

Vibrational properties of four consecutive carbon picotubes

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Four different picotubes have been synthesized up to now. These highly symmetric, ringlike hydrocarbons are closely related to the smallest armchair nanotubes available. We investigate vibrational properties of the different picotubes using first principles calculations and polarization-dependent Raman spectroscopy. Our results emphasize the strong relationship between picotubes and nanotubes.

In this context, two features in the picotube spectra are of particular interest: The high-energy bands and breathing-like modes. Vibrational patterns calculated for the high-energy modes of picotubes are similar to the axial and transversal high-energy vibrations of armchair nanotubes. Concerning the radial breathing modes of picotubes, our calculations suggest a d^{-1} -dependence of the radial breathing mode (RBM) frequency, which is again in analogy to nanotubes.

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1 Introduction Carbon nanostructures developed as a key issue in the physics community since the discovery of fullerenes and carbon nanotubes. Beginning in 1996, the synthesis of picotubes established a new class of highly interesting nanostructures. The first picotube to be synthesized was the tetramer molecule [1]. Its structural similarity to a (4,4) carbon nanotube was shown to be reflected on the electronic and vibrational properties [2]. Next on the scene were the semitrimer, corresponding to a (3,3) armchair nanotube and Kammermeierphane, a substructure of a (5,5) nanotube [3,4]. Both compounds reveal strong analogies to the tetramer as well as to nanotubes, as will be discussed below. Another molecule, referred to as tetradehydrodianthracene (TDDA), represents a substructure of the smallest possible armchair tube, the (2,2) nanotube and thus completes the series of armchair-like picotubes [1,5].

The successful synthesis of picotubes represents a crucial step in the field of organic chemistry [6]. Besides their fascinating chemical properties, picotubes are of significant importance with regard to a possible specific synthesis of nanotubes [7]. Up to date methods for the production of carbon nanotubes are based on self-organization and therefore yield mixtures of nanotubes of different chiralities and

lengths. In order to use nanotubes for electronic devices, tubes of a defined chirality are required. Hence, a controlled, specific production of carbon nanotubes is one of the big challenges in nanotube research. Picotubes are possible suitable starting points to achieve this goal [7,8].

In this paper, we present vibrational properties of the above mentioned picotubes in the context of their corresponding nanotubes. Our considerations rely on first principles calculations performed on TDDA, semitrimer and Kammermeierphane molecules as well as a further analysis of the results on semitrimer crystals presented in Ref. 3. Data on the tetramer picotube has been taken from Ref. 2. The computational methods are described in Sec. 2, followed by a brief overview of the picotube structures in Sec. 3. Our results on the vibrational properties are discussed in Sec. 4. Based on a well-defined assignment of vibrational eigenvectors to the main semitrimer Raman peaks, we compare semitrimer and tetramer high-energy modes and relate them to theoretical results on the high-energy modes of TDDA and Kammermeierphane. Furthermore, we discuss breathing-like modes of the different picotubes. Such modes have been identified in the spectra of (3,3) and (4,4) picotubes [2,3]. Our calculations performed on TDDA and Kammermeierphane predict radial breathing

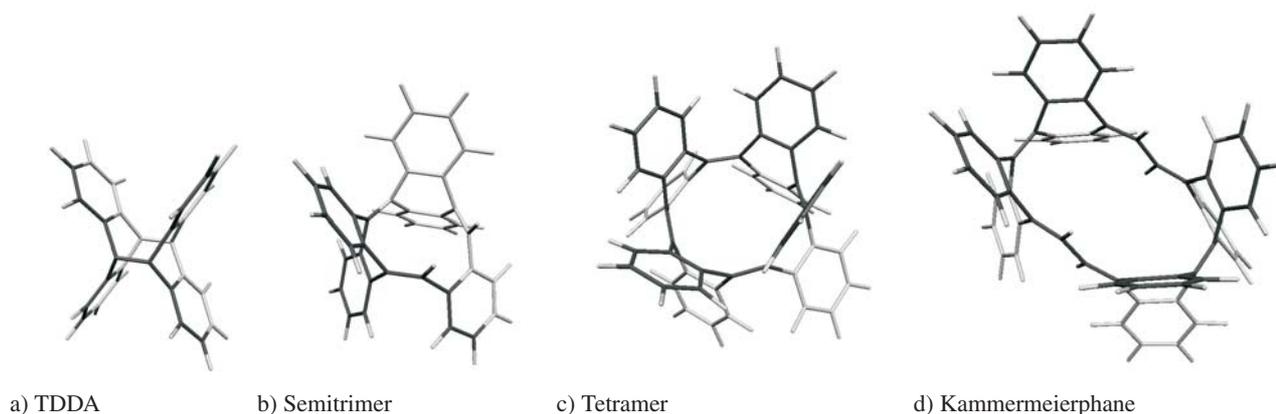


Figure 1 Calculated atomic structures of the investigated picotubes. Foreground (background) carbon-carbon bonds are indicated black (gray).

modes as well. Like in the case of nanotubes, the RBM frequencies of picotubes seem to depend on the inverse tube diameter [9].

2 Computational details First principles calculations have been performed on isolated TDDA, semitrimer, and Kammermeierphane molecules. The results on semitrimer picotubes discussed in this paper have been derived using the electronic structure program *Gaussian03* with the computational parameters given in Ref. [10].

TDDA and Kammermeierphane were calculated with the SIESTA code [11,12]. The local-density approximation was used along with norm-conserving pseudopotentials for the core electrons. The valence electrons were described by a double- ζ basis set, the confinement of which was determined by an energy shift of 30 meV. An equivalent plane-wave cutoff of 100Ry defined the fineness of the grid in real space. The coordinates of the structures were relaxed until all atomic forces were below 0.04 eV/\AA .

In order to check the comparability of calculations performed with SIESTA and *Gaussian*, we also calculated the semitrimer using SIESTA and found a very good agreement to the results derived with *Gaussian* concerning both structural and vibrational properties.

3 The picotube family A survey of the picotubes covered in this paper is presented in Fig. 1. The shown structures result from first principles calculations on single molecules with the tetramer data being taken from Ref. [2]. With a diameter of only 2.4 \AA , TDDA is the smallest possible picotube [5]. Our calculations on the TDDA molecule confirm the experimentally determined radius [5]. This highly strained molecule belongs to the dihedral group D_{2h} (see Fig. 1a). As to the semitrimer, which is next in size, the symmetry is reduced significantly compared to the other picotubes due to a missing wing (see Fig. 1b). The resulting group is C_{1h} , also referred to as C_s in the literature. Concerning the size of the semitrimer, our calculations predict a diameter of 4.0 \AA , close to the diam-

eter of 4.2 \AA calculated for a closed (3,3) nanotube [13]. A detailed discussion of the semitrimer structure will be reported elsewhere [14]. Another highly symmetric picotube is the tetramer shown in Fig. 1c [2]. In excellent agreement between experiment and theory, the diameter of this molecule was found to be 5.4 \AA . This value is again very close to the diameter of the corresponding (4,4) nanotube of 5.5 \AA [2]. In contrast to the picotubes described above, the cross-section of Kammermeierphane differs considerably from a uniform circle, which makes the definition of a diameter difficult (see Fig. 1d). Averaging over several atomic distances in the central ring of the molecule, we find a value of 6.5 \AA in agreement with the theoretically predicted value for a closed (5,5) nanotube of 6.8 \AA [15]. Nevertheless, the molecule, which has C_{2h} symmetry, represents a subunit of a (5,5) carbon nanotube. Table 1 summarizes the structural parameters of picotubes.

4 Vibrational properties Raman measurements performed on both semitrimer and tetramer picotubes reveal strong similarities among each other as well as to the vibrational spectrum of carbon nanotubes [2,3]. A more detailed investigation of the eigenmodes reconfirms these analogies. Following the procedure described in Ref. 3, polarized Raman measurements combined with first principles calculations enable us to assign eigenvectors to measured Raman peaks. By now, a well-defined assignment is found for most of the main semitrimer Raman peaks, allowing a direct comparison of tetramer and semitrimer eigenmodes. In the following, we concentrate on two characteristic bands in the Raman spectra of picotubes: The high-energy-band and the breathing-like modes in the low energy region. Thereby, respective eigenmodes calculated for TDDA and Kammermeierphane picotubes are discussed as well.

4.1 High-energy bands Structured high-energy bands at about 1600 cm^{-1} are typical for curved sp^2 carbon compounds. In the case of armchair nanotubes, this band contains vibrations parallel and perpendicular to the tube axis. Calculations on picotube molecules predict analogous dis-

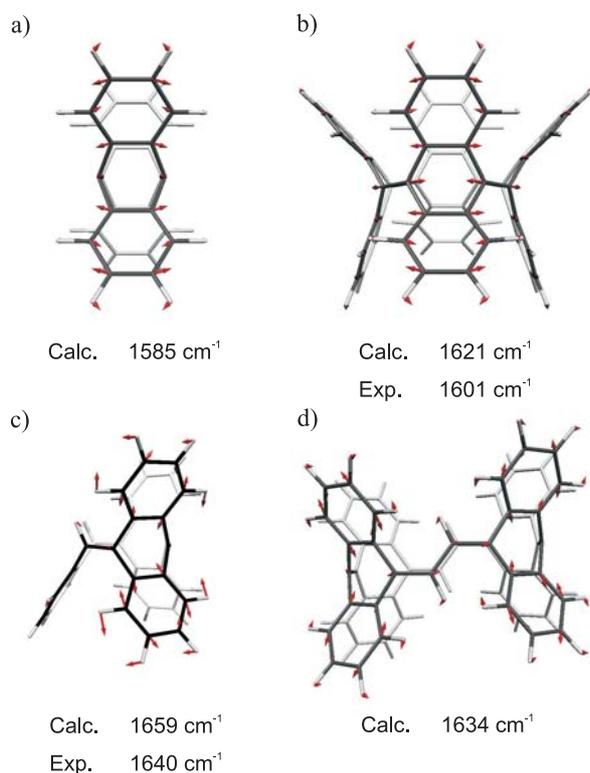


Figure 2 Selected calculated high-energy eigenmodes of picotube molecules. They all belong to the A_1 representation. For clarity, foreground (background) carbon-carbon bonds are indicated black (gray) and the atomic displacements of the background atoms are omitted.

placement patterns for all types of picotubes [2]. Selected eigenvectors thereof are presented in Fig. 2. The exemplary TDDA and tetramer modes shown in Figs. 2a and 2b reveal atomic motion predominantly perpendicular to the picotube axes, which we refer to as transversal. Two examples of axial vibrations are presented in Figs. 2c and 2d for semitrimer and Kammermeierphane picotubes. The symmetries of the two latter compounds allow both axial and transversal A_1 modes. This does not apply to TDDA and the tetramer, where axial modes are of lower symmetry compared to the structure of the molecule. Therefore, longitudinal modes are not expected to contribute to the high-energy Raman bands of TDDA and tetramer picotubes in good agreement to the results on (4,4) picotubes [2]. This behavior is in strong analogy to that of armchair nanotubes where the axial E_{1g} high-energy modes are not expected to yield considerable Raman intensity [9]. In contrast, the high-energy band of semitrimer picotubes contains, besides axial ones, transversal eigenmodes like the pattern shown in Fig. 2c. We therefore observe an extended Raman band in this region compared to the tetramer spectrum [3]. Raman measurements on Kammermeierphane picotubes most likely would yield similar results.

4.2 Picotube radial breathing modes The appearance of radial breathing modes in the vibrational spectra of semitrimer and tetramer picotubes illustrates the strong relationship between nanotubes and their tiny substructures. For these two picotubes, calculated breathing-like eigenvectors have been assigned to measured Raman peaks [2,3]. Our calculations on TDDA and Kammermeierphane predict breathing-like modes in these compounds, too. Figure 3 shows the RBM eigenvectors derived for the four different picotubes along with their calculated frequencies and the experimentally determined frequencies for semitrimer and tetramer [2,3]. Although the molecular structure of picotubes deviates considerably from that of closed nanotubes, the calculated atomic displacements are predominantly in radial direction and in phase. The strongest deviance from a breathing-like motion occurs in the eight wings of Kammermeierphane (see Fig. 3d). Due to the elongated cross section of the molecule, a radial direction is not explicitly defined. Furthermore, Kammermeierphane has two centers of mass linked by two comparably long carbon chains, which implies a less even breathing mode than in the other picotubes.

An interesting aspect concerns the RBM frequencies of

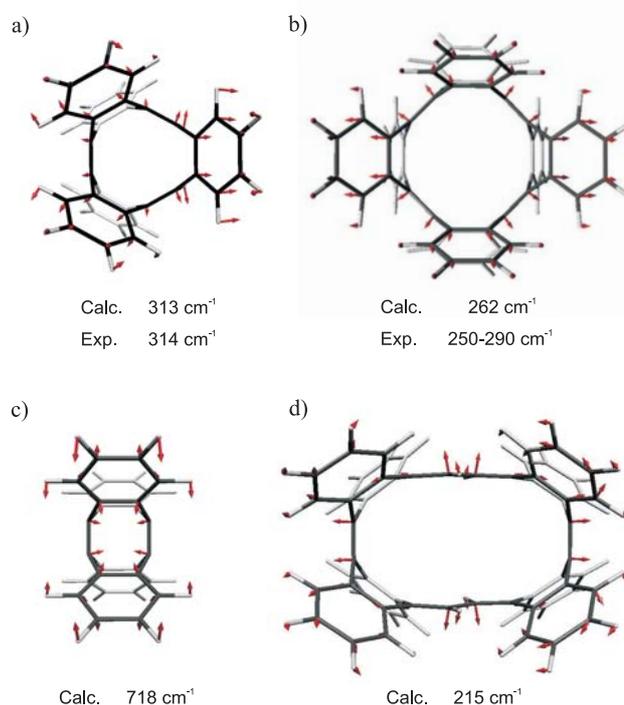


Figure 3 Calculated eigenvectors of breathing-like modes of picotube molecules. For clarity, foreground (background) carbon-carbon bonds are indicated black (gray), and the atomic displacements of the background atoms are omitted.

Table 1 Characteristic structural and vibrational parameters of carbon picotubes. The radii and symmetries as well as the given RBM frequencies result from first principles calculations [2]. The RBM frequencies of the corresponding nanotubes are derived using the frequency-diameter dependence found by Telg *et al.* and calculated nanotube diameters [2, 13, 15, 16].

| | Radius (Å) | Symmetry | $\omega_{RBM}(\text{cm}^{-1})$ | $\omega_{RBM}^{\text{nanotube}}(\text{cm}^{-1})$ |
|------------------|------------|----------|--------------------------------|--|
| TDDA | 2.4 | D_{2h} | 718 | |
| semitrimer | 4.0 | C_{1h} | 313 | 531 |
| tetramer | 5.4 | D_{2d} | 262 | 408 |
| Kammermeierphane | 6.5 | C_{2h} | 215 | 334 |

picotubes (see Tab. 1). Due to lower symmetry constraints in picotubes compared to nanotubes, we expect the RBMs at lower energies in picotubes than in nanotubes in accordance with the observations made on semitrimer and tetramer picotubes [2, 3]. The RBM frequency of a nanotube increases with decreasing tube diameter, since smaller tubes are more strained. In principle, we expect the same effect among picotubes. The theoretically determined RBM frequencies of the investigated picotubes versus picotube diameter are plotted in Fig. 4. We used tube diameters as stated in Sec. 3. The red fitted curve was calculated using the known frequency-diameter relation in carbon nanotubes $\omega_{RBM} = C_1/d + C_2$ [9]. Obviously, the picotube data available up to now roughly satisfies this relation using the parameters $C_1 = 1902 \text{ cm}^{-1} \text{ nm}$ and $C_2 = -98 \text{ cm}^{-1}$. However, the RBM frequency of the semitrimer is lower than according to the d^{-1} -dependence. This possibly originates from the fact that the structure of the molecule is further relaxed due to one missing wing. A full trimer, which has not been synthesized yet, most likely yields a higher RBM frequency.

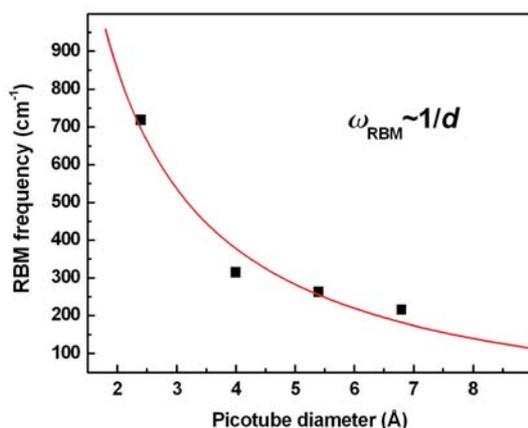


Figure 4 Calculated frequencies of radial-breathing modes in picotubes plotted versus tube diameter. The red fitted curve was calculated assuming a reciprocal dependence of the frequency on the diameter.

5 Summary We presented a comparative study of the vibrational properties of four different picotubes. First principles calculations show characteristic high-energy modes in strong analogy to carbon nanotubes. Combining the calculations to previous Raman measurements allows us to assign eigenvectors to all main peaks in the semitrimer Raman spectrum, including those in the high-energy band. This enables us to explain the different shapes of the high-energy bands of semitrimer and tetramer picotubes. Furthermore, our calculations yield picotube analogs to the radial breathing mode in carbon nanotubes. The RBM frequencies of picotubes roughly satisfy a d^{-1} -dependence in accordance with the relation in carbon nanotubes.

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