

Infrared absorption spectroscopy of functionalized single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWCNT) as well as functionalized nanotubes were studied by means of low temperature Fourier transform infrared (FTIR) absorption spectroscopy. Embedment of carbon nanotubes into KBr (potassium bromide) pellets was found to be one of the most convenient methods to study the nanotubes at room and low temperatures. Low temperature allows us to observe several spectral bands associated with vibrations in the nanotubes. These vibrations were found to be sensitive to the ordering of the carbon atoms in the nanotube therefore it could be used as a signature of the nanotube quality. Infrared spectroscopy was found to be sensitive enough for the monitoring of nanotube functionalization and identification of the particular functional groups attached to the nanotubes. Assignment of spectral bands to particular vibrations of atoms localized in the functional groups attached to the nanotube is supported by *ab initio* calculations.

Key words: functionalized single-walled carbon nanotubes, infrared spectroscopy

INTRODUCTION

Carbon nanotubes due to their structure have very different properties in comparison to another allotropic carbon species such as graphite, diamond or fullerenes. Due to their unique properties carbon nanotubes are the subject of a vast number of studies since their first discovery by Iijima in 1991 [1–2]. Mechanical and electrical properties of carbon nanotubes make them very attractive in different fields of applications [3–4]. Chemical and physical properties of the carbon nanotubes can be significantly altered by attaching additional chemical groups to the nanotube. Recent advances in chemical functionalization of carbon nanotubes allow to apply them in a very wide range of fields including chemistry, biology and even as drug delivery systems or cancer treatment in medicine [5–7]. However, production of carbon nanotubes in large amounts encounters some problems. This is especially true for the functionalized single-walled carbon nanotubes with the specific requirements to their chemical and physical properties. Even more, the determination of the quality of

structure and chemical properties of produced carbon nanotubes remains a great scientific and technological problem. There are not so many techniques for complete characterization of carbon nanotubes and in order to have a full analysis one has to use several of them. Currently the most popular means of the nanotube analysis are as follows: Thermogravimetric analysis; X-ray photoelectron spectroscopy; Scanning tunneling microscopy; Neutron diffraction; X-ray diffraction; Transmission electronic microscopy; Infrared spectroscopy; Raman spectroscopy; Nuclear magnetic resonance [3, 8]. In some studies the potential of visible and ultraviolet spectroscopy is also demonstrated [9].

In order to fully understand properties of untreated and functionalized nanotubes and increase fields of their application, their properties must be understood at the molecular level. Raman scattering and infrared (IR) absorption spectroscopy combined with theoretical molecular modeling provides a very powerful tool to study molecular systems. However, the most recent theoretical calculations concentrate on calculating possible geometries and potential energies of nanotubes or interaction potentials of nanotubes and functional groups [10–11]. Infrared active phonon transitions

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have been studied using a number of theoretical approaches: group theory analysis, generalized bond-charge mode [12], spectral moment method [13], and first-principles calculations based on the density functional theory [14]. All these calculations predict three infrared active phonons for armchair (n, n) and zigzag (n, 0) nanotubes. The low frequency RBM (radial breathing mode) varies very significantly with the change of the nanotube diameter in the range of 100–500 cm^{-1} , remaining two middle infrared region modes around 800–900 cm^{-1} and 1500–1600 cm^{-1} are less sensitive to the change of the tube diameter [13–14]. Chiral (n, m) nanotubes have 6 infrared active phonon modes: one low frequency mode in the range of 200–500 cm^{-1} , three modes in the range of 600–850 cm^{-1} and two bands in the range of 1450–1500 cm^{-1} . However, these calculations assume perfect nanotubes without defects and do not take into account individual atom vibrations close to the ends of nanotubes, defects or functional groups. There are only several attempts to calculate vibrational frequencies of -COOH functionalized single-walled carbon nanotubes [15]. Unfortunately, authors present their study based only on one C=O stretch vibration therefore full comparison with the experimental data is impossible. This is especially true when the study of the influence of nanotube functionalization on the inner vibrations of nanotube atoms is conducted. Moreover, the use of DFT methods for such a complicated molecular system as the carbon nanotube is not completely justified.

Infrared spectroscopy has been used for the studies of untreated and functionalized nanotubes since their discovery [16]. Authors of the first papers discuss only presence of two spectral bands at 1575 and 868 cm^{-1} [16], these observations are in very good agreement with theoretical calculations. However, more infrared absorption bands are observed in the spectra of carbon nanotubes in the later experimental studies [17–19]. There are several disagreements in the assignments of spectral bands in these works, mainly due to the fact that it is hard to get completely pure nanotubes without organic molecules and amorphous carbon or graphite impurities. The defects in the walls of carbon nanotubes can also result in the appearance of additional spectral bands [18].

In many experimental studies infrared spectroscopy is also used to analyze functionalized carbon nanotubes as an additional method without performing a detailed analysis of vibrational spectral bands [20]. The detection of functional groups is based on appearance of several additional bands in the infrared spectra after chemical functionalization of the nanotubes [6, 7, 20]. In order to establish peculiarities of interaction between attached chemical groups and nanotubes a more detailed vibrational analysis of the observed spectra is required. The spectral bands could serve as a marker for the determination whereas the functionalization takes place due to physical adsorption of the molecules governed by Van der Waals forces or due to formation of covalent chemical bonds.

Methods for obtaining infrared absorption spectra of carbon nanotubes should be justified as well. There are four

basic infrared spectroscopy techniques applied to study carbon nanotubes: embedment in potassium bromide (KBr) pellet, deposition from a solvent/nanotube suspension onto IR transparent substrates, attenuated total reflection (ATR) and reflection absorption spectroscopy (RAIRS) of the samples grown on infrared reflective surfaces such as copper. The main problem with both latter techniques is that reflected infrared radiation could have a diffuse reflection component, due to the light scattering from the nanotubes as their dimensions are of the same order as the wavelength of incident radiation, distorting the absorption spectra [21, 22]. Results obtained by the KBr pellet technique also need to be checked by alternative techniques to confirm that there is no interaction between KBr and nanotubes.

The main objective of this work is to systematically analyze infrared absorption spectra of untreated and functionalized nanotubes with the aid of *ab initio* calculations in order to determine sets of infrared spectral bands characteristic to a particular functional group (-OH or -COOH) and to establish these characteristic bands as definitive markers for identification of attachment of -OH or -COOH groups to the single-walled carbon nanotubes.

Advantages and possibilities of low temperature infrared spectroscopy for the studies of the single-walled carbon nanotube structures are also demonstrated in this work.

EXPERIMENTAL

Untreated single-walled as well as carboxyl group (-COOH) and hydroxyl group (-OH) functionalized nanotubes were purchased from two companies: Sigma-Aldrich and Arry. Sigma-Aldrich SWNTs material is produced by the electric arc discharge technique, $D \times L$: 4–5 nm \times 0.5–1.5 μm functionalization 10.0 atom%; purity 90%. Arry SWNTs material is produced by the chemical vapor deposition method (CVD), $D \times L$: 1–2 nm \times 3.0–5.0 μm functionalization 10.0% weight, purity 90%. Nanotubes were used for experiments without any additional treatment.

An infrared microscope Hyperion 3000 coupled with a Vertex 70 interferometer (Bruker) was used to record the infrared spectra of pure SWCNT. The nanotubes were dispersed on the ZnSe optical window and placed under the objective of the microscope. Visible light in the transmission mode was used to select the areas of nanotube bundles for the infrared absorption measurements. Spectra were recorded in the 4000–500 cm^{-1} spectral range at 1 cm^{-1} resolution using a KBr beamsplitter global source and a MCT detector cooled with liquid nitrogen. In order to record the signal only from the desired area of nanotubes bundle the spatial aperture was used. Depending on the sample from 4000 to 10000 scans were recorded and averaged to increase the signal to the noise ratio of the spectra.

Embedment of the nanotubes in the KBr pellets were used for the experiments in the temperature range between 9–300 K. Nanotubes were mixed with the KBr powder (Uva-

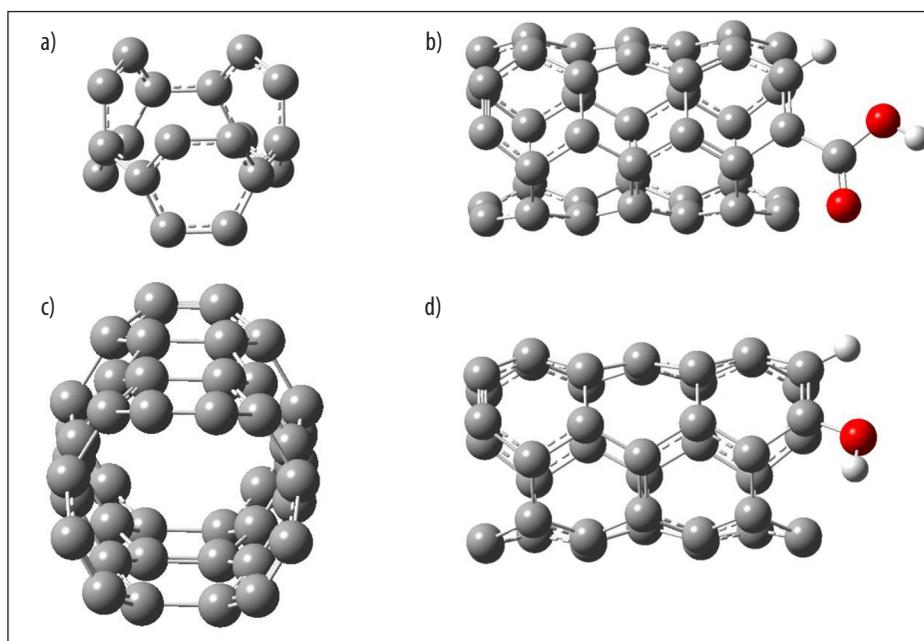


Fig. 1. Cyclic carbon structures: a) cycloparaphenylene; b) fragment of single-walled carbon nanotube, c) COOH tip functionalized single-walled carbon nanotube; d) OH tip functionalized single-walled carbon nanotube

sol, Merck) at the rate 1 : 5 000 and pressed using a hydraulic press exerting 740 MPa pressure. Pallets were attached to the copper frame of a closed-cycle helium cryostat (Leybold Heraeus, working temperature range 9–300 K) using indium gaskets to ensure a good thermal contact between the cold frame and the sample. Infrared absorption spectra were recorded on a Bruker IFS 113 spectrometer in the 4000–500 cm^{-1} range. Typically 0.5 cm^{-1} resolution was used with the KBr beamsplitter, global source and MCT detector. 512 scans were recorded and averaged to get a good signal to the noise ratio. In the low temperature experiments some spectra were recorded with 0.05 cm^{-1} resolution in order to reduce the width of the instrument function and observe the non-perturbed bandwidth of sharp spectral bands.

Raman scattering spectra of SWCNT in the KBr pellet were recorded in order to verify the purity of the nanotubes. These spectra were recorded using a Bruker FT-Raman spectrometer MultiRAM equipped with a Nd:YAG laser source (1064 nm), and a liquid-nitrogen cooled Ge detector. Spectra were recorded using 10 mW power laser excitation and 4 cm^{-1} spectral resolution, 10 000 spectra were averaged in order to get a good signal to the noise ratio.

Calculations

Geometrical parameters and vibrational frequencies of the fragment of untreated single-walled as well as OH and COOH functionalized nanotubes were calculated using the *ab initio* HF/6-31G method implemented in the Gaussian03 software package [23]. The fragment consisting of 3 units of cycloparaphenylene (Fig. 1) along the axis of the tube (total 42 carbon atoms) was used. In this way tubes of 3.3 chirality (armchair) were generated for the model calculations. The limitation of the

number of atoms included into the calculations was needed to reduce the computing time and make it reasonable. The model used for the calculations is not expected to give very good agreement with the experimental values of the nanotube vibrations. Nevertheless such length of the tube should be enough for the calculation of the vibrations of functional groups attached to the nanotubes and the vibrations of the nanotube atoms close to the functional groups [15], which is the main objective of this study. The functional groups were attached to the end of the nanotube which is considered to be the most likely place of the defect occurrence (tip functionalization) [15] (Fig. 1).

RESULTS AND DISCUSSIONS

Spectra of untreated nanotubes

The spectra of pure single-walled carbon nanotubes and the nanotubes embedded in the KBr pellet are presented in Fig. 2. As it is mentioned in the experimental section, the spectra of the pure nanotubes were measured using the infrared microscope attached to the FTIR spectrometer. Unfortunately, these measurements are time-consuming due to the use of the small spatial apertures. In order to obtain a decent signal to the noise ratio averaging of 4000 to 10 000 scans depending on the sample was required which is equivalent to 1–5 hours of measurement time. The measurements of the same nanotubes embedded in the KBr pellets are much faster due to a much larger amount of the sample in the beampass. Normally 500 scans were enough to obtain a good signal to the noise ratio (10 min measurement). Detailed examination of these two spectra (Fig. 2) does not reveal any significant differences. This allows to conclude that embedment of carbon nanotubes in KBr pellets does not affect their vibrational

Table. Calculated (only bands with high infrared absorption intensity) and experimentally observed vibrational bands of untreated and functionalized single-walled carbon nanotubes, wavenumber values in cm^{-1} . Intensities of calculated bands are given in parenthesis (km/mol)

Calculated HF/6–31 g			Experimental			Vibration description
SWCNT	SWCNT-OH	SWCNT-COOH	SWCNT	SWCNT-OH	SWCNT-COOH	
			695	695	695	
763 (59)	768 (36)	767 (26)	725	725	725	Radial def.
	785 (19)	776 (17)		717	717	Radial def.
		795 (19)				Radial def.
	810 (18)					Radial def.
			797	797	797	
			779	779	779	
844 (20)	888 (19)	845 (23)	862	862	862	Breathing-longitudinal str.
877 (13)		873 (23)				C=CCC umbrella
	892 (33)	889(26)		878	878	Radial def.
	896 (36)	893 (32)		897	897	Radial def.
	977 (36)					Radial def.
1 050 (148)	1 064 (58)	1 048 (56)				Radial def. + CC antisym. str.
			1 077	1 077	1 077	Amorphous carbon
	1 070 (73)	1 076 (38)				CCH bend
		1 093 (21)				CCH bend
1 123 (13)	1 121 (13)	1 129 (12)	1 275	1 275	1 275	Longitudinal def.
	1 132 (22)					CCC def.
1 147 (23)	1 158 (21)	1 153 (15)				C6 breathing + def.
			1 163	1 163	1 163	Defect C-O-C
		1 172 (52)				CO str.
		1 189 (51)				COH def.
		1 216 (35)				OH def.
		1 254 (175)			1 234	OH def. + CCC sym. str.
	1 263 (60)					OH def.
	1 272 (48)	1 271 (28)				OH def.
	1 281 (83)	1 282(103)			1 259	OH def.
	1 288 (125)	1 289 (51)				OH def.
		1 318 (68)			1 315	CCC def. + COH def.
			1 372	1 372	1 372	
1 412 (10)	1 410 (5)		1 431	1 431	1 431	C6 def.
			1 463	1 463	1 463	
1 489 (34)	1 477 (15)	1 474 (18)	1 583	1 583	1 583	CC antisym. str. + layers rotation
	1 487 (22)					CC str. + OH def.
		1 500 (67)			1 476	CCO def.
	1 512 (63)	1 508 (14)		1 530		CC str. + CO str.
		1 521 (96)				CCO def.
		1 551 (74)			1 542	CC antisym. str.
	1 545 (60)			1 586		COH bend
	1 573 (70)	1 575 (35)		1 652	1 652	CC str.
	1 618 (32)					CC str.
	1 632 (26)					CC str.
	1 650 (27)					CC str.
	1 663 (56)			1 630		CC out of phase str.
		1 667 (25)			1 640	C=C str. + CCC def.
	1 722 (73)					C=C str.
		1 731 (42)			1 712	C=C str.
			1 720	1 720	1 720	
	1 783 (60)			1 737		C=C str.
		1 897 (120)			1 742	C=O str.

Antisym. – antisymmetrical vibration, def. – deformational vibration, sym. – symmetrical vibration, str. – stretch vibration.

states. Therefore KBr pellets were used in further studies of the untreated and functionalized nanotubes.

The untreated nanotubes exhibit several infrared absorption bands (Fig. 2 and Table). These bands are characteristic of all the tubes used in this study. Our spectra resemble IR spectra observed in previous works when SWCNTs were studied without additional purification [8, 17]. The strong absorption in the 1100 cm^{-1} region indicates that the SWCNT has defects or residual amorphous carbon impurities or both. The maximum of

the observed band is at 1077 cm^{-1} which is in agreement with absorption of amorphous carbon as indicated in [18].

It is interesting to note that the band position is in good agreement with the calculated value of a short nanotube fragment (1050 cm^{-1}) used in our model calculations (Table) therefore it is possible that small fragments together with amorphous carbon are present as well.

In order to check the purity of the SWCNT in KBr, the Raman spectrum was recorded (Fig. 3) as well. Raman

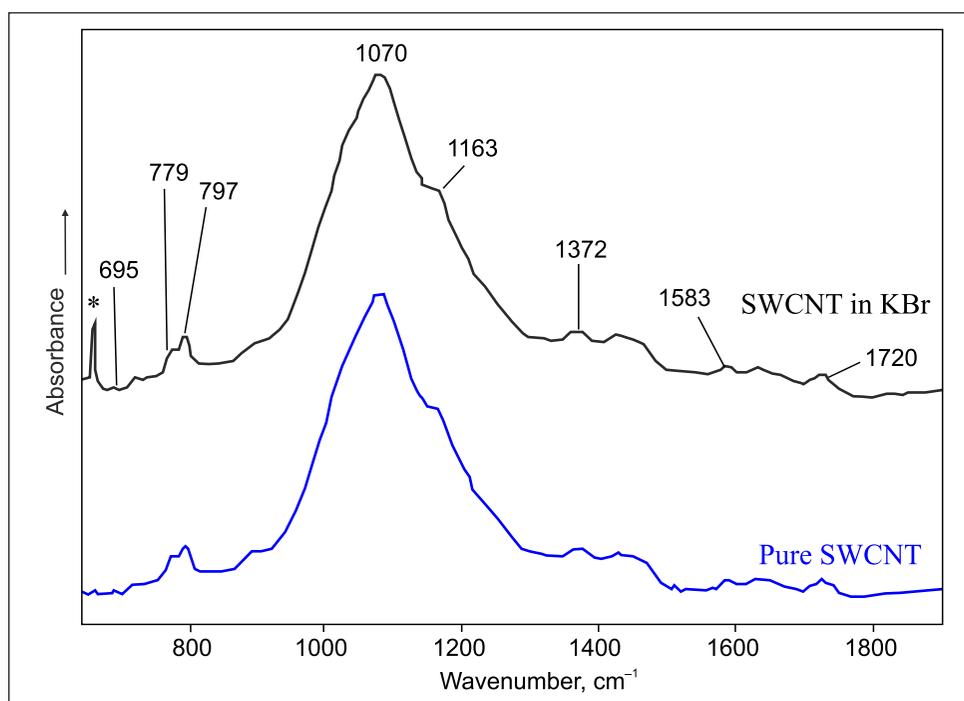


Fig. 2. Infrared absorption spectra of pure single-walled nanotubes (bottom) and the same nanotubes embedded in KBr pellet (top). Asterisk denotes absorption due to residual CO_2 trapped in KBr pellet

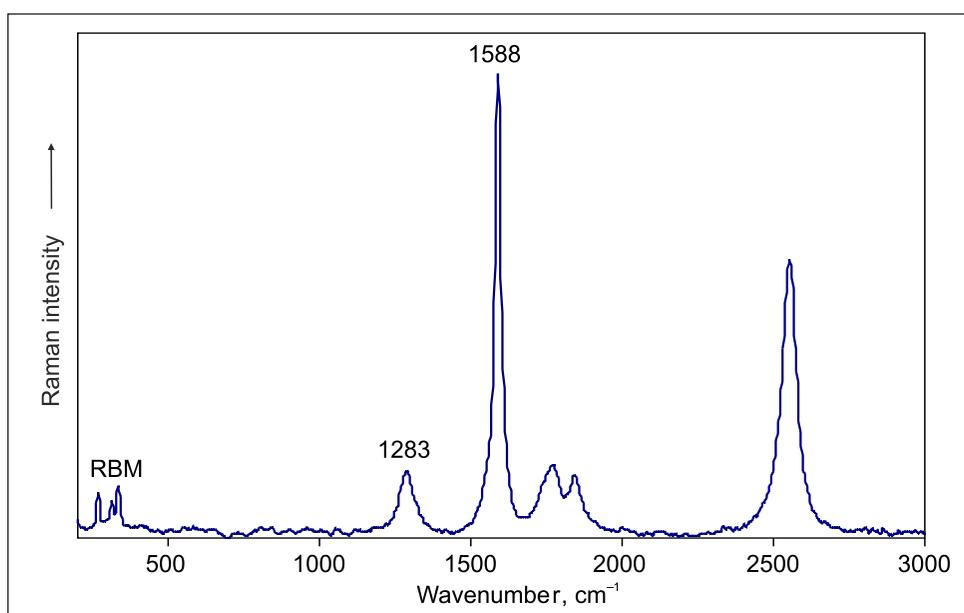


Fig. 3. Raman spectrum of single-walled carbon nanotubes

spectral bands observed at 1283 cm^{-1} and 1588 cm^{-1} are called D and G modes of carbon nanotubes and their ratio is used as a measure of the defects and impurities in the nanotube sample [3]. Indeed, rather high intensity of the 1283 cm^{-1} band is a sign that the nanotubes have defects and, most likely, some graphite impurities as well. However, clear observation of RBM modes in the $200\text{--}300\text{ cm}^{-1}$ region manifest that the major component in the sample is SWCNT.

Raman spectrum allows concluding that there are defects in the nanotubes. Therefore an experimentally observed shoulder band around 1663 cm^{-1} in the infrared absorption spectra is likely caused by residual C-O-C type vibrations in the defected areas of the nanotube.

Theoretical calculations predict 2 active phonon vibrations in the middle infrared region for armchair and 5 for zigzag type SWCNT [14]. The nanotubes were not additionally purified therefore both types of SWCNT are expected to be present in the sample [17]. Therefore it is possible to expect at least 7 bands due to the phonon of the nanotubes.

The lowest frequency band observed with our experimental setup is a weak band at 695 cm^{-1} . This band is in good agreement with observations of [17]. A similar band in this reference was observed at 682 cm^{-1} . This is in the range of theoretically predicted value 692 cm^{-1} for chiral nanotubes (see Table III [14]).

Relatively sharp spectral bands with medium intensity observed experimentally at 779 cm^{-1} and 797 cm^{-1} could be assigned to the vibrations of chiral SWCNT based on the theoretically predicted bands at 768 and 793 cm^{-1} (see Table III [14]). Weak band observed at 862 cm^{-1} is a radial mode of armchair type nanotube based on theoretical predictions $827\text{--}880\text{ cm}^{-1}$ depending on the diameter of SWCNT [14]. This band is reported at 854 [17], 860 and 865 cm^{-1} [19] depending on the SWCNT under the study.

The spectral band at 1372 cm^{-1} is associated with tangential type vibration. A similar band is observed [17] at 1369 cm^{-1} and theory predicts vibration in the $1365\text{--}1370\text{ cm}^{-1}$ region.

Experimentally observed bands at $1431, 1463\text{ cm}^{-1}$ could be assigned to the chiral nanotubes based on the data [14] predicting two bands at 1486.8 and 1496.5 cm^{-1} . Spectral bands at 1443 and 1446 cm^{-1} were reported in [17], however, the authors [17] do not have clear assignment for these two bands.

Spectral band at 1583 cm^{-1} is attributed to the tangential mode of the armchair type SWCNT. This band was clearly observed in the previous studies: 1587 cm^{-1} [18], 1585 cm^{-1} [17] and 1580 cm^{-1} [6, 19]. Recent DFT calculations predict the value to be in the range of $1520\text{--}1580\text{ cm}^{-1}$ depending on the diameter of the nanotube. Our theoretical model using a short fragment of the tube predicted value at 1489 cm^{-1} . This indicates that the direct comparison of the vibrational frequencies is possible only for the vibrations of the functional groups and nanotube atom vibrations connected to

functional groups, but the model is too small for the accurate representation of the whole nanotube vibrations.

The highest frequency band observed at 1720 cm^{-1} cannot be easily attributed to the normal vibrations of the nanotube as the calculations do not predict any bands with significant intensity in this spectral region. There are two possible explanations of the origin of the band. One is C=O stretch band form possible residual organic impurities [19], another possibility is an overtone or combination band [17], unfortunately, the present experimental data does not allow to discriminate between the two options.

The overall number of observed spectral bands in our study is much higher than in [18, 19] and in most cases it is similar to the data of [17]. However, our experimental data is not sufficient to completely resolve the argument and it is not the scope of this study. Based on IR and Raman spectra we can conclude that the sample is SWCNT but the existence of short nanotube fragments and impurities of amorphous carbon cannot be excluded. Functionalized nanotubes used in the following study were obtained from the untreated ones therefore they have the same impurities which spectral bands are already known from the spectra of untreated nanotubes.

Spectral bands due to functionalization of the nanotubes

A number of additional spectral bands were observed in the infrared absorption spectra of the functionalized nanotubes (Fig. 4). The observed bands can be separated into two groups: bands which appear independently on the chemical group (carboxyl COOH, or hydroxyl OH) attached to the nanotube and the bands specific to each chemical group. The additional bands appearing in the spectra are of relatively low intensity due to the fact that the functionalization of the nanotubes is in the order of 10% as specified by the manufacturer.

In the low frequency range of the infrared absorption spectrum there are two bands at 878 and 897 cm^{-1} (Fig. 4) which appear when either of chemical groups are attached to the nanotube. These vibrations can be attributed to the radial vibrations of the carbon nanotube, which becomes active due to the decreased symmetry of the nanotube when the additional chemical groups are attached to the tube. Another functional group independent band is observed at 1652 cm^{-1} . This band is attributed to the C-C vibrations close to the attached functional group, theoretical calculations fail to predict correctly the frequency of this band in both OH and COOH functionalized nanotubes respectively at 1573 and 1575 cm^{-1} . This is most likely due to the fact that in model calculations only a very short fragment of the tube is considered and this might result in the wrong estimation of functional group influence on the vibrations of the carbon atoms in the nanotube. It is interesting to note that the band doublet at $1431, 1463\text{ cm}^{-1}$ gains in intensity after functionalization. Also the intensity distribution in this doublet is different than in the untreated nanotubes and is

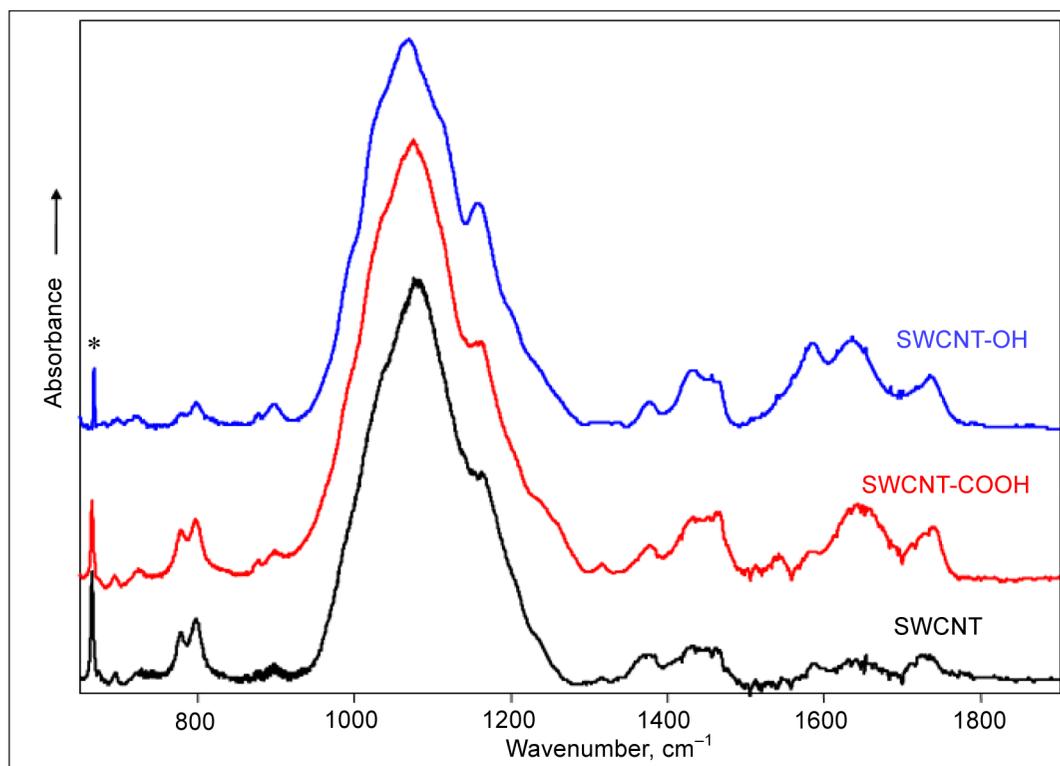


Fig. 4. Infrared absorption spectra of single-walled carbon nanotubes in KBr pellet. Bottom: untreated SWCNT; middle: COOH functionalized SWCNT; top: OH functionalized SWCNT

functional group dependant. In the OH functionalized nanotubes the band at 1431 cm^{-1} is more intense while the band at 1463 cm^{-1} is more intense in COOH nanotubes. Such changes could be explained by the fact that the total system symmetry is lowered after the functionalization.

OH functionalized nanotubes

The largest spectral differences between the untreated and OH functionalized nanotubes are observed in the region between 1500 and 1800 cm^{-1} . The most distinct and easily observable is the spectral band at 1586 cm^{-1} attributed to the COH bending vibration of the attached hydroxyl group. The frequency of the bending vibration is close to the frequency of HOH bending vibration in water molecule which is slightly above 1600 cm^{-1} . The observed band position at 1586 cm^{-1} indicates the chemical bonding of the OH group to the nanotube.

The OH bending band at 1586 cm^{-1} is much stronger than the band at 1583 cm^{-1} observed in the untreated nanotube sample what makes this band impossible to separate.

Multivariate curve fit analysis (OPUS 5.5) in the spectral range of 1600 – 1770 cm^{-1} allows identification of four additional bands. The band at 1652 cm^{-1} is assigned to the C-C stretch vibration of the atoms attached to the functional group. The same band is observed in the nanotubes functionalized with the carboxyl group. The spectral band at 1720 cm^{-1} is common to all nanotubes and is also observed in untreated SWCNT. Remaining spectral bands at 1630 cm^{-1}

and 1737 cm^{-1} are characteristic to the tubes functionalized with the OH group. Comparison with the results of theoretical calculations allows easy assignment of the 1737 cm^{-1} band to the C=C stretch vibration in the group where one of the carbon atoms is directly attached to the hydroxyl functional group. This vibration is well localized and does not involve vibrations of other atoms in the nanotube. The calculated position of this vibration is 1783 cm^{-1} . The calculated frequency of the C=C stretch vibration in OH functionalized nanotubes is the highest from all calculated bands having intensity high enough to be observable in the experimental infrared absorption spectra. The assignment of the remaining band at 1630 cm^{-1} is not that straightforward. The calculations predict two rather strong bands at 1663 and 1722 cm^{-1} . Both calculated vibrations involve C-C=C stretch type movements delocalized in the whole nanotube. Such vibrations can be very strongly coupled and experimentally often observable as one broad band, thus current experimental data do not allow more precise assignment of this experimental band. Theoretical calculations predict four strong bands in the range of 1260 – 1290 cm^{-1} . Unfortunately, this range is perturbed by very strong and broad absorption from the vibrations of untreated nanotubes and these theoretically predicted bands cannot be easily identified in the experimental spectrum. A strong band involving C-C-C and C-C-O deformation motions according to the calculations is expected to be around 1512 cm^{-1} . In the experimental spectrum a broad shoulder is observed on the 1583 cm^{-1} band which suggests existence of

a superimposed low wavenumber band. Multivariate curve analysis allows identification of a broad and medium intensity band located at around 1530 cm^{-1} .

COOH functionalized nanotubes

A carboxylic group is chemically more complicated than a hydroxyl group, therefore even more additional spectral bands are expected. Detailed analysis of the spectral region in the range of $1300\text{--}1500\text{ cm}^{-1}$ revealed seven spectral bands specific to the COOH functionalized carbon nanotubes. A weak spectral band observed in the experimental spectrum at 1315 cm^{-1} can be assigned to the theoretically calculated vibration at 1318 cm^{-1} . This vibration is a combination of COH deformation vibration from the carboxylic group and CCC deformation from the nanotube atoms attached to the carboxylic group. The spectral band at 1476 cm^{-1} is not clearly seen as it is perturbed by the neighboring band at 1463 cm^{-1} common to the untreated nanotubes. This band could be assigned to the C-C-O deformation vibrations. The assignment is based on two calculated bands at 1500 cm^{-1} and 1521 cm^{-1} both involving C-C-O deformation motions. Coupling of these two bands most likely results in appearance of one band in the experimental spectrum. The spectral band observed at 1542 cm^{-1} is assigned to the theoretically predicted band at 1551 cm^{-1} involving the C-C stretch vibration of the nanotube atom group directly connected to the functional group. The spectral band at 1640 cm^{-1} is a part of close overlapped doublet with another band located at 1652 cm^{-1} . 1652 cm^{-1} band is also observed for the OH functionalized nanotubes and assigned to the C-C stretch vibrations of the nanotube atom group attached directly to the functional group. The spectral band at 1640 cm^{-1} is specific only to the carboxylic functional group and based on theoretical calculations is assigned to the theoretically predicted band at 1667 cm^{-1} . This band involves the C=C stretch and C-C-C bond deformation vibrations of the nanotube carbon atoms. In the untreated nanotubes these types of vibrations result in very weak infrared absorption bands. System symmetry is changed when the carboxylic group is attached to the nanotube and it results in increase of the intensity of some weak bands.

A broad band in the spectral range between $1700\text{--}1880\text{ cm}^{-1}$ seems to have an internal structure. It is possible to find three bands at 1712 , 1720 and 1742 cm^{-1} in this spectral range using the multivariate curve analysis. A relatively weak and broad band at 1720 cm^{-1} is observed in all the nanotubes including untreated ones. The band at 1712 cm^{-1} is assigned to the antisymmetric C=C stretch vibration. The band at 1742 cm^{-1} is assigned to the theoretically predicted band at 1897 cm^{-1} . This band is the most characteristic feature of the carboxylic group. It involves well localized C=O stretch vibration. Theoretical calculations performed with a low basis set usually overestimate the position of this band, predicting its frequency to be 10% higher than experimental one. The position of this

band is close to the one observed in the carboxylic acids, for example, in methanoic (formic) acid this band is found around 1770 cm^{-1} depending on environment [19]. The calculations performed at the same level as for the functionalized nanotubes predict the position of the C=O stretch band in methanoic acid at 1900 cm^{-1} . Our assignment of the bands at 1712 and 1742 cm^{-1} is in good agreement with previous observations [6, 7, 17, 20].

Analysis of the infrared absorption spectral bands of carboxylic group functionalized nanotubes reveals that the presence of the spectral bands at 1315 , 1542 , 1640 and 1740 cm^{-1} can be used for the definite identification of the carboxylic group attached to the carbon nanotube.

Low temperature spectral results

Infrared absorption spectra of the untreated and functionalized carbon nanotubes embedded in the KBr pellets were recorded at several different temperatures in the range of 9 to 300 K. The shape and structure of all observed bands at 300 K temperature do not change in all temperature range down to 9 K. However, at low temperature two additional bands were observed for both untreated and functionalized nanotubes at 1275 cm^{-1} and 1385 cm^{-1} (Fig. 5). The observed bands are much sharper than any other bands observed at high temperatures. At the lowest temperature (9 K) the width of the band at 1275 cm^{-1} is 0.2 cm^{-1} (FWHM) and for the band located at 1385 cm^{-1} the width is 0.3 cm^{-1} . These bands exhibit clear temperature dependence and the variation with temperature is different for each band. The band at 1275 cm^{-1} broadens very rapidly with the increase of temperature, the band is hardly observable at 50 K temperature and completely undetectable at around 80–90 K. The behavior of this band is similar to the phonon bands in crystals which are also usually observable only in low temperatures. The fact that the band becomes very sharp at low temperatures reveals that the vibration gets strongly localized which is consistent with phonon vibrations. Theoretical calculations predict a vibration at 1123 cm^{-1} which involves C-C symmetric stretches resulting in the change of the length of whole tube. These vibrations are very highly coupled resulting in the experimental band broadening at high temperature. At temperatures below 10 K vibrations become strictly localized resulting in a very sharp band. The increase of the temperature to 40–50 K allows partial delocalization followed by the band broadening. The width of this band is 0.5 cm^{-1} at 20 K and 2.1 cm^{-1} at 50 K.

The 1385 cm^{-1} band is not that strongly dependant on the temperature change and is clearly visible up to 200 K. However, the width and position of this band changes with the increase of temperature. The band shifts from 1385.4 cm^{-1} at 9 K to 1384.7 cm^{-1} at 200 K and to 1384.2 cm^{-1} at 260 K. Above this temperature the band becomes too broad for the accurate detection. The band width increases from 0.3 cm^{-1} to 1.5 cm^{-1} when temperature is increased from 9 K to 200 K and reaches 1.7 cm^{-1} at 260 K. The broadening and red shift

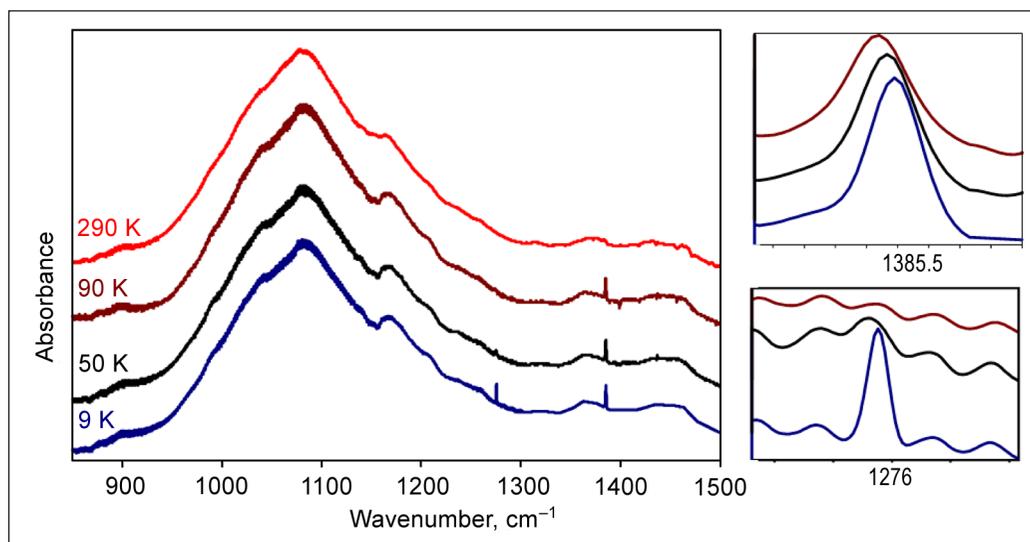


Fig. 5. Infrared absorption spectra of single-walled carbon nanotubes in KBr pellet at different temperatures (only 9, 50 and 90 K spectra are shown in the figures of single bands)

of the band is a sign showing that with the increase of temperature the number of higher lying energy states becomes populated. This allows to assign this band to the phonon type vibrations in the nanotube. In order to verify that these bands are related to the nanotubes and not caused by an impurity low temperature spectra (9 K) of pure KBr pellet, graphite in KBr and fullerene in KBr were recorded. In neither of these samples spectral bands 1275 and 1384.2 cm^{-1} were observed. Moreover, the band shape increase with temperature indicates that the vibration gets localized at low temperature which will not be expected to happen to any impurity under conditions of our experiment.

The band at 1275 cm^{-1} is very sensitive to the structure of any nanotube. The intensity of this band is decreased by factor of 3 for the OH or COOH functionalized nanotubes in comparison with untreated nanotubes (Fig. 6). In the experiments performed with the multi-walled nanotubes this band is barely visible and the intensity ratio with single-walled nanotubes is roughly 1 : 9.

In contrary, the band at 1385 cm^{-1} does not depend on the functionalization of the nanotube, e. g. it is not sensitive to any structural changes in the nanotube. Different behavior upon change of the structure confirms the different origin of the bands at 1275 and 1385 cm^{-1} .

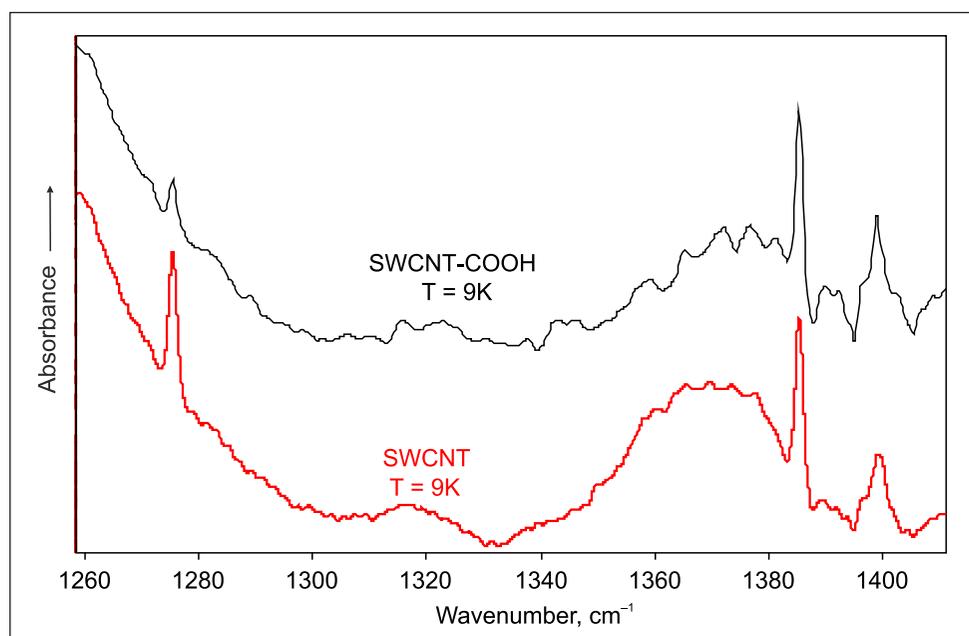


Fig. 6. Infrared absorption spectra of single-walled carbon nanotubes and COOH functionalized single-walled carbon nanotubes in KBr pellet at 9 K temperature

Strong dependence of the spectral band at 1275 cm^{-1} on the structure of the nanotube is a very good marker for the determination of the structural defects in the nanotubes and after calibration measurements with nanotubes of different quality could be potentially used for the determination of the unknown sample quality.

CONCLUSIONS

Results of infrared absorption experiments with untreated single-walled carbon nanotubes and the nanotubes embedded in the KBr pellet allow to conclude that the vibrational states of the nanotubes are not significantly affected by the KBr environment and this technique can be used for the future studies of the nanotubes.

Detailed analysis of the infrared spectra of the functionalized nanotubes revealed that there are perturbations on the nanotube structure which are to the same extent independent from the chemical group attached to the nanotube. Therefore infrared spectroscopy could be used as a tool for the detection of defects in the carbon nanotubes. Detailed analysis of the infrared spectra allows precise identification of chemical groups attached to the carbon nanotubes.

Theoretical calculations of the vibrational bands of chemical groups attached to the carbon nanotube and experimental data are in good agreement (within 10%) even using a rather low basis set and a small tube fragment with the exception of the C=O stretch band, which frequency is known to be overestimated in other molecular systems as well [23].

A very sharp band at 1275 cm^{-1} is observed in the low temperature infrared absorption spectra of single-walled carbon nanotubes. It is very sensitive to the structural defects in the nanotube and potentially could be used to evaluate amounts of structural defects in the single-walled carbon nanotubes using the low temperature ($T < 20\text{ K}$) infrared absorption spectroscopy as an additional method.

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FUNKCIONALIZUOTŲ VIENASIENIŲ ANGLIES NANOVAMZDELIŲ TYRIMAS INFRARAUDONOSIOS SUGERTIES SPEKTROMETRIJOS METODU

Santrauka

Anglies nanovamzdeliai (nuo pat jų atradimo 1991 metais) dėl savo ypatingos struktūros bei cheminių ir fizinių savybių tyrinėjami įvairiais metodais. Nepaisant didelio tyrimų skaičiaus vis dar lieka neatsakytų klausimų apie nanovamzdelių struktūrą bei chemines savybes. Tai ypač svarbu įvairiomis cheminėmis grupėmis funkcionalizuojant anglies nanovamzdelius. Norint suprasti funkcionalizavimo ypatybes bei praplėsti funkcionalizuotų nanovamzdelių taikymo sritis siektina suprasti procesus, vykstančius nanovamzdeliuose (molekuliniame lygmenyje). Infraraudonosios sugerties (IR)

spektrometrija kartu su kvantinės chemijos skaičiavimo metodais suteikia labai plačias galimybes tirti įvairias molekulinės sistemas. Infraraudonosios sugerties spektrai tampa informatyvesni juos užregistravus, bandinį atšaldžius iki labai žemų temperatūrų, dėl sumažėjusios aukštesnių energijos lygmenų užpildos.

Darbe pristatoma detali, grynų vienasienių anglies nanovamzdelių (SWCNT) bei hidroksilo (-OH) ir karboksilo (-COOH) cheminėmis grupėmis funkcionalizuotų vienasienių anglies nanovamzdelių, IR sugerties spektrų analizė paremta kvantinės chemijos skaičiavimų, atliktų naudojant HF/6-31G metodą, rezultatais. Užregistruoti grynų SWCNT bei SWCNT, izoliuotų kalio bromido tabletėse (KBr) IR sugerties spektrai. Grynų ir izoliuotų KBr SWCNT sugerties spektrai neturi didesnių skirtumų, todėl izoliavimo KBr tabletėse metodika yra taikytina tolimesniuose SWCNT tyrimuose IR sugerties metodu. Kambario temperatūros grynų SWCNT IR sugerties spektruose identifikuotos sugerties juostos, jos priskirtos normaliesiems atomų virpesiams bei fononams, remiantis teorinių skaičiavimų rezultatais bei ankstesnių darbų analize. Šios spektrinės juostos taip pat yra stebimos ir funkcionalizuotų SWCNT IR sugerties spektruose.

Funkcionalizuotų SWCNT IR sugerties spektruose aptiktos dvejų tipų sugerties juostos. Vienos būdingos visiems funkcionalizuotiems SWCNT, nepriklausomai nuo cheminės grupės, prijungtos prie nanovamzdelio tipo. Tai spektrinės juostos ties 878, 897, 1 652 ir 1 720 cm^{-1} . Šių juostų atsiradimas IR spektre leidžia identifikuoti struktūrinius defektus, atsirandančius funkcionalizuojant SWCNT. Kitos IR sugerties juostos būdingos tik konkrečiai cheminei grupei. Spektrinės juostos ties 1 586, 1 630 ir 1 737 cm^{-1} leidžia identifikuoti hidroksilo grupę, o juostos ties 1 315, 1 542, 1 640 ir 1 740 cm^{-1} – karboksilo grupę, kovalentiniu ryšiu prijungtą prie SWCNT.

SWCNT, atšaldytų iki 9K, IR sugerties spektruose pastebėtos naujos labai siauros (0,2 cm^{-1}) spektrinės juostos, priskirtos fononiniams virpesiams anglies nanovamzdelyje. Spektrinės juostos, esančios ties 1 275 cm^{-1} , intensyvumas labai kinta atsirandant struktūriniams defektams nanovamzdelyje. Funkcionalizuotų nanovamzdelių spektruose santykinis šios juostos intensyvumas sumažėja 3 kartus, o daugiasienių vamzdelių spektruose – 9 kartus. Spektrinės juostos ties 1 275 cm^{-1} intensyvumo priklausomybė nuo nanovamzdelių struktūros tvarkingumo leidžia defektų SWCNT identifikavimui taikyti žemos temperatūros infraraudonosios sugerties spektrometrijos metodą.