



Infrared active phonons in single-walled carbon nanotubes

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Received 5 May 1998

Abstract

We present IR reflectance spectra of samples containing single-walled carbon nanotubes and compare them with measurements made on graphite. Weak structures near the graphite modes but shifted towards higher frequencies were found. We assign these structures to IR-active phonons of single-walled nanotubes. Our experimental results suggest that while roughly in agreement with the experiment, further and more accurate calculations of the phonon frequencies of single-walled carbon nanotubes are necessary. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The discovery of carbon nanotubes (NT) by Iijima [1] in 1991 stimulated theoretical research on the electronic and vibronic properties of these novel materials [2,3] as well as intensive experimental work. The calculations revealed that these properties depend strongly on the structure and symmetry of the NT (for structural aspects and a summary of research see Ref. [4]). The phonon spectra of single-walled nanotubes (SWNT) consist of 15–16 Raman and 7–9 infrared active vibrational modes, depending on their symmetry (i.e. armchair, chiral or zigzag). It was found, that the position of the low-energy modes below 400 cm^{-1} varies considerably with changing diameter, whereas others show only a little variation. The latter are the preferred candidates for observation since in an ensemble of nanotubes with different diameters they should constructively contribute to a single Raman or infrared line [4]. As far as the Raman experiments are considered, their

results seem to be in rather good correspondence with theory [5,6]. However, there is only one publication related to infrared spectroscopy on SWNT [7] in which the observation of phonon modes at 633 and 1382 cm^{-1} is claimed.

Comparing the predictions for IR spectra of SWNT in Refs. [4,8] for different symmetries, phonon modes around 850 and 1590 cm^{-1} appear in all symmetries almost independently of the diameter and are therefore expected to produce clearly recognizable structures in absorbance or reflectance spectra of a variety of SWNT. According to the theoretical model, which is based on force-constants, the frequencies for small-diameter SWNT are lower than the corresponding modes in a two-dimensional graphite layer and converge to the position of the graphite modes with increasing diameter. The low-frequency modes of the SWNT (below 400 cm^{-1}) depend strongly on the diameter in the opposite sense, i.e. they soften with increasing diameter. These modes could therefore give a means to distinguish

SWNT of different size or symmetry by their spectra if one of these properties is known. Following the prediction that predominantly those modes contribute to the spectra which have similar frequencies for various symmetries and tube diameters, we restricted our investigation to the frequency range from 700 to 7000 cm^{-1} , with our main attention on the positions around the graphite phonon modes at 869 and 1590 cm^{-1} .

2. Sample preparation and experiment

We investigated samples prepared by the arc-discharge technique [9]. They consisted of fluffy soft soot bundles not suitable for reflection spectroscopy. A TEM study of this material revealed an inhomogeneous composition of SWNT with $1.4(\pm 0.1)$ nm diameter, amorphous carbon and Ni nanoparticles with about 20 nm diameter. Ni is used in SWNT production as a catalyst. The variation of the diameter of the SWNT is small, as far as the TEM pictures are considered and is presumably related to the production parameters. Journet et al. [9] reported that 80–90% of the sample consisted of nanotubes, our TEM studies suggest the amount to be somewhat smaller. Among the amorphous carbon, some graphitic material was found which has to be taken into account when interpreting the results.

To obtain reflection spectra the material was pressed between polished copper plates until it turned into thin and almost flat sheets. Raman spectroscopy performed on the sample before and after the pressing revealed comparable intensities of the characteristic Raman lines and confirmed that the NT were not mechanically or otherwise damaged in this process.

The reflection spectra were obtained using a Bruker IFS 66v FT-IR Spectrometer with a liquid N_2 -cooled mercury cadmium telluride (MCT) in comparison with a gold mirror. The spectral resolution was set to 2 cm^{-1} . Different sets of samples were prepared and measurements were performed on several sample spots with an aperture of 1 to 3 mm diameter. Additionally we determined the reflectance of highly oriented pyrolytic graphite (HOPG) and polycrystalline graphite using the same measurement parameters as for SWNT.

3. Results and discussion

Fig. 1 shows the reflectivity of the SWNT sample in comparison with graphite and HOPG, restricted to the region of interest. The average reflectance in this spectral region of the SWNT sample is about 8%, the difference to the graphite reflectance is mainly due to scattering on the nonperfect sample surface. HOPG and graphite exhibit the E_{1u} mode at 1590 cm^{-1} , which is an in-plane vibration; the graphite mode is broader. The A_{2u} mode at 869 cm^{-1} , an out-of-plane vibration, cannot be stimulated in HOPG when illuminated along the c-axis and appears therefore only in polycrystalline graphite where the crystallites are oriented randomly. The spectra of graphite and HOPG agree with what is known from the literature [10,11] with respect to frequency and linewidth. Comparing the spectra of Burger et al. [7] of SWNT with the results on graphite it is surprising that they find a linewidth of only 2 cm^{-1} , whereas the graphite mode in HOPG has a linewidth of 13 cm^{-1} .

The spectra of SWNT in Fig. 1 do not show strong features. A weak structure around 1590 cm^{-1} resembles a strongly broadened graphite mode. No structures seem to appear around 869 cm^{-1} at first sight. To amplify structures which may be hardly visible in this representation we took the first derivative of the spectra. The reflectance of a damped lattice oscillation has on the high-frequency side a

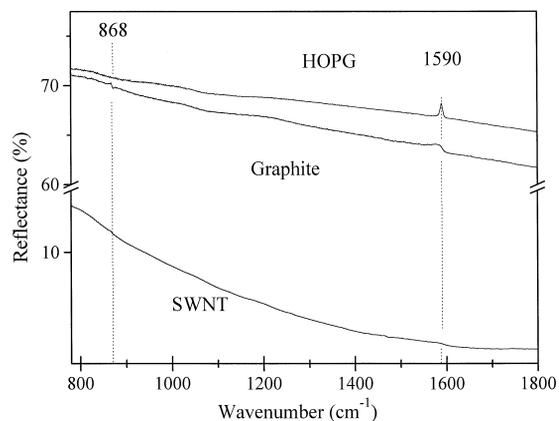


Fig. 1. FT-IR reflectance spectra of single-walled nanotubes (SWNT), graphite and HOPG. The positions of the IR-active vibrational modes of graphite are indicated. The SWNT spectrum is shown on a different scale for better comparison.

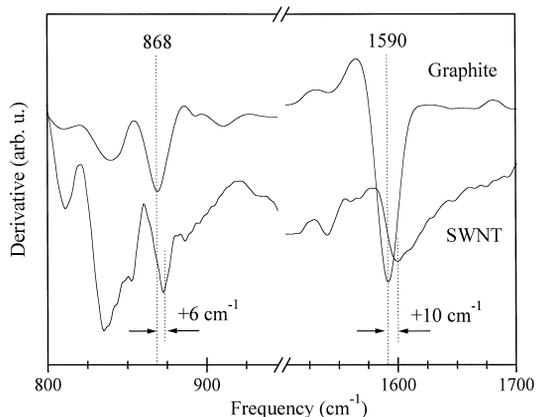


Fig. 2. First derivative of the reflectance spectra of polycrystalline graphite and SWNT. Only regions of interest around the graphite phonons are drawn.

sharp decay, marking the position of the LO mode, from the highest reflectance to a value much lower, before ascending again to the value of the background reflectance. This LO position appears in the derivative as a minimum, which we take for our further analysis. The effect of increasing damping is simply a small shift ($< 1 \text{ cm}^{-1}$) of this position towards lower frequencies along with a broadening of the structure. Hence, if the weak structure in the SWNT spectra of Fig. 1 originates from graphitic

regions of the samples, the minimum of the derivative should nonetheless remain at the position found in the spectra of graphite or HOPG.

Fig. 2 shows the results of deriving the graphite and SWNT spectra. There is an obvious difference in the LO minima in graphite and SWNT as indicated by the dashed lines. The minimum of the feature at 1590 cm^{-1} is shifted to higher frequencies by 10 cm^{-1} . A similar structure appears at 869 cm^{-1} shifted by 6 cm^{-1} . As mentioned, over 20 measurements were performed on different samples and sample spots. In Fig. 3 we present the results as a histogram of the determined frequencies per unit interval over wavenumber.

The features in the high-frequency range are shifted significantly by up to 14 cm^{-1} compared to the position of the graphite E_{1u} mode with a maximum around $+6 \text{ cm}^{-1}$. The low-frequency structure likewise shows a shift, but it is smaller and frequencies below 869 cm^{-1} are found, too. However, this might be due to the fact that the minimum in the derivative around this frequency was more difficult to determine. The mean linewidth of these structures was found to be 22 cm^{-1} . The derivative of the spectra revealed further features at other frequencies which could not be assigned unambiguously to the sample and will not be discussed in this Letter.

Several questions arise from these results. One is

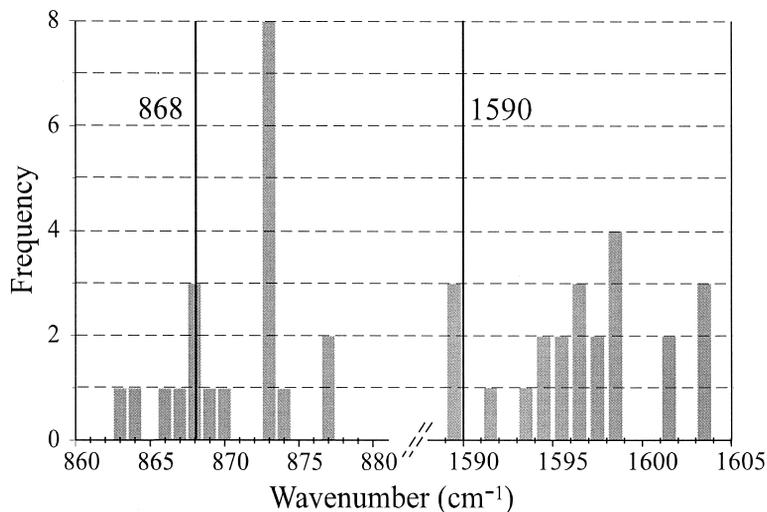


Fig. 3. Frequency distribution of features found in the derivative of SWNT reflectance spectra. The graphite modes are indicated.

whether these features instead of being related to SWNT could originate from strongly disordered graphite, amorphous material or Ni. As discussed above, the damping of a phonon, as a result of disorder can result only in a lowering of the phonon frequency contrary to what is observed. Amorphous carbon as a completely disordered material has no sharp phonon modes at all. Ni, on the other hand, has no IR active phonon modes. We thus excluded the possibility that the observed features originate from other than the SWNT in the sample.

Next we ask how the variability of the observed frequencies in Fig. 3 can be explained. Since the measurements were taken with an aperture of at least 1 mm diameter, the spectra represent a mean value over a multitude of nanotubes and do not show individual ones. In accordance with the TEM pictures there is not much variety in tube diameters (1.4 ± 0.1 nm), so that only different symmetries of tubes could produce different mode positions. There would thus be an inhomogeneous distribution of nanotubes with different symmetries and a bunching of specific symmetries on the different spots that we measured. Another possible explanation is that the observed structure is produced by an overlap of a specific nanotube phonon mode with the graphite E_{1u} mode at 1590 cm^{-1} . The variety of observed frequencies could then be explained with a variation in intensities of SWNT and graphitic material in the sample spot under examination.

Having shown that the observed features originate from SWNT phonon modes, the open question remains as to why these modes have frequencies higher than the respective ones of graphite. As mentioned above, the common force-constant model for vibrational modes of SWNT reveals IR frequencies lower than the corresponding modes of graphite. However, the force-constant models used may lack some detail with respect to the three-dimensional structure of the tubes because the parameters commonly used are taken from fits to 2d-graphite layers and organic compounds of carbon and may not be of sufficient accuracy for the specific structure of nanotubes.

More theoretical work may give further insight into this problem.

4. Conclusions

A reflection study on samples containing mostly SWNT revealed structures in the infrared reflectance spectra around 1598 ± 3 and $874 \pm 2\text{ cm}^{-1}$ (mean values and standard deviation). We showed that these features most likely originate from phonons in SWNT, which roughly correspond in frequency to calculations of phonon spectra of SWNT so far performed. The frequencies deviate, however, from the corresponding graphite frequencies to higher values by 8 and 5 cm^{-1} , a fact which cannot be explained by current force-constant models. Our results suggest further theoretical research, which may include an alternative approach to the phonon frequencies by means of first-principle methods.

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