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Infrared Reflectance of Single-Walled Carbon Nanotubes

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Abstract A mid-infrared reflection study on single-walled carbon nanotubes revealed weak absorption structures which we assign to the vibrational modes of the tubes. The results are in good agreement with theoretical predictions for nanotubes. In comparison to graphite phonons a small shift to higher frequencies was found. First measurements at different temperatures indicate no temperature dependence of the phonon frequencies.
Keywords: Infrared and Raman spectroscopy; Fullerenes and derivatives

1 Introduction

The vibrational spectra of single-walled carbon nanotubes (SWNT) consist of 15-16 Raman and 7-9 infrared active vibrational modes, their number depending on symmetry. [1] Whereas Raman spectroscopy on carbon nanotubes is a well established tool for investigation of the vibrational modes of SWNT [2, 3], there is no publication on the infrared active vibrations with results of comparable quality. The main obstacle is the poor sample quality of raw material produced by either laser-ablation or arc discharge techniques. Only small amounts of purified sample material were obtained by purification processes up to now. As an additional difficulty the modes, which are almost independent of the tube diameter and therefore are expected to contribute constructively to detectable absorptions, lie close to the frequencies of graphite at 868 cm^{-1} and 1590 cm^{-1}. It may be difficult to distinguish them from SWNT, if the presence of graphitic particles cannot be excluded.

2 Sample Preparation and Experiment

The samples were prepared by the arc discharge technique [4] and consist of soft soot bundles. The material is inhomogeneously composed of SWNT (> 50 %), Ni nanoparticles (a catalyst for SWNT production) and amorphous carbon, as verified by transmission electron microscopy (TEM). A few graphitic particles were detected, too. The tube diameters were estimated from the TEM images to be 1.4 (±0.1) nm. The as grown material was not suited for the reflection measurements, therefore it was pressed between polished copper plates until it turned into thin and almost flat sheets. It was verified by Raman spectroscopy that the sample composition did not change during this procedure. The reflection spectra were obtained employing a BRUKER IFS 66v FT-IR spectrometer in combination with a liquid N_2 cooled MCT-detector. The reflectance was referred to a gold mirror. In addition, the temperature dependence of the spectra was measured by cooling the mirror and the sample with a He-flow cryostat. Polycrystalline graphite and higly oriented pyrolytic graphite (HOPG) samples were investigated for comparison.

3 Results and Discussion

Figure 1 shows the reflectivity of the SWNT sample in comparison to polycrystalline graphite. The weak structure in the SWNT spectrum at 1590 cm^{-1} resembles a strongly

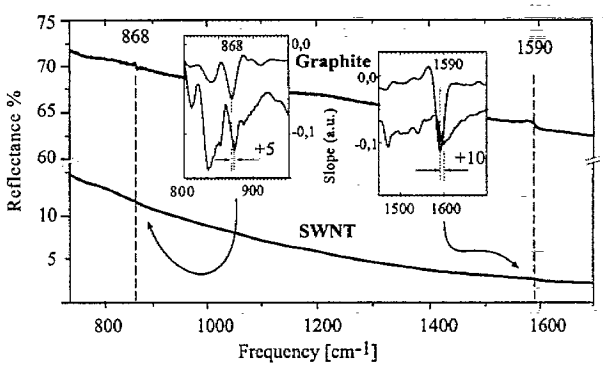

Fig. 1: Infrared reflectance spectra of polycrystalline graphite (upper curve) and SWNT. Graphite has two infrared active phonons, the A_{2u} mode at 868 cm^{-1} and the E_{1u} mode at 1590 cm^{-1}. The first derivatives of the spectra around these positions are shown in the insets.

broadened graphite mode. To enhance this structure and to determine its position, we took the first derivative of the spectra, which is shown in the inset to Fig.1. Applying

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this operation to the graphite spectrum, the mimima of the first derivative indicate the position of the graphite LO modes at 868 cm^{-1} and 1590 cm^{-1}, in good agreement with literature. [5]

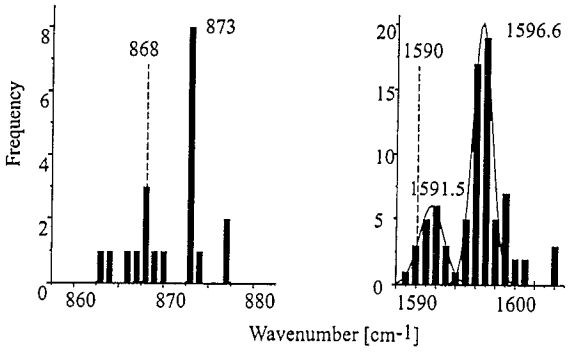

Fig. 2: Frequency distribution of features found in the 1st derivative of SWNT reflectance spectra. The graphite mode positions are indicated with dashed lines.

Figure 2 shows a compilation of several measurements (80 at 1590 cm^{-1} and >20 at 868 cm^{-1}) on different SWNT samples. The positions were determined by the 1st derivative of the spectra around 870 cm^{-1} and 1590 cm^{-1}. In both cases there is a difference between maxima in the distributions and the graphite modes. The minima of the high frequency features at 1590 cm^{-1} are bimodally distributed with peaks at 1591.5 cm^{-1} and 1596.6 cm^{-1}. A similar distribution appears at 868 cm^{-1}, with a prominent peak at 873 cm^{-1}. There is no evidence that these structures could originate from amorphous carbon or the Ni nanoparticles found in the sample. [4, 6] A possible explanation is that the peaks near the graphite modes are contributions from graphitic material in the sample, whereas the upshifted peaks originate from SWNT phonons. It has not been entirely clarified, whether the SWNT modes should have frequencies higher than the respective ones of graphite. [7] Further measurements comparing the reflectance and absorbance of these samples with first principles calculations may give more insight into this problem.

Figure 3 shows the measurements on SWNT and graphite in the temperature range from 50 K to room temperature. The results reveal no uniform temperature behavior of the SWNT samples in contrast to graphite, where the hardening of the lattice vibrations with decreasing temperature is clearly discernible. The temperature series ▽ which gives evidence of a similar dependence could not be reproduced. With decreasing temperature the SWNT spectra become clearer together with an increasing background reflectivity.

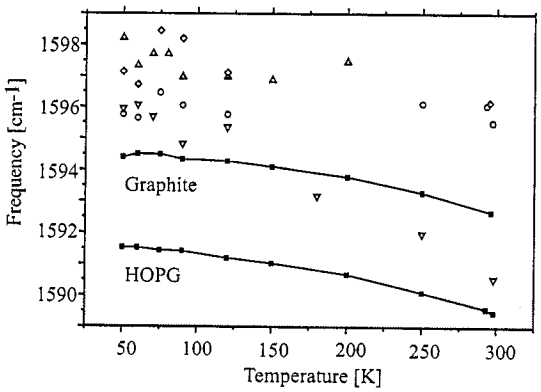

Fig. 3: Frequencies of HOPG and graphite E_{1u} mode and SWNT structure positions over measurement temperature. The symbols ○,◇,△ and ▽ represent different measurement series on SWNT. Only data set ▽ shows a strong temperature dependence similar to graphite.

4 Conclusion

We presented an infrared reflection study on pressed flakes of a sample containing mostly SWNT which revealed structures around 1597 cm^{-1} and 874 cm^{-1}. These features originate most likely from SWNT vibrational modes, which is in correspondence to frequency calculations so far performed. Reflectance measurements at different temperatures revealed no reproducible temperature dependence of these modes.

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