

Nonresonant Raman spectrum of C_{60} nanopeapod: C_{60} polymerization effects

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We present a force constants model for the vibrational modes in C_{60} dimer and polymer phases. The results of this model are used to calculate the nonresonant Raman spectra of infinitely long isolated C_{60} dimer and polymer peapod in the framework of bond-polarization theory by using the spectral moment's method. The changes of the Raman spectrum in terms of the structure of the C_{60} molecules inside the nanotubes are identified. We show that the lowest Raman frequency region of the nanotube is more affected by the C_{60} chain insertion in comparison with the higher one.

Keywords: nanopeapod, Fullerene, Raman spectroscopy, nanotube, spectral moment method.

I. INTRODUCTION

New forms of carbon such as fullerenes and single-wall carbon nanotubes (SWCNTs) have been attracting considerable interest for a number of years [1]. It has been experimentally shown that fullerenes can be inserted into SWCNTs, forming a peapod-like structure. Electron microscopy images [2] of peapod have revealed the one-dimensional character of the C_{60} chain inside the carbon nanotube. The formation mechanism of the peapods has not been completely comprehended [3, 4], and the structure of C_{60} chain inside the nanotube is not yet well known in the precision limit of the present experimental facilities. So, in order to understand the peapod properties, it is necessary to study the structures of the C_{60} molecule chain within the nanotubes. Experiments [5–7] correlated with recent calculations [8–10] have stated that the center-to-center distance between two C_{60} s in peapods is smaller than in three-dimensional crystals but larger than in solids based on polymerized fullerenes. High resolution transmission electron microscopy (HRTEM) observations have stated that C_{60} s can be unequally separated [11, 12].

The successful synthesis of practically pure samples of dimers (D), orthorhombic (O) 1D chain, tetragonal (T) and rhombohedral (R) 2D lattices by HPHTT allowed investigation of their structure and of their irrational dynamics by using Raman and infrared spectroscopy [13, 14]. A number of theoretical works [15–17]

have been investigated the phenomenon of C_{60} dimerization. These publications have established that the most energetically favourable bonding between two C_{60} molecules is accomplished by a [2+2] cycloaddition reaction which leads to nearly rigid molecules that are bound by a four membered square ring. Due to this remarkable property of the C_{60} s molecules to form covalent bonds through different routes, an orthorhombic structure phase can be formed, in which the C_{60} molecules form linear polymer chain [18–20]. In recent years, a variety of theoretical methods have been applied to the calculation of internal modes of C_{60} polymer material: *ab initio* calculations [21], tight binding hamiltonian models [22] and force constant model [23]. In the last model, introduced by Shober *et al.*, the on-ball C-C interactions are calculated using a force field proposed by Jishi *et al.* [24]. The covalent inter-cage bonds were modelled by a longitudinal force constant (f.c) and two angular f.c. Force constants were fitted only to produce the low frequency [0,25 meV] Global Density Of State (GDOS) obtained from inelastic neutron-scattering measurements of samples of RbC_{60} in its dimer and polymerized phases. Although this force constants model provided a good fit to the low frequency lattice, the high frequency region where the intramolecular vibrations are concerned was not analyzed. To obtain a good fits of these parameters, in this work, a slight modification will be made on the

force constants model in order to fit both the density of state and Raman-active modes in C_{60} dimer and polymer phases.

Raman spectroscopy has been demonstrated to be a key technique to study structural changes in C_{60} as well as in SWCNT. Recently Raman measurements of a synthesized peapod have been performed [25]. The authors recorded Raman spectra at helium temperature to derive the peapods response before polymerization. A new Raman active mode located at 90 cm^{-1} which is close to the interball C_{60} dimer mode, was observed at low temperature. In our previous work, within the bond polarizability model, the nonresonant Raman spectra of linear and zigzag chain of C_{60} s monomers inside SWCNTs have been calculated [26]. We have shown that the splitting of the non degenerated radial breathing-like mode that was experimentally observed in real peapods samples can be related either to a low C_{60} filling factor or to the presence of zigzag C_{60} chains inside the nanotubes. In this paper, we present the results of lattice dynamic calculations of Raman spectra of peapods made from a dimer structures for the encapsulated C_{60} chain. After a brief description of the model used to compute the Raman spectra of the nanopeapods (section II), we present the force constants model within which the vibrational normal modes of the C_{60} dimer and polymer are calculated.

II. MODELS AND METHODS

The geometry of C_{60} dimer molecule can be obtained by joining two C_{60} molecules by parallel double bonds. Other orientations and relative connections between molecules would be possible in principle, but previous calculations have shown that they are either energetically unfavourable with respect to [2,2] cycloaddition [15, 21] or, in the case of single bonded chains, stabilized only by doping anions [27]. The carbon atoms participating in the [2,2] cycloaddition are shifted in such a way as to change the bond lengths of this for-C ring to 0.15 nm and 0.153 nm for intrafullerene bonds and 0.153 nm for interfullerene bonds. The formation of intermolecular bonds reduces the geometric symmetry of individual C_{60} from I_h to D_{2h} . In order to calculate the C_{60} dimer and C_{60} polymer dynamical matrix, a slight modification has been made in the force constants employed previously by Shober *et al* [23]. These modifications are made in order to remedy some deficiencies revealed in Raman spectroscopy. The SWCNT C-C intratube interactions are described using a force constants model

formally introduced by Saito [28]. This model was previously used in our group to calculate the Raman spectra of isolated single wall carbon nanotubes with finite length [29].

The calculations were performed using a Lennard-Jones potential,

$$U_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right],$$

to describe the van der Waals interactions between both adjacent fullerene molecules and fullerenes and the surrounding nanotube. The values of the Lennard-Jones parameters were chosen

$\sigma = 3.407\text{ \AA}$ and $\epsilon = 0.002964\text{ eV}$ and these values have recently been found to describe correctly the van der Waals contribution to the C_{60} bulk cohesive energy [30]. To derive the elements of the dynamical matrix, we used a van der Waals cut-off radius of 0.74 nm.

The optimal fullerene-fullerene gap is calculated by minimization of the Lennard-Jones inter fullerene and fullerene-nanotube interactions. We found a gap around 1.0 nm for all optimised peapods. This value is in good agreement with the previously reported peapod interball separation of 0.97 nm from electron-diffraction profiles [31] and 0.95 nm from high-resolution transmission electron microscopy (TEM) data [32]. Calculations of the Raman spectra, before and after the energy minimization, with respect to the relative Euler angles of rotation, do not show any significant difference in the mode frequencies.

The intensities of the Raman lines were calculated within the empirical non-resonant bond polarisability model [33]. Raman spectra are calculated using direct diagonalization of the dynamical matrix for small samples (few hundreds atoms) and the spectral moments method (SMM) [29, 34] for larger ones. For small samples, both approaches lead exactly to the same position and intensity for the different peaks.

I. RESULTS AND DISCUSSION

In this section, first, we are interested in lattice dynamical model of C_{60} in the dimer and polymer states, we present the adjusted force constants for the dimer and polymer models. Next, we report the results of calculated Raman spectra for infinite isolated SWCNTs filled with C_{60} dimer chain. In all our calculations, we consider the Z direction as the nanotube axis direction, the Y direction as the light

propagation direction, and a carbon atom is along the X axis of the nanotube reference frame. We use ZZ, ZX and XY polarization geometries, where the letters indicate the polarization direction of the (incident, scattered) light.

1- C₆₀ dimer and polymer phases force constants models

Any phenomenological lattice dynamical models are usually determined via fitting to available experimental data on the

Model	Stretching	Value	Bending	value
D ₀	S _p	3.95	a _p	1.0
	S _h	2.30	b _h	0.25
	S ₂	1.21	b	0.095
	S ₃	-1.05	c	0.235
D	K _{str}	2.1	K ₁	0.36
			K ₂	0.34
P	K _{str}	4.0	K ₁	0.8
			K ₂	0.7

Table 1: Force-constant parameters for intrafullerene bonds (D₀ model). D1 and P models represent interfullerene dimer and polymer force-constants respectively. The bond stretching force constants are expressed in mdyn/Å, whereas the angle-bending force are expressed in mdyn Å/(rad)².

to the low frequency part of the GDOS measured for a RbC₆₀ dimer and polymer samples. The force constants values (model D1 and P1) of the cycloaddition bonds are given in table II of reference [23]. The structure of RbC₆₀ used in the calculations was not optimized. Of particular interest is the shift of about 10 wave numbers from 1469 cm⁻¹ in the pristine solid of C₆₀ to 1459 cm⁻¹ in the phototransformed material. Within a bond polarization model and using the force constants of Shober, Raman active modes in dimer and infinite polymer chain are calculated. No shift is obtained for either optimized or no optimized structures. To remedy these deficiencies, since the bond length of carbon atoms participating in the [2+2] cycloaddition are changed after dimerization, a slight modification has been made to the force constants employed both for on ball C-C (D0 model) and C-C interfullerene interactions (D model for the dimer and the P model for the polymer), otherwise our model is unchanged in the sense that we consider the same set of parameters. The adjusted force constants, in the same units as the Born von Karman force constants of Jishi, that we have used to obtain the best fit to the experimental Raman data are given in table 1. We use the same units as the Born von Karman force constants of Jishi for the bond stretching (mdyn/Å), and the angle-

same or similar structures. To obtain a good approximation description of the phonon modes in C₆₀ dimer and polymer states, it is necessary to start with an accurate model for the phonon modes in isolated C₆₀ molecule. Shober *et al* have been used a force constants model of Jishi [24] to describe the interfullerene interactions. The inter-cage bonds were modelled by a longitudinal force constant (f.c) and two angular f.c. Authors fitted only the two interfullerene (f.c)

bending force (mdyn/(rad)²). The profile of the Density Of States (DOS) calculated using the new set of force constants is displayed in figure 1. The comparison between the experimental [23, 35] and calculated GDOS shows a very good description of the principal experimental GDOS. The new intermolecular modes between 10 and 22 meV which corresponds to translational and librational inter-ball modes are well reproduced by intermolecular covalent bonds.

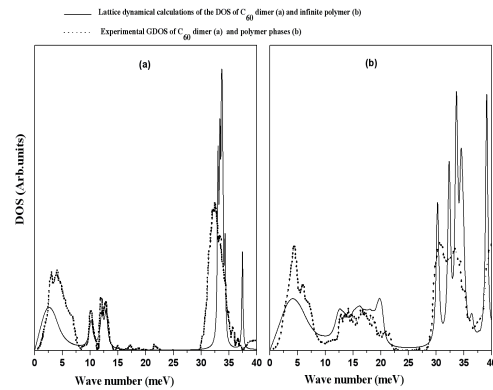


Figure 1 comparison between lattice dynamical calculations and experimental density of states (DOS) of C₆₀ dimer (curve a) and infinite polymer (curve b).

Concerning the Raman spectra obtained for the C_{60} dimer and infinite chain, and using our corrected model together with the bond-charge polarizability model and C_{60} polarizability parameters of Snoke and Cardona [36], we have computed the parallel polarized Raman spectra for C_{60} dimer and infinite polymer chain (figure 2). The calculated shift is of particular interest, as shown in Figure 2, for the peak which, in C_{60} , is the high-frequency $A_g(2)$ mode. This shift is from 1468 cm^{-1} in C_{60} to 1458 cm^{-1} for the dimer and to 1439 cm^{-1} in the infinite chain. The calculated 10 cm^{-1} shift in going from C_{60} to the dimer agrees well with the observed shift of 10 cm^{-1} in going from pristine solid C_{60} to the photopolymerized solid [37, 38] and obtained by *ab initio* calculations [21]. The $H_g(8)$ mode is also downshifted from 1582 cm^{-1} to 1580 cm^{-1} . But in the experiment finding is a 6 cm^{-1} downward shift for this peak. The $H_g(1)$ mode at 270 cm^{-1} in C_{60} , exhibits a clear splitting into 265 cm^{-1} , 272 cm^{-1} and 301 cm^{-1} (242 cm^{-1} , 270 cm^{-1} , 280 cm^{-1} and 348 cm^{-1}) in C_{60} dimer (infinite polymer chain). Experiment [37] shows a peak at 270 cm^{-1} for pure C_{60} , and peaks at 301 , 271 , and 258 cm^{-1} for the photopolymerized material. For the $A_g(1)$ peak, the experiment shows no shift for this mode. In the dimer, we obtain no shift for this peak whereas we calculate a downshift by 5 cm^{-1} for the infinite chain. For the other peaks, $H_g(2)$, $H_g(3)$, and $H_g(4)$, our agreement with experiment is qualitatively good, but the multiplicity of splitting makes the agreement difficult to quantify. Concerning the new low-frequency modes (in the $0\text{-}200 \text{ cm}^{-1}$), observed in the Raman spectra, There are the inter-ball modes which, in pristine face-centred-cubic solid C_{60} , appear only through the Van der Waals interaction. In the dimer, there are three modes at 106 , 99 , and 82 cm^{-1} . The most Raman active of the three modes is at 86 cm^{-1} which is the analogue of the stretching mode in diatomic molecules. This inter C_{60} Raman active stretching bond mode has been recently observed at approximately 90 cm^{-1} [39] for a C_{60} linear polymer chain. Previous theoretical calculations determined its frequency between 69 cm^{-1} [21] and 101 cm^{-1} [22]. In the infinite chain there are five modes in this range at 77 , 78 , 100 , 122 and 135 cm^{-1} . However, in experiment, only a new active mode at 118 cm^{-1} was found [37, 38].

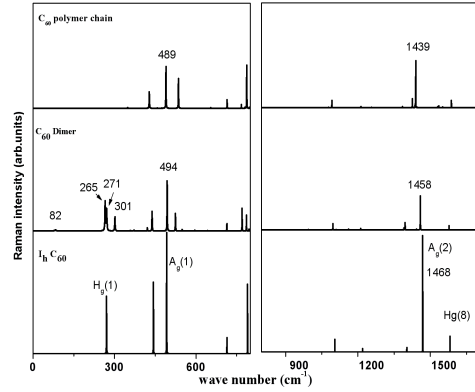


Figure 2: The calculated polarized ZZ Raman spectra of C_{60} monomer, C_{60} dimer, and infinite C_{60} polymer. Spectra are displayed in lower (left) and higher (right) frequency region.

1- Polarized Raman spectra of infinite crystal of single C_{60} dimer and polymer nanopeapod

After studying the structure and the force constants model of the isolated C_{60} polymer chain, we studied the combined system of a C_{60} polymer chain together with the encapsulating SWCNT. Recently we have studied the optimum configurations of C_{60} molecules inside single wall carbon nanotubes (SWCNTs) [26], we found a linear or zigzag C_{60} monomer chains inside the nanotubes depending on the diameter of the nanotube host. The same behaviour can be expected in the case of C_{60} polymer chain inside SWCNT. In this work we restrict ourselves to cases where the linear C_{60} s polymer chains are positioned exactly in the nanotube axis. We deal with the case of completely filled nanotubes. The only SWCNTs that come into consideration are the ones which have a diameter between 1.25 and 1.4 nm .

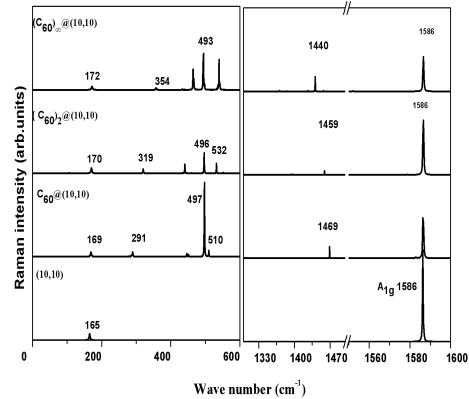


Figure 3: The calculated ZZ polarized Raman spectra of the infinite $(10,10)$ SWCNT and their corresponding infinite C_{60} n -mer ($n=1$ (monomer), $n=2$ (dimer) and $n=\infty$ (polymer)) peapods.

The calculated ZZ polarized Raman spectra of the infinite SWCNT (10,10), and their corresponding nanopeapod ((C₆₀)_n@(10, 10)) (n=1 (monomer), 2 (dimer), and ∞ (polymer)) are depicted in Figure 3. We show that the RBLM of SWCNT shows an upshift for all infinite filled (C₆₀)_n@(10,10) from 165 cm⁻¹ to 169 cm⁻¹, 170 cm⁻¹ and 171 cm⁻¹ for n = 1, n = 2 and n=∞ (infinite polymer chain) respectively. Around the C₆₀ Ag(1) mode, one can distinguish two strong components for all considered C₆₀ n-mer peapods. The position of the highest (lowest) component shifts from 510 cm⁻¹ (498 cm⁻¹) in infinite C₆₀ monomer peapod to 538 cm⁻¹ (493 cm⁻¹) in the infinite C₆₀ polymer peapod. In the low energy Raman spectra, for the infinite C₆₀ dimer nanopeapod, one can see a shift from 82 cm⁻¹ in C₆₀ dimer to 103 cm⁻¹ in infinite (C₆₀)₂@(10,10) peapod. Finally, in the high frequency range, we show that the tangential like modes (TLM) are not or slightly affected for all considered peapods structures, in contrast with the radial breathing-like modes (RBLM).

ii.

CONCLUSION

In conclusion, we have presented a force constants model for calculating the irrational frequencies in C₆₀ dimer and polymer phases. This model is used to calculate the polarized nonresonant Raman spectra of infinite SWCNT's encasing linear chain of C₆₀ dimer and infinite polymer molecules. We found that the polymerization of the peas has no significant effect on the RBLM mode in C₆₀ peapods. Furthermore, the totally symmetric C₆₀ Ag(1) mode exhibits a clear splitting in the C₆₀ dimer and polymer peapods. The new Raman active mode located at 90 cm⁻¹ obtained experimentally can be explanted in our model, by a dimerization of C₆₀ molecules inside nanotubes.

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