The Optical Spectra of Carbon Nanotubes

by

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This is to certify that I have examined the above MPhil thesis and have found that it is complete and satisfactory in all respects, and that any and all revisions required by the thesis examination committee have been made.

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Abstract

Single wall carbon nanotubes (SWCNs) of mono size and unique chirality are formed inside micro-channel array of a zeolite single crystal. Since they are forced to align along the c-axis of the crystal, they show strong polarization anisotropy in the optical absorption from near infrared to visible region. We have developed an effective and systematic way to measure the UV- FIR polarized optical absorption spectrum of nanotubes.

The polarization anisotropy of SWCNs in the infrared were studied by using the technique of Fourier Transform Infrared Spectroscopy (FTIR). Polarized optical absorption spectra in UV-NIR of SWCNs were measured with conventional dispersive spectrometry. We observed strong polarization anisotropy of the samples and carbon nanotubes are well arrayed in the zeolite. Absorption peaks with energy at 1.78eV and 3.4eV are being observed when the light electric field (E) is parallel to the tube direction (C), which are attributed to the inter-band transition of the nanotubes. This result agrees well with the calculation of density of state based on the local density function approximation.
Chapter 1

Introduction

Carbon nanotubes are the currently the focus of intense study worldwide. Carbon nanotubes are fullerene-related structures that consist of graphene cylinders closed at either end with caps containing pentagonal rings. Iijima discovered carbon nanotubes in 1991; Iijima's samples were created by a direct-current arc discharge between carbon electrodes immersed in a noble gas. [1] Since the tubule diameters in some cases are small enough to reveal the effect of one-dimensional periodicity, many new applications of Carbon Nanotubes are constantly being discovered and many are yet to be discovered.
1.1 Carbon Nature

Carbon belongs to group IV in the periodic table. Group IV elements have four outermost shell electrons and two of them are in s-orbital and the other two in p-orbital. These elements can undergo hybridization forming different bonds. A free carbon atom has the electronic structure \( (1s)^2(2s)^2(2p)^2 \). In order to form covalent bonds, one of the 2s electrons is promoted to 2p, and the orbital are then hybridized in one of the three possible ways: \( sp^1 \), \( sp^2 \) and \( sp^3 \) as shown in figure 1.1. The mixing of s and p orbitals is called hybridization.

Typical form of carbon that uses \( sp^2 \) hybridization is graphite. The structure of graphite consists of layers in which carbon atoms are arranged in an open honeycomb network. One of the 2s electrons hybridizes with two of the 2p to give three \( sp^2 \) orbital at 120 degree to each other in a plane, with the remaining orbital having a \( p_z \) configuration, at 90 degree to this plane. The \( sp^2 \) orbital form the strong \( \sigma \) bonds between carbon atoms in the graphite plane, while the \( p_z \), or \( \pi \), orbital provide the weak van der Waals bonds between the planes. The overlap of \( \pi \) orbital on adjacent atoms in a given plane provides the electron bond network which responsible for the high electrical conductivity of graphite.
In naturally occurring or high-quality synthetic graphite, the stacking sequence of the layers is known as graphene sheets.

Diamond is formed when carbon undergoes sp\(^3\) hybridization, which is the hardest solid in the world. In diamond, each carbon atom is joined by four neighbors in a tetrahedral structure.

There is a new form of carbon, fullerene, which is formed when carbon atoms undergo mixed sp\(^2\)/sp\(^3\) hybridization. The smallest fullerene molecule, C\(_{60}\), has a soccer ball structure. The carbon atoms are bonded in an icosahedral structure made up of 20 hexagons and 12 pentagons. Each of the carbon atoms in C\(_{60}\) is joined to three neighbors, the bonding is essentially sp\(^2\), and there is a small amount of sp\(^3\) character due to the curvature. Note that all 60 carbons atoms are identical, so that the strain is evenly distributed over the molecule. The bonding in carbon nanoparticles and nanotubes is also primarily sp\(^2\), although once again there may be some sp\(^3\) character in region of high curvature.
Figure 1.1: Schematic presentation of (a) sp$^1$, (b)sp$^2$ and (c) sp$^3$ bonding hybridizations.
1.2 Structure of SWCNs

There are three types of nanotubes shown in Fig.1.2 [1], depending on how to roll the two-dimensional graphene sheet, called armchair, zigzag and chiral nanotubes. Nanotubes can be considered as prototypes for a one-dimensional quantum wire. Within the band-folding scheme, the diameter and the chirality of a SWCN determine whether the nanotubes is metallic or semiconducting.
Figure 1.2: Three kinds of SWCNs: The upper one is armchair nanotubes, the middle one is zigzag nanotubes, and the bottom one is chiral nanotubes. It can be seen that the orientations of hexagonal rings relative to the tubule axes are different.
Figure 1.3: Schematic of a 2D graphene sheet illustrating lattice vectors $\hat{a}_i$ and $\hat{a}_2$, and the roll-up vector $C_h = n\hat{a}_1 + m\hat{a}_2$. When we connect lattice sites O and A, and sites B and B', a nanotubes can be constructed. The translation vector $\mathbf{T}$ is along the nanotubes axis and defines the 1D unit cell. The figure is constructed for an $(n, m) = (4, 2)$ nanotubes.
In the unit cell of a carbon nanotubes, refer to Figure 1.3, chiral vector of the nanotubes, $C_h$, is defined by

$$C_h=n\hat{a}_1 + m\hat{a}_2$$

(1.1),

where $\hat{a}_1$ and $\hat{a}_2$ are unit vectors in the two-dimensional hexagonal lattice, and $n$ and $m$ are integers. Another important parameter is the chiral angle $\theta$ of the nanotubes between $C_h$ and $\hat{a}_1$. Nanotubes are formed when the graphene sheet is rolled up from the cylinders; the ends of the chiral vector meet each other. The chiral vector thus forms the circumference of the nanotubes; different nanotubes structure can be formed by different values of $n$ and $m$. 
Armchair nanotubes are formed when \( n = m \) and the chiral angle is 30°. Zigzag nanotubes are formed when either \( n \) or \( m \) is zero and the chiral angle is 0°. Chiral nanotubes are formed when chiral angles is between 0° and 30°. The properties of nanotubes are determined by their diameter, chiral angle and the value of \( n \) and \( m \).

The diameter, \( d_i \), is simply 1/4 the length of the chiral vector and defined by

\[
d_i = \left( \frac{\sqrt{3}}{\pi} a_{c-c} \right) \sqrt{m^2 + mn + n^2}
\]  

(1.2)

, where \( a_{c-c} \) is the distance between neighboring carbon atoms in the flat sheet.
In turn, the chiral angle is given by

\[ \theta = \tan^{-1}\left(\sqrt{3n} / (2m + n) \right) \]  \hspace{1cm} (1.3)

Another important parameter is the translational vector, \( T \), is the vector parallel to the tubule axis and normal to \( C \) referring to Fig.1.2, and given by:

\[ T = t_1 \hat{a}_1 + t_2 \hat{a}_2 = (t_1, t_2). \]  \hspace{1cm} (1.4)

where \( t_1 = (2m+n)/D \), \( t_2 = -(2n+m)/D \) and \( D \) is the greatest common divisor of \( (2n+m) \) and \( (2m+n) \).

For \((n, n)\) nanotubes, \( T \) is always \((1, -1)\) and for \((n, 0)\) nanotubes, \( T \) is always \((1, -2)\). With \( T \) and \( C \), the unit cell of the one dimensional carbon nanotubes the rectangle \( OAB'B' \) in Figure 1 is defined. The number of hexagons per unit cell \( N \) is given by:

\[ N = 2(m^2 + mn + n^2) / D, \]  \hspace{1cm} (1.5)

and there are \( 2N \) carbon atoms in each unit cell.
Furthermore, we denote the carbon atom site vectors with the unit cell by \( iR \)

where \( i \) is an integer. The symmetry vector \( R \) is defined as the site vector \( OR \) (see Figure 1.2), and is given by:

\[
R = p\hat{a}_1 + q\hat{a}_2, \tag{1.6}
\]

where \( t_1q - t_2p = 1 \).

The solution of \( p \) and \( q \) is uniquely determined if \( t_1 \) and \( t_2 \) do not have a common divisor except for unity.
1.3 Electronic structure of SWCN

The unique electronic properties of carbon nanotubes are due to the quantum confinement of electrons normal to the nanotubes axis. In radial direction, electrons are confined by the monolayer of the graphene sheet. Around the circumference of the nanotubes, periodic boundary conditions come into play. For example, if a zigzag or armchair nanotubes has 10 hexagons around its circumference, the 11th hexagonal will coincide with the first. Going around the cylinder once introduces a phase of difference of $2\pi$.

Because of this quantum confinement, electrons can only propagate along the nanotubes axis, and so their wavevectors point in this direction. The resulting number of one-dimensional conduction and valence bands effectively depends on the standing waves that are set up around the circumference of the nanotubes. These simple ideas can be used to calculate the dispersion relations of the one-dimensional bands, which link wavevector to energy, from the well-known dispersion relation in a graphene sheet. Dispersion relation show that about one-third of small-diameter nanotubes are metallic, while the rest are semiconducting, depending on their diameter and chiral angle. In general, carbon
nanotubes will be metallic when \( n - m = 3q \), where \( q \) is an integer. All armchair nanotubes are metallic, as are one-third of all possible zigzag nanotubes.

The density of electronic states as a function of energy has been calculated for a variety of nanotubes. As an example, consider the density of states for metallic (8,8), (9,9), (10,10) and (11,11) armchair nanotubes. While conventional metals have a smooth density of states, these nanotubes are characterized by a number of singularities, where each peak corresponds to a single quantum subband. These singularities are important when interpreting experimental results, such as measurements obtained from scanning tunneling spectroscopy and resonant Raman spectra, the two techniques that have contributed the most to our understanding of the one-dimensional properties of nanotubes.
1.4 Vibrational modes in SWCNs

Group theory is used to determine infrared active modes and Raman active modes. The modes can be decomposed into the irreducible representations of the point group appropriate to the tube.

The symmetry classification of a carbon nanotubes is as either being achiral (symmorphic) or chiral (non-symmorphic) [3]. There are only two cases of achiral nanotubes; armchair and zigzag nanotubes. The achiral nanotubes belong to the point group $D_n$. The $D_n$ group has a different group structures, depending on whether $n$ is even ($n=2j$) or odd ($n=2j+1$). The total symmetry of achiral nanotubes is expressed by the direct product of the groups $D_n \otimes C_i$, where the group $C_i$ consists of the identity and inversion operators, $E$ and $i$.

From reference [4], if we consider armchair tubes with $D_{nh}$ symmetry and assume that $n$ is an even integer, the vibrational modes will be decomposed into the following irreducible representations.

$$
\Gamma^{\text{ vib}} = 4A_1 + 2A_{1u} + 4A_{2g} + 2A_{2u} + 2B_{1g} + 4B_{1u} + 2B_{2g} + 4B_{2u} + 4E_{1g} + 8E_{1u} + 8E_{2g} + 4E_{2u} + \ldots + 8E_{(n/2-1)g} + 4E_{(n/2-1)u}.
$$

(1.7)
If $n/2$ is even, the 8 and 4 in the last two terms will be interchanged. Consider the (6,6) armchair tube, for which $N = 12$, this will have 72 phonon branches, and a total of 48 distinct mode frequencies (since the final two terms disappear).

Appropriate character tables can be used to determine which modes are IR active and which are Raman active. For the $D_{nh}$ group, the $A_{2u}$ and $E_{1u}$ modes are IR active, while the $A_{1g}$, $E_{1g}$ and $E_{2g}$ are Raman active.

Thus there are 8 IR mode frequencies ($A_{2u} + 7E_{1u}$) and 16 Raman active frequencies ($4A_{1g} + 4E_{1g} + 8E_{2g}$) at zone center. It is important to note that the number of IR and Raman active modes is independent of nanotubes diameters; this is also true for all other classes of tube. However, by increasing the diameter of the nanotubes, modes with different symmetries are added but the number and symmetry of the optically active modes remain the same.

In the case of armchair tubes with $D_{nd}$ symmetry that $n$ is odd integer, similar arguments show that there will be 7 IR active frequencies and 15 Raman active frequencies. Zig-zag tubes, whether $D_{nh}$ or $D_{nd}$, will also have 7 IR active frequencies and 15 Raman active frequencies.
Consider now the chiral tube, that belong to non-symorphic Abelian group $C_N$, for which the vibrational modes contain the following symmetries.

\[ \Gamma^{ub} = 6A + 6B + 6E_1 + 6E_2 + \cdots + 6E_{N/2 - 1} \] (1.8)

For chiral nanotubes, the A and $E_1$ modes are IR active, and the A, $E_1$ and $E_2$ modes are Raman active.

Since there are $2N$ carbon atoms in the unit cell of a carbon nanotubes, the total number of vibrational modes will be $6N$. The vibrational mode frequencies of nanotubes can be calculated from those of a two dimensional graphene sheet using the equation

\[ \omega_{1D}(k) = \omega_{2D}(kK_2 + \mu K_1) \] (1.9)

\[ \mu = 0,1,2,\ldots,N - 1, \]

where $\omega_{1D}$ is the vibrational mode frequency for 1D tube, $\omega_{2D}$ is the frequency for a 2D graphene sheet, $k$ is a wavevector in the direction $K_2$ in reciprocal space (i.e. along the tube axis) and $\mu$ is an integer used to label the wavevectors along the $K_1$ direction in reciprocal space, perpendicular to the tube axis.
1.5 Mode frequency dependence on tubule diameter

It should be noted that the number of Raman- and IR-active modes is independent of the nanotubes diameter.

For the armchair, chiral and zig-zag, a common general behaviour is observed for both the IR-active and Raman-active modes. The highest frequency modes exhibit much less frequency dependence on diameter than the lowest frequency modes [5].

The highest frequency modes exhibit much less frequency dependence on diameter than the lowest frequency modes. Taking the large-diameter tube frequencies as our reference, we see that the four lowest modes stiffen dramatically (150-400cm\(^{-1}\)) as the tube diameter approaches ~1nm. Conversely, the modes above ~800cm\(^{-1}\) in the large-diameter tubules are seen to be relatively less sensitive to tube diameter.
1.6 Purpose of this Research

There is still limited experimental information available for 1D properties of Carbon nanotubes. Many new applications of Carbon Nanotubes are constantly being discovered and many are yet to be discovered. With a systematic and effective way to measure the polarization anisotropy optical spectrum in UV to IR, we can investigate the optical property of SWCNs, and through which a better understanding of the electronic and vibrational properties of the SWCNs.
Chapter 2 Experimental Procedures

In this chapter, the fabrication of SWCNs and the experimental procedures of absorption spectroscopy will be explained.

2.1 Fabrication of Carbon Nanotubes

In the fabrication of Carbon Nanotubes, zeolite crystals are used as temples to accommodate the SWCNs. Zeolite is a general name of series of porous crystal and used in this research is aluminophosphate (AIPO₄-5) crystal, named AFI. The inner diameter is 0.73nm and the separation distance between two neighboring channels is 1.37nm as shown in figure 2.2.

TPA is a kind of organic molecules. Its molecular formula is N(CH₂CH₂CH₃)₃. It is the raw material for making carbon nanotubes. TPA encapsulated AFI crystals are put in a glass tube and pumped to a vacuum of 10⁻⁴ Torr at temperature of about 600°C. At this temperature, the N-C and H-C bonds of TPA are broken, leaving the carbon atoms in the channels and forming carbon nanotubes.
The experimental setup for the synthesis is shown as Fig.2.1. The zeolite is put into a long quartz test tube with the open end connected to a vacuum pump. The close end of the tube is put into an oven.

A TPA-AFI crystal is transparent in visible region. After the carbon nanotubes formed inside (named C-AFI), the C-AFI crystal turns slightly black in color and behaves as a good polarizer. It has high absorption of light polarized parallel to the crystal axis direction (E//C) and with high transparency for the light polarized perpendicular to crystal axis direction (E ⊥ C). This is consistent with the one-dimensional characteristics of nanotubes.
Fig.2.1: This is the setup for synthesizing SWCNs inside zeolite. TPA-AFI is

put into a Quartz test tube and heated to 600°C in oven under vacuum.
Figure 2.2: (a) The framework structure of an AFI single crystal view along the [001] direction. (b) A schematic show of the AFI single crystal and light polarization configuration.
2.2 Experimental Procedures of Absorption Spectroscopy in the near-IR

The absorption spectrum of C-AFI is measured in order to gain the knowledge about the electronic structure of carbon nanotubes. In Figure 2.3 and 2.4, it is shown that SWCNs sample is fixed in the paper slit with a layer of aluminum foil with a hole just under the tube to let light pass through.

The transmission of the C-AFI is measured at room temperature. Before the incident goes to lens, it goes to the FTIR and polarizer with polarization of either parallel or perpendicular to the axis of the nanotubes. Then, the light is focused onto the sample by a microscope objective lens. The transmission light is collected by another lens and coupled to a silicon detector. A pre-amplifier is further amplified using a lock-in amplifier. The data is then transferred to a personal computer. The apparatus is shown in Figure 2.5.
Fig. 2.3: The photo of a sample (black in color) fixed in the paper slit. Underneath the sample is a layer of aluminum foil with a hole (see Figure b) to let light pass through. The sample looks black because it has high absorption of light polarized parallel to the carbon nanotube axis direction: (a) $E \perp C$, (b) $E // C$.
Figure 2.4: The components of the sample holder, including the slit, the aluminum foil and the metal plate.
Figure 2.5: The near-IR setup and ray path for measuring absorption spectrum.
2.3 Experimental Procedures of Absorption Spectroscopy in UV/VIS

The transmission of the C-AFI is measured at room temperature. Before the light pass through lens, light goes through an iris, chopper and polarizer with polarization of either parallel or perpendicular to the axis of the nanotubes. Then, the incident light is focused onto the sample by a microscope objective lens. The transmission light is collected by another lens. The light is finally coupled to an optical fiber. The chopper is connected to a controller and a lock-in amplifier. The optical fiber is connected to a monochromator. The dispersed light is detected using a photomultiplier tube (PMT), and is further amplified using a lock-in amplifier. The data is then transferred to a personal computer. The apparatus is shown in Figure 2.6.
Figure 2.6: The UV/VIS setup and the ray path for measuring absorption spectrum.
In order to normalize the transmission spectrum of sample with polarization parallel to axis and perpendicular to axis, the background spectrum is also measured. The intensity of the transmission light is fitted using the equation:

\[ I = I_0 e^{-\sigma(\lambda)d} \]  

(2.1)

where \( I \) is the intensity of light passing through the sample and \( I_0 \) is the intensity passing through a pure AFI crystal. The thickness of the sample \( (d) \) is kept constant throughout the experiment and the absorption coefficient \( (\sigma) \) which is a function of wavelength can be obtained.
Chapter 3 Experimental Results and Discussion

The absorption spectra of carbon nanotubes are measured in order to learn more about the electronic structure and lattice vibration of carbon nanotubes. Many samples have been tested, but only some of them have strong polarization anisotropy.

3.1. Polarization Anisotropy

We expect that the transmitted light intensity vary with the polarization angle \( \theta \) and would like to see the maximum and minimum transmitted light intensity while the polarization angle is changed with axis c. Schematics in Figure 3.1 shows two extreme cases of transmitted light.

Figure 3.2(a) and (b) shows the intensity of light passing through the sample with polarization parallel to axis and perpendicular to axis in UV-NIR. There is strong polarization anisotropy from 1.1eV to 2.8eV. The transmission of light with polarization perpendicular to the axis is much larger, consistent with the expected property of carbon nanotubes. However, as shown in Figure 3.2 (c), there is no significant anisotropy in the intensity of light passing through the empty zeolite with polarization parallel to axis and perpendicular to the axis in UV-NIR.
Therefore the observed transmission anisotropy of carbon nanotubes containing zeolite samples is due to the nanotubes.

From Figure 3.2(d), it can be seen that a broad absorption peak is near 2.5eV for the c-tube sample c3 in the 90 degree polarization angle. There are also some absorption peaks for sample f2 and z3 in Figure 3.2(e) and (f), but they are not corresponding to the certain band-transition for chirality (3,3), (4,2) and (5,0). Absorption peaks are corresponding to the band-transition for chirality (4,2) would be discussed in section 3.3.

Figure 3.1: Transmitted light intensity is maximum when \( I_\perp \) and is minimum when \( I_\parallel \).
Figure 3.2 (a): Transmission spectra of light passed through the C-AFI sample as a function of photon energy. The intensity for E//C is much less than that E⊥C polarization.

Figure 3.2 (b): Transmission spectra of C-tube sample f2 in different polarization angles.
Figure 3.2 (c): Transmission spectra of empty zeolite z3 in different polarization angles.
Figure 3.2 (d): Absorption spectrum of c-tube sample c3 in different polarization angles.

Figure 3.2 (d): Absorption spectrum of c-tube sample f2 in different polarization angles.
Figure 3.2 (f): Absorption spectrum of empty zeolite in different polarization angles.
3.2 Degree of Polarization in UV-VIS

From Figure 3.3, it is seen that the transmitted light intensity of the AFI-nanotubes sample varies with the polarization angle and there are periodical extreme values, which indicates the maximum and minimum of the light intensity. The minimum of light intensity is due to absorption of the parallel-polarized light by the carbon nanotubes.

Mono-sized, aligned and single-walled carbon nanotubes (SWCNs) of about 0.4nm diameter are formed inside the micro-channel array of a zeolite single crystal. Since they are forced to align along c-axis of the crystal, they show strong polarization anisotropy in the optical absorption from near infrared to ultraviolet region. The transmission is maximum at 90° and minimum at 0° and 180°. The spectrum at 30° matches well with that at 150°, and the spectrum at 60° matches well with that at 120°, showing well the cosθ dependence of the spectra.
Figure 3.3: The transmitted intensity $I$ varies with polarization angle $\theta$ of C-tube in the UV-visible region.
3.3 Inter-band transition

In the absorption spectrum shown in Figure 3.4, when the light electric field (E) is polarized parallel to the tube direction (c), the spectrum display a broad peak (A) at 1.78eV, which is due to the inter-band transition of electrons in our nanotubes. Most of the samples examined show similar spectra like sample C3. A list of all the samples studied is given in Table 3.1.

In the absorption spectrum of another sample F5 shown in Figure 3.5, when the light electric field (E) is polarized parallel to the tube direction (c), the spectrum display a broad peak (B) at 3.4eV to be the inter-band transition of electrons in our nanotubes. Only one sample has been found to have absorption spectrum like that.

The calculated DOS shown in Figure 3.6 have been performed using a planewave pseudopotential formulation within the framework of local density approximation (LDA) [6]. Unlike the nanotubes of larger diameters, the density of states is by no means symmetric about the Fermi level, a consequence of the small radius and large curvature. It is clearly seen from the figure that the (4,2) tube is semi-conducting, and the DOS has characteristic one-dimensional singularity with quantized energy levels. The inter-band transition energy is about 1.78eV and 3.4eV.
Figure 3.7 shows that the calculated imaginary part of the dielectric function ($\varepsilon_2$) of the three SWNT for the case of light polarized parallel to the nanotubes axis.

For the (4,2) tube, there is a sharp peak at about 1.9eV and small peak at about 3.6eV. These energies match well the absorption peaks in Figs. 3.4 and 3.5.

![Graph showing absorption spectrum](image)

**Figure 3.4:** The polarized optical absorption spectrum of the SWNT containing AFI crystal.
Figure 3.5: The polarized optical absorption spectrum of the SWNT containing AFI crystal.

total DOS of tube(4,2)

Figure 3.6: The density-of-state of (4,2) chiral nanotubes. The SWCN is semiconductor [6].
Figure 3.7: Imaginary part ($\varepsilon_2$) of the dielectric function (parallel to the tube axis) for the tubes (5,0), (3,3) and (4,2).

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<tr>
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</table>

Table 3.1 Size of samples
3.4 Phonon modes

Figure 3.8 shows the intensity of light passing through the sample with slit in the mid-infrared range, using the FT spectrometer with IR microscope at MCPF.

Figure 3.9(b) shows the intensity of light passing through the empty zeolite with slit in the mid-infrared range. Zeolite crystal blocks the light in two regions (700-1720 cm\(^{-1}\)) and (2715- 3682 cm\(^{-1}\)), in which no light leakage is found. Compare with Figure 3.9 (a), transmission intensity of light passing through the sample without slit is also measured. It is seen that light is not completely blocked in these two regions. This is due to light leakage around the sample that cannot be completely blocked out by the microscope aperture. The slit is used to fix carbon nanotubes and prevent light leakage for UV-FIR since aluminum foil can block UV-FIR.

Since the significant phonon IR-active modes are near 800cm\(^{-1}\) and 1600cm\(^{-1}\) as shown in Figure 3.10, from the transmission spectrum shown in Figure 3.8, no open window can be found under 1900cm\(^{-1}\), therefore we cannot find the significant phonon IR-active modes. To see modes under 1800cm\(^{-1}\), we have to thin down the c-tube to let more light pass through in future work.
Figure 3.8: Transmission spectrum of c-tube fixed in slit

Figure 3.9(a): Transmission spectrum of c-tube without slit
Fig 3.9 (b): The plot of the transmission of light passed through the AFI sample as a function of wavenumber.
Figure 3.10 Diameter dependence of IR-active mode frequencies for nanotubes [5]
3.5 Polarization Anisotropy in MIR

The polarization anisotropy spectra of each sample is obtained by ratio the transmission spectrum of each sample at 0° by the one at 90°. There are some regions with polarization anisotropy in the transmission spectra of carbon nanotubes samples. Absorption due to carbon nanotubes can only be observed in these open windows.

Figure 3.13 shows that carbon nanotubes sample f17 has strong polarization anisotropy only in 3800 to 6000cm⁻¹ and in 1350 to 1550cm⁻¹, and nearly zero polarization anisotropy in 1700 to 2600cm⁻¹. Figure 3.11 shows that carbon nanotubes sample f15 has strong polarization anisotropy in 1700 to 2600cm⁻¹ and 3800 to 6000cm⁻¹.

F17 is a tropical sample since most of the well-measured samples (f12, f9 and c3) have similar transmission plot as f17 (Figure 3.13). In the transmission plot, three open windows can be found and only the second window (1700 to 2700 cm⁻¹) has no anisotropy. However, there is an exception case in f15. In Figure 3.11, the first window is not observed and the second window has non-zero anisotropy, while the third window has anisotropy as in the case of F17.

The broad anisotropy background observed is probably due to the weak electronic transition near the Fermi level where the density of state is low. From
Figure 3.6, it can be seen that tube (4,2) is semiconducting with a small band gap of 0.2eV. In the zero anisotropy open window of f17 and others, the window width is about 0.15eV. Comparing with the Density of State of different chirality in Figure 3.15, only (4,2) tubes have open gap. From the weak absorption strength and gap length, most of the samples measured are probably (4,2) ones. There are only three possible types of tube because of the small diameter of carbon nanotubes. Since the curve structures of f15 and f17 are different, f17 is (4,2), then f15 must be (3,3) or (5,0) or mixture of (3,3) and (5,0).

![Graph](Image)

Figure 3.11 Transmission spectra of light passed through the C-AFI sample f15 as a function of photon energy.
Figure 3.12: The transmission ratio between 0degree and 90degree polarization C-tube sample f15

Figure 3.13 Transmission spectra of light passed through the C-AFI sample f17 as a function of photon energy.
Figure 3.14: The transmission ratio between 0degree and 90degree polarization
C-tube sample f17
Figure 3.15 Density of states for (a) (5,0) (b) (3,3) and (c) (4,2) tubes. The Fermi level is 0eV.
3.6 Carbon nanotubes in epoxy after thin-down

A carbon nanotubes sample fixed in epoxy has been thin down to reduce its strong absorption. In Figure 3.16, the red curve is the intensity of epoxy without carbon nanotubes in the parallel polarization angle, while the green curve is the intensity of carbon nanotubes fixed in epoxy in the parallel polarization angle. From Figure 3.9(b), there is still transmission below 2100cm\(^{-1}\) for zeolite crystal. However, it is seen from Figure 3.16 that the absorption is complete below 2100cm\(^{-1}\). This is due to the absorption of epoxy that is not completely removed at the bottom of the carbon nanotubes sample.

Figure 3.17 shows the plot of intensity of C-tube over the intensity of Epoxy. From this ratio curve, it can be seen that there are epoxy absorption near 2900cm\(^{-1}\) and zeolite absorption from (3000 to 3500) cm\(^{-1}\).

Figure 3.18 shows the ratio of the 0 degree spectrum over that of the 90 degree polarization for Epoxy and C-tube. For Epoxy, there is interference fringe in the range of 2000 to 3700 cm\(^{-1}\), and weak anisotropy near 4800cm\(^{-1}\) and 6600cm\(^{-1}\). There is a significant anisotropy double-dip near 3600cm\(^{-1}\), it may be caused by the absorption from the overtone phonon transitions in carbon nanotubes.
For the samples without thin down and the zeolite absorption in the region 3000 to 4000 cm\(^{-1}\) is large. Compare with Figure 3.16, the carbon nanotubes after thinning down still have transmission in the 3000 to 4000 cm\(^{-1}\). Therefore, thinning down is necessary for carbon nanotubes so that the more structure of carbon nanotubes in 3000 to 4000 cm\(^{-1}\) can be seen. From Figure 3.18, the absorption dips are found near 3600 cm\(^{-1}\).

![Graph](image)

*Figure 3.16 Intensity of C-tube fixed in Epoxy and Epoxy with parallel-polarized angle in the MIR region.*
Figure 3.17: The ratio of intensity of C-tube over Epoxy in different polarization angle.

Figure 3.18: Plot of (0 degree over 90 degree) transmission ratio of Epoxy and C-tube.
Chapter 4: Conclusion and Future Works

By studying the polarization anisotropy of the samples, we found some strong anisotropy spectral regions that are due to carbon nanotubes absorption. We also developed an effective and systematic way to measure the UV- FIR polarized optical absorption spectrum of nanotubes, and have observed that the carbon nanotubes are well arrayed in the zeolite.

Polarized absorption spectra were measured. Absorption peaks were observed near 1.78eV and 3.4eV. By comparing the result of density of state calculation using local density approximation, this absorption band was attributed to the nearest inter-band transition of the electrons in the (4,2) nanotubes. Also, by comparing with the length of zero-anisotropy window in transmission spectrum of nanotubes and the gap separation in the Density of State of (4,2), we identified our samples as (4,2) tube.

The realization of 0.4nm SWCNs is a major breakthrough in carbon nanotube research. Many complex properties are still under investigation. Due to strong absorption by the zeolite crystal, we cannot see the structure of carbon nanotubes below 1900cm⁻¹, where most of the nanotube phonon modes are. After thinning down of carbon nanotubes, phonon modes can be seen. This opens up the possibility to study the details of the IR active phonons.
References

1. AV Eletskii, Physics-Uspelchi 40 (9), 899 (1007)
6. The calculation result of density of state is provided by H.J. Liu
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