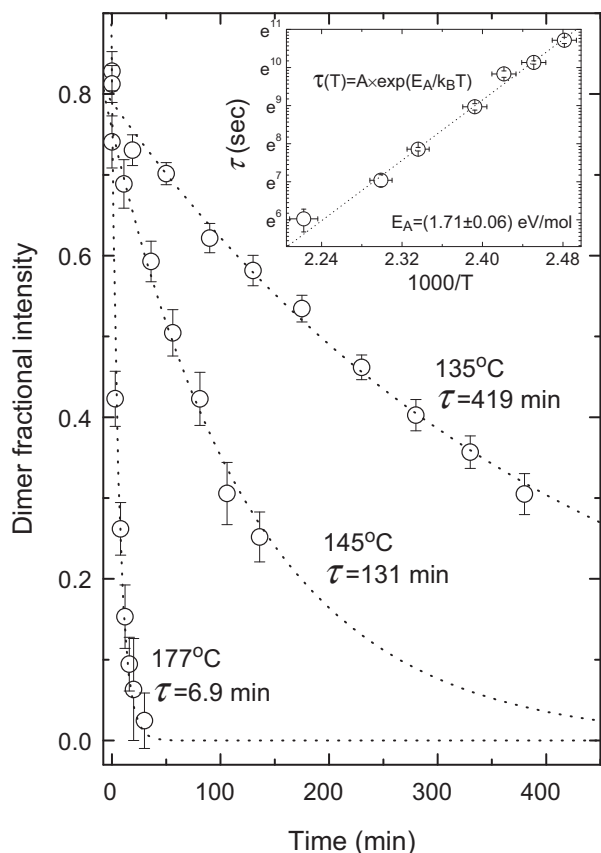


Fig. 4. Time dependence of the fractional intensity of the dimers at 135, 145 and 177 °C treatment temperatures (circles) and the fit of the experimental data by exponential decay functions (dotted lines). Inset: Arrhenius dependence of the exponential decay time constant on the treatment temperature.

and 2D-R polymers (Raman) are in good agreement with the theoretically calculated values.

It is interesting to compare the experimental data related to the dimers decomposition obtained by DSC measurements [3,4] with those obtained in the present work and in Ref. [9]. The DSC study of dimers synthesized by a solid-state mechanochemical reaction of C_{60} with potassium cyanide performed at a rate of 1 °C/min exhibits an endothermic peak centered at 162 °C. In addition, these dimers were found to dissociate totally by heating their solution at 175 °C for 15 min [3]. Using the values for the activation energy E_A and the constant A obtained from the Arrhenius plot of Fig. 4, we calculated the temperature at which the dimers content drops to 1% within 15 min of thermal treatment to be ~ 180 °C. This temperature is in good agreement with Ref. [3], as well as with the corresponding data obtained in Ref. [9]. Nevertheless, it differs a lot from the value of ~ 280 °C obtained by the DSC measurements of dimers synthesized by a high pressure technique that uses the organic compound Et_2C_{60} as the starting material [4].

According to the DSC measurements, the total energy minimum related to the fcc monomeric state of C_{60} is higher than the total energy minimum related to the polymeric structures of C_{60} [4]. The stability of the C_{60} monomer at ambient conditions is due to the energy barrier that separates the polymeric and the monomeric states. The height of the barrier from the polymer side is the activation energy of the polymer dissociation whereas the barrier height from the monomer side is the activation energy of the polymerization reaction. The difference between these two values is the enthalpy of polymerization reaction that can be determined by DSC experiments directly from the endothermic peak area.

The enthalpy of the 2D-R polymer dissociation obtained by DSC experiments in Refs. [4,6] is about ~ 0.13 eV/molecule and ~ 0.11 eV/molecule, respectively, while the deduced enthalpy of the dimer dissociation is 0.7 eV/molecule [4]. We can estimate the enthalpy of the dimers dissociation taking into account that the activation energy of the HPHT synthesis of dimers was found $E_A = (1.39 \pm 0.06)$ eV/molecule [19]. The activation energy of the HPHT dimer dissociation obtained in the present work is $E_A = (1.71 \pm 0.06)$ eV/molecule, resulting in a dissociation enthalpy, defined as their difference, of $\Delta H = (0.32 \pm 0.06)$ eV/molecule. This value is considerably smaller than that reported in Ref. [4], but it agrees very well with the cohesive energy of the dumb-bell dimers of C_{60} , 0.32 eV, theoretically calculated by the DF-TB method [13].

Summarizing, the Raman spectra of the HPHT DS of C_{60} measured at temperatures higher than 130 °C show a gradual decomposition of the dimers to C_{60} monomers that becomes drastically faster for thermal treatment at 177 °C. The decomposition of DS under HTT is characterized by the exponential decrease of the dimer content with the treatment time, as well as by the decrease of the exponential decay time constant with treatment temperature, indicating the activation-type behavior of the dimer decomposition. The dependence of the decay time constant on the treatment temperature is well described by the Arrhenius law that gives the activation energy of the dimer decomposition reaction as $E_A = (1.71 \pm 0.06)$ eV/molecule. The HPHT dimers dissociation enthalpy, defined as the difference between the activation energy of dimer decomposition and the activation energy of the dimer creation, is $\Delta H = (0.32 \pm 0.06)$ eV/molecule. The experimentally obtained values agree very well with those calculated theoretically on the basis of the DF-TB method for the dumb-bell dimers of C_{60} [13].

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