Raman Scattering And Electronic Properties Of The Cyclic Anthracene Tetramer (Picotube)

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Abstract. We present a study on the electronic and vibrational properties of the cyclic anthracene tetramer. FTRaman and Raman spectroscopy in the visible were used to investigate the vibrational properties of the molecule. Gaussian'98 and Gaussian'03 were employed to calculate the Raman response; the electronic properties were modeled by VASP, resulting in a gap energy of $E_g = 2.24$ eV. A strong correlation of the calculated modes to the measured Raman frequencies provides evidence for the D_{2d} symmetry.

Keywords: Picotube, Raman scattering, VASP.

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INTRODUCTION

We present recent spectroscopic results from the cyclic anthracene tetramer (picotube). This compound was first prepared by R. Herges *et al.* [1,2]. It consists of four anthracene units arranged in a tube-like configuration, thus resembling a (4,4) nanotube. However, unlike the usually considered infinitely long tube, this system has molecular character, as the picotube only represents 3 unit cells of the analogous (4,4) tube, with a length of 8.2 A. It was previously not possible to grow tubes with such a small diameter of only 5.4 A. The exception to this is found in the well known lower limit for zeolite grown nanotubes, which are unstable outside the zeolite channels. The system also provides us with a new approach to nanotube production by chemical methods. Here we focus on the vibrational and electronic properties of this novel system.

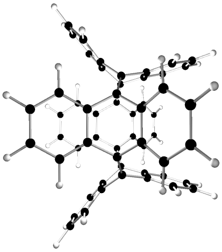

FIGURE 1: The chemical shape of the picotube. The four anthracene units are saturated with hydrogens, and connected by only one double bond to form a tube-like configuration. The image represents the optimized structure with D_{2d}-symmetry obtained by Gaussian'98.

Figure 1 depicts the chemical shape of the picotube. Due to the tilting of the upper and lower anthracene unit the systems symmetry is reduced from D_{4h} to D_{2d}. This is in contrast to NMR- and X-ray diffraction experiments [3], which show the higher symmetry D_{4h}. The discrepancy between the calculation and the experiments originates from a thermal averaging of the tilting of the anthracene planes.

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EXPERIMENTAL, VIBRATIONAL ANALYSIS AND CALCULATIONS

FTRaman spectra were recorded from a Bruker FRA106/s IR/FTRaman spectrometer, with an excitation wavelength of 1064 nm in 180° backscattering geometry. Alternatively, Raman spectra were also recorded in the visible spectral region from a Dilor xy triple spectrometer with blue laser excitation. All spectra were recorded in normal resolution mode, which corresponds to a resolution of 3 cm^{-1} for blue lasers. The FTRaman was recorded with a spectral resolution of 2 cm^{-1}. The calculation of the Raman active modes was performed for both geometries by Gaussian'03. To get the accurate line positions Voigtian lines were fit to the spectral response.

A vibrational analysis of the molecule in its D_{2d} symmetry yields a total of representation of the modes as

$$\Gamma^{(tot)} = 34\cdot A_1(Raman) + 34\cdot A_2(silent) + 34\cdot B_1(Raman) + 34\cdot B_2(Raman, IR) + 64\cdot E(Raman, IR) \qquad (1)$$

230 of these modes are Raman-active, as indicated.

The analysis of the D_{4h}-symmetric geometry yields

$$\Gamma^{(tot)} = 16\cdot A_{1u}(silent) + 17\cdot A_{1g}(Raman) + 15\cdot A_{2u}(IR) + 16\cdot A_{2g}(silent) + 16\cdot B_{1u}(silent) + 17\cdot B_{1g}(Raman) + 16\cdot B_{2u}(silent) + 17\cdot B_{2g}(Raman) + 33\cdot E_u(IR) + 31\cdot E_g(Raman) \qquad (2)$$

which would result in a total of 82 Raman-active modes.

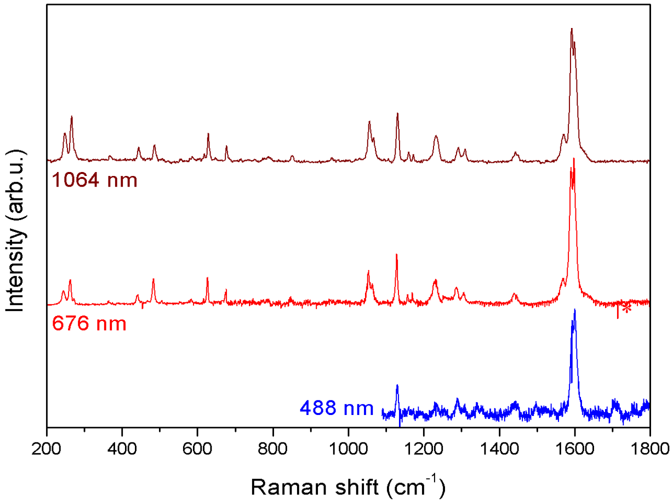

FIGURE 2: Recorded Raman spectra for excitation wavelengths as indicated. (*) supplied by the Bundestechnische Versuchsanstalt Braunschweig.

RESULTS

Raman spectra are depicted in Figure 2 as excited with various lasers. Notice the absence of any dispersive modes, as expected for the molecule. Also, best visible in the FTRaman spectrum if the spectral scale is blown up, the strongest component of the spectrum at 1600 cm^{-1} contains at least 7 Voigtian features, clearly indicating the proposed D_{2d} symmetry.

As we used different excitation wavelengths, we could tune towards the region of resonance which for this molecule would be in the UV spectral region at 319 nm. However, so far measurements from this spectral range did not yield proper results due to sample degradation by the high energy UV light. The spectra excited with blue lasers were rather noisy due to a strong luminescence background. Figure 3 shows the excellent agreement of measurement and calculation if the D_{2d} symmetry is assumed, while the D_{4h} symmetry reproduces the measured spectra to a lesser degree.

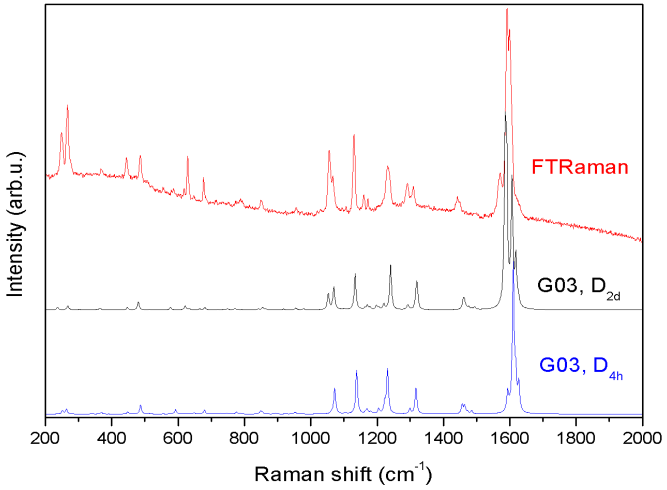

FIGURE 3: Comparison of the measured Raman response and calculations by Gaussian'03 for the D_{2d} and the D_{4h} symmetry. The calculated spectra were downscaled by 2 %.

A scaling factor of 2 % was applied to the calculated spectra in order to match the strongest line to the strongest component in the measured spectrum. The request for downscaling is well known for the Gaussian codes[4]. As far as the frequencies are concerned, excellent agreement is obtained. Interestingly, relative Raman intensities are also well reproduced from the calculation except for a systematic suppresion of intensities towards lower frequencies. Still, the excellent agreement allows us to correlate the individual calculated vibrational modes to the respective features in the measured spectrum.

TABLE 1: Correlation of the 14 strongest Raman modes of the experiment to calculated results. Given are calculated and measured frequencies, the relative intensities and the relative intensity ratios.

Calculated Frequency (cm-1)	I/I_{max}	***FTR*** **Frequency** (cm-1)	I/I_{max}	$\Delta\nu$ (cm^{-1})	$(I/I_{(max)})_{exp}$ / $(I / I_{(max)})_{calc}$
236.18	0.02	248	0.13	11.8	6.5
267.54	0.02	266	0.25	-1.5	12.5
479.22	0.04	486	0.08	6.8	2
620.34	0.02	626	0.09	5.7	4.5
679.14	0.01	677	0.22	-2.1	22
1068.20	0.12	1066	0.22	-2.2	1.8
1132.88	0.20	1130	0.26	-2.9	1.3
1238.72	0.15	1234	0.09	-4.7	0.6
1291.64	0.03	1291	0.13	-0.6	4.3
1317.12	0.12	1309	0.15	-8.1	1.3
1461.18	0.06	1449	0.02	-12.2	0.3
1586.62	1	1573	0.16	-4.4	0.16
1588.58	0.91	1591	1	-2.4	1.1
1604.26	0.72	1602	0.71	2.3	1

The correlation for the blue excitation was more difficult due to strong luminescence. Not all modes were visible in this region. This is indicated by the ratio of measured versus calculated intensities, after the application of a normalisation to the strongest component of the spectra. Only the modes bigger than 10 % of the strongest component were taken into account.

The electronic states of the picotube were calculated by VASP using PAW[5,6]. Figure 4 presents results. Part (a) depicts the density of states for the D_{2d} symmetry.

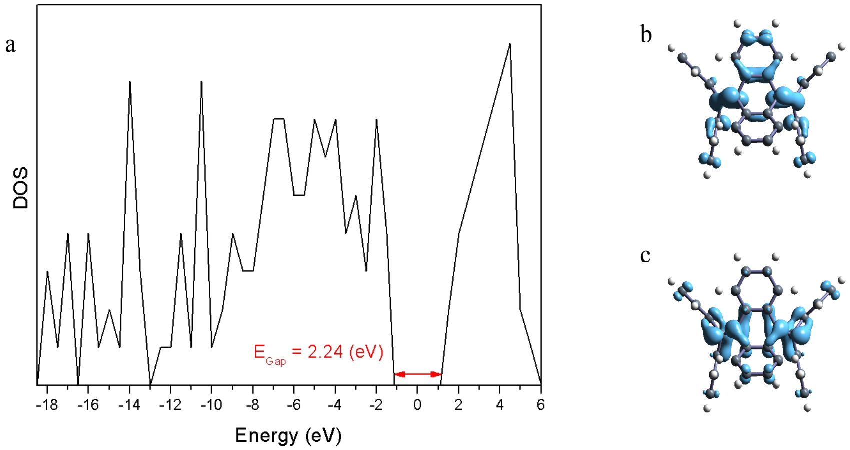

FIGURE 4: The calculated DOS, plotted per 0.5 eV (a); the isosurface for the HOMO state (b), and the isosurface for the LUMO state (c).

It shows several interesting features. The width of the gap is as low as 2.24 eV. As depicted in parts (b) and (c) of the figure, in the HOMO and LUMO states 70 % of the electrons are concentrated to the ring of double bonds connecting the anthracene units. Preliminary results from the calculations indicate that the anthracene units close up if the picotube is inserted into a SWCNT.

CONCLUSIONS

In conclusion, we have presented an experiemental and theoretical study of the electronic and vibrational properties of the picotube. This enabled us to give an assignment of the individual features of the measured spectra to the normal coordinates. Further prospects indicate a prossibility to close the picotube up to form a real piece of a (4,4) armchair tube.

ACKNOWLEDGEMENTS

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