

Vibrational properties of semitrimer picotubes

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The semitrimer picotube is a ring-shaped hydrocarbon closely related to a very short (3,3) carbon nanotube. We study the vibrational properties of the semitrimer by means of Raman spectroscopy and find the structural similarity to nanotubes to be reflected also in the vibrational spectra. In particular, combining polarization-dependent Raman measurements and *ab initio* calculations we can identify a fully symmetric vibration corresponding to the radial breathing mode in nanotubes.

1. INTRODUCTION

The interest in carbon materials increased rapidly since the discovery of carbon nanotubes with their remarkable properties [1]. This field of research was widened in 1996 by the synthesis of the tetramer picotube, a highly symmetric hydrocarbon, similar by structure to a (4,4) nanotube [2]. In 2006, the picotube family was extended: the semitrimer was synthesized. This picotube resembles a short (3,3) nanotube, whereas the symmetry is reduced compared to the tetramer. The synthesis of the picotube molecules represents a milestone in organic chemistry. They were the first ring-like hydrocarbon compounds with fully conjugated *p* orbitals which are oriented radially. In the following we concentrate on the study of the semitrimer.

As the optical and electronic properties of carbon nanotubes strongly depend on the chirality of the tubes, selective growth is one of the great goals in nanotube research [1]. The self-organization methods currently used do not achieve satisfying results in this respect. Pico-

tubes seem to be a promising starting point for the specific synthesis of nanotubes [4].

Furthermore, the study of picotubes can lead to a deeper understanding of small nanotubes. Properties of large nanotubes can be well approximated from graphene. At smaller diameters however, this approach does no longer describe electronic and optical properties correctly [1]. In contrast, picotubes show the same curvature effects as small nanotubes, which is of great use for the study of the electronic structure [6].

In this Letter, we present vibrational properties of semitrimer crystals. Our Raman measurements show similarities to the spectra of tetramer picotubes and single-walled nanotubes. The equivalencies include features in the high-energy region at around 1600 cm^{-1} as well as the appearance of a radial breathing-like mode, which can be identified by comparing the measurements with *ab initio* calculations. Polarization-dependent measurements allow us to obtain the symmetries of the main peaks.

2. EXPERIMENTAL AND COMPUTATIONAL DETAILS

For our measurements we used semitrimer crystals, which in contrast to tetramer crystals do not seem to have a characteristic shape [6]. The synthesis and crystallisation procedure as well as a detailed discussion of the atomic structure will be reported elsewhere [7]. We recorded micro-Raman spectra in backscattering geometry using a He-Ne laser at an excitation wavelength of 633 nm and a single-grating spectrometer [8]. Our experimental setup allowed a resolution of $4\text{--}5\text{ cm}^{-1}$. The polarization-dependence was studied by rotating the sample under parallel and crossed polarization of the incoming and outgoing light. All measurements were performed at room temperature and under ambient pressure.

Apart from the Raman experiments, the vibrational properties of the semitrimer have been subject to *ab initio* calculations, which were performed with the electronic structure program *Gaussian03* [9]. A B3LYP functional was used along with a $6\text{--}31\text{ G (d)}$ basis set.

3. RESULTS AND DISCUSSION

The atomic structure of the semitrimer is shown in Figure 1 [7]. With a reflection plane being the only symmetry operation, the molecule belongs to the symmetry group C_s , also referred to as C_{1h} in the literature. The dynamical representation can be decomposed as $87 A' \oplus 87 A''$, including translations and rotations. From group theory, all normal modes are expected to be Raman active [10].

A non-polarized Raman spectrum of a semitrimer crystal is shown in Figure 2. The lower symmetry of the structure compared to nanotubes or tetramer crystals results in a wealth of Raman peaks. The most intense feature appears at around 1600 cm^{-1} , which is typical for sp^2 carbon compounds. Each of the two main peaks in this band consists of two modes, located at 1592 and 1602 cm^{-1} for the less energetic peak and accordingly at 1633 and 1640 cm^{-1} for the high energetic one. The high-energy band shows strong similarity to the one in the tetramer Ra-

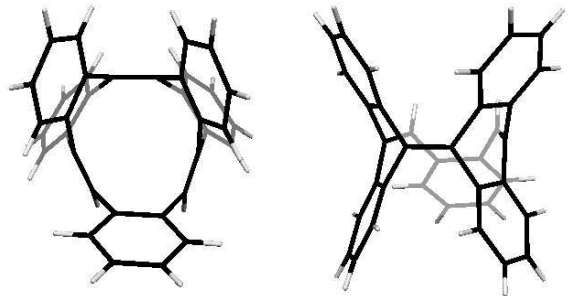


Figure 1. (a) The semitrimer molecule as seen from the top taken from x-ray measurements. Foreground (Background) carbon-carbon bonds are indicated black (dark grey). (b) Lateral view of the same molecule [7].

man spectrum, where two modes could be resolved at 1592 and 1601 cm^{-1} [6]. Further analogies in the spectra of the two picotube species are observed in the region between 1000 and 1500 cm^{-1} . The most prominent peaks in this range of the semitrimer spectrum are found at 1027 and 1138 cm^{-1} , whereas the frequencies of the possible counterparts in the tetramer spectrum are 1056 and 1131 cm^{-1} . Several peaks between 1200 and 1400 cm^{-1} bear additional similarity between the vibrational spectra of both picotubes. All peaks described above correspond to in-plane vibrational modes.

One feature of great interest is found in the low-energy region. Besides a set of peaks of considerably smaller intensity compared to the ones discussed above, especially the peak at 314 cm^{-1} caught our attention. It can be assigned to a radial breathing mode, as described in detail below.

In order to determine the symmetry of the measured modes, we recorded polarization-dependent Raman spectra. Figure 3 shows the dependence of the Raman intensity on the angle between the polarization of the exciting laser light and a fixed crystal axis for the mode at 314 cm^{-1} . Since there is no characteristic shape of the semitrimer crystals, this fixed axis is just defined by the coincidental initial orientation of the sample and there-

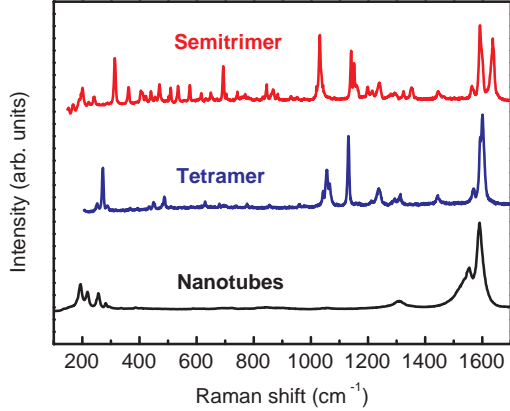


Figure 2. Unpolarized micro-Raman spectra of a semitrimer crystal, a tetramer crystal, and single walled carbon nanotubes (top down) [6].

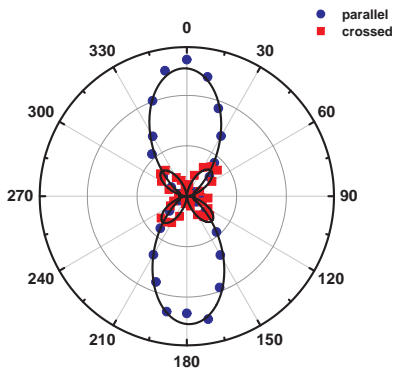
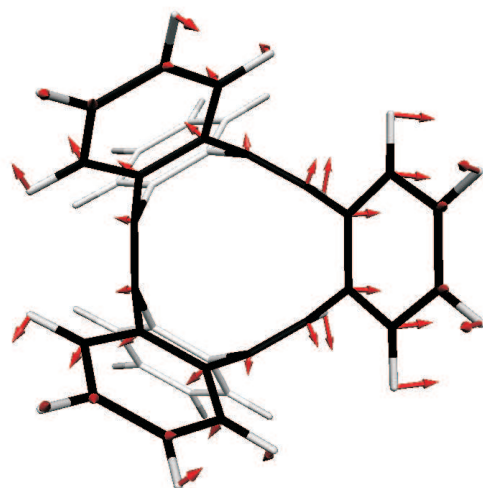


Figure 3. Raman intensity of the mode at 314 cm^{-1} as a function of the angle between the polarization of the incident light and a fixed crystal axis. Blue dots correspond to parallel polarized incident and scattered light, red squares to perpendicularly polarized incident and scattered light. Black lines are fits to our model for an A_1 mode.

fore in principle not related to any symmetry axis, which has to be taken into account when modeling the Raman intensity. The polarization dependence of the intensity shows a twofold symmetry in the case of parallel polarized incident and scattered light (blue dots) and a fourfold symmetry, when the scattered light is perpendicularly polarized with respect to the incoming laser (red squares). These characteristics are in general described by an A_1 Raman tensor. We calculated fits to our experimental data in analogy to the procedure described in Ref. [6]. The method will be discussed in more detail in Ref. [7]. Figure 3 demonstrates the excellent agreement of our model to the measured values. In this case, the intensity was calculated using the A_1 Raman tensor. We thus find the peak at 314 cm^{-1} to correspond to a fully symmetric vibrational mode. In the same way, the symmetry of the main modes in the semitrimer Raman spectrum can be determined. The most intense peaks correspond to A_1 modes.

To assign the measured modes to atomic displacement patterns, *ab initio* calculations were performed. Focusing again on the low-energy region, we find only one suitable candidate to correspond to the mode at 314 cm^{-1} . In this frequency range, a single A_1 mode is found at 313 cm^{-1} . Concerning this mode, the calculations reveal the atoms to vibrate in phase predominantly in radial direction with respect to the main axis of the molecule (see Fig. 4). Hence, we found a mode very similar to the typical radial breathing mode in carbon nanotubes. This is a remarkable result, since the semitrimer structure and symmetry deviate considerably from those of a closed tube. Our *ab initio* calculations for a (3,3) carbon nanotube, which is the corresponding closed structure to the semitrimer, show the radial breathing mode at a frequency of 545 cm^{-1} . Using the experimentally determined diameter dependence of the radial breathing mode frequency, we obtain a value of 531 cm^{-1} in good agreement to our calculations [11]. The shift of the breathing mode to higher energies in nanotubes is due to the much higher symmetry and rigidity of the closed tubes. Comparing tetramer molecules with (4,4) nanotubes, we observe the same effect with a very



Calc. 313 cm^{-1}

Exp. 314 cm^{-1}

Figure 4. Calculated phonon eigenvector of the radial breathing mode in the semitrimer with calculated frequency as well as assigned experimental frequency. For clarity, bonds in the foreground (background) are presented in black (gray) and the atomic displacement arrows of the atoms in the background are omitted.

similar relative energy shift [6]. The appearance of a breathing-like mode, however, again reflects the strong similarity between picotubes and nanotubes.

4. SUMMARY

We presented an experimental and theoretical study of the vibrational properties of semitrimer picotubes. Strong similarities were found in the Raman spectra of the two picotube species semitrimer and tetramer as well as in the spectra of picotubes and carbon nanotubes. *Via* polarization-dependent Raman spectroscopy, we determined the symmetry of the modes in the semitrimer spectrum. Furthermore, comparing

experimental data with *ab initio* calculations allowed us to assign vibration patterns to the Raman peaks. The most striking result in this respect is the appearance of a radial breathing-like mode.

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