The effect of light polarization on the interband transition spectra of zigzag carbon nanotubes and its diameter dependence

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HIGHLIGHTS

- Polarization dependence of absorption in zigzag nanotubes is studied for 0–11 eV.
- A modified angular quantum number is used for the selection rules.
- Transition probability is significant for perpendicular light at certain energies.
- In small diameter tubes, perpendicular light is favorable for absorption of UV light.
- In the IR/VIS region, parallel polarization has a higher probability of absorption.

ARTICLE INFO

ABSTRACT

Although the optical absorption spectra of carbon nanotubes with perpendicularly polarized light are known to be suppressed due to the depolarization effect, peaks with significant magnitudes have been reported in photoluminescence absorption spectra of single-walled nanotubes under perpendicular polarization. We study the effect of light polarization on the interband optical transition spectra of nanotubes, independently from the depolarization effect. We employ the density functional theory to calculate the absorption spectra of periodic zigzag carbon nanotubes for parallel and perpendicular polarization of light in a wide, infrared-visible-ultraviolet range (0–11 eV). We have chosen (4,0), (8,0), and (16,0) nanotubes with diameters of ~ 0.34, ~ 0.63, and ~ 1.27 nm, respectively, to also investigate the dependence of the polarization effect on nanotube diameter. Although the overall spectrum for perpendicular polarization is sparse compared to the one for parallel polarization, the transition probability can be quite significant at certain photon energies for perpendicular polarization. For an (8,0) nanotube, for example, we observe sharp peaks at 1.2 eV, 1.8 eV and 10.6 eV. As the nanotube diameter decreases, parallel polarization seems to become progressively more favorable for absorption than perpendicular polarization in the infrared/visible range. Surprisingly, in the ultraviolet region, this trend is reversed; for nanotubes with small diameter, we notice a higher probability of absorption for ultraviolet light with perpendicular polarization compared to the one with parallel polarization. This can be important in optoelectronic applications of carbon nanotubes for ultraviolet absorption and emission.

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1. Introduction

The unique optical properties of carbon nanotubes (CNTs) that arise from their one-dimensionality and sharp van Hove singularity (VHS) points in their density of states, have been widely investigated in both theoretical and experimental research [1–5]. Several groups have measured the absorption spectra of CNTs and explored the structural dependence of these spectra [6–10]. These properties have also been explored theoretically using methods ranging from the analyses of dipole moments and transition rates based on the tight-binding (TB)/zonefolding approximation to first-principles calculations of the absorption spectra [11–15].

Both the theoretical and experimental studies have shown a strong dependence on chirality and diameter for optical absorption. The spectra also depend on the polarization of the incident light, due to the one-dimensional nature of nanotubes. For perpendicularly polarized light, the absorption spectrum is known to be suppressed due to the depolarization effect [16], i.e., the reduction of the effective electric field as a result of the induced charges on the nanotube walls. The polarization dependence of the optical absorption spectrum has been studied experimentally for 4 Å nanotubes (nanotubes with diameter of $\sim$4 Å) in zeolite [17]. Theoretical calculations that take into account the local-field

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effects (LFE) have also confirmed the weakening of the perpendicular polarization spectra of 4 Å nanotubes due to the depolarization effect [18]. The depolarization effect has also been observed in Raman spectroscopy of CNTs [19–21].

However, despite the depolarization effect, distinct peaks have been observed in the photoluminescence spectra of individual single-walled nanotubes (SWNTs) under the perpendicular polarization [22]. This suggests that although the depolarization effect (often referred to as the "antenna effect" in the nanotube literature) is known to play a major role, other factors might also be influential in the polarization dependence of the absorption spectra of nanotubes. Hence, exploring the effect of light polarization beyond the depolarization effect is important. Band-to-band transition rates are at the root of optical absorption spectra. Therefore, the goal of this work is to investigate the effect of light polarization on the interband optical transition spectra of zigzag nanotubes independently of the antenna effect and to explore its dependence on the nanotube diameter.

2. Methodology

We employed a first-principles method to calculate the optical absorption spectra of zigzag CNTs for parallel and perpendicular polarizations of light. We studied the band-to-band transition spectra without including the LFE in order to examine the effect of light polarization on the dipole moments and interband transitions separately from the depolarization effect. In order to investigate the diameter dependence of the polarization effect, we calculated the spectra for three zigzag nanotubes with significantly different diameters. For this purpose, we chose (4,0), (8,0), and (16,0) nanotubes with diameters of ~ 0.34, ~ 0.63, and ~ 1.27 nm, respectively. Structural relaxation and energy calculations were performed in Gaussian 09 [23]. Periodic boundary conditions were applied to one unit cell of the nanotube and the band energies and wave functions were obtained from density functional theory (DFT) calculations using Becke–Lee–Yang–Parr (BLYP) [24,25] exchange-correlation potentials with the 6-31G basis set. We have previously observed that results form BLYP/6-31G calculations of the optical spectra for parallel polarization are in reasonable agreement with experimental data [26]. Our study is based on calculating the wave functions and obtaining the transition rates based on Fermi's golden rule, according to which, the transition rate, W_{if}, between an initial state, Ψ_i, and a final state, Ψ_f, has the form

$$W_{if} \propto \frac{1}{\omega^2}|P.D|^2\rho, \tag{1}$$

where ω and P are the angular frequency and the polarization vector of the incident light, respectively, ρ is the density of states (joint density of states (JDOS) in this work), and D is the electric dipole vector given by

$$D = \langle \Psi_f|\nabla|\Psi_i\rangle. \tag{2}$$

Dipole moments were calculated only at the Γ point ($k_z = 0$), which is the only k-point at which Gaussian software provides the wave functions. In case of zigzag nanotubes, the Γ point is where the VHS occur and, therefore, the overall transition rate to a specific subband is expected to mostly originate from the dipole moment at this k-point. In order to calculate the dipole moment according to Eq. (2), the derivative of the wave function corresponding to the studied valence band was calculated using the method of finite differences and the integral was performed in the three-dimensional space. The number of grid points in the directions perpendicular to the nanotube axis (x and y) varied according to the nanotube diameter. For instance, a $300 \times 300 \times 221$ ($N_x \times N_y \times N_z$) grid was used for discretizing the wave functions of an (8,0) nanotube. Further refining of the grid led to negligible changes in our results. We calculated the dipole moment for all the possible optical transitions between the first 12 valence and 16 conduction bands, including both π and σ bands. However, for the purposes of comparison, all the optical spectra are plotted only in the 0–11 eV range.

3. Results and discussion

3.1. Effect of polarization

Fig. 1 shows the optical transition spectrum of an (8,0) nanotube for light polarized parallel and perpendicular to the nanotube axis. The overall spectrum for perpendicularly polarized light is sparse compared to the one for parallel polarization.
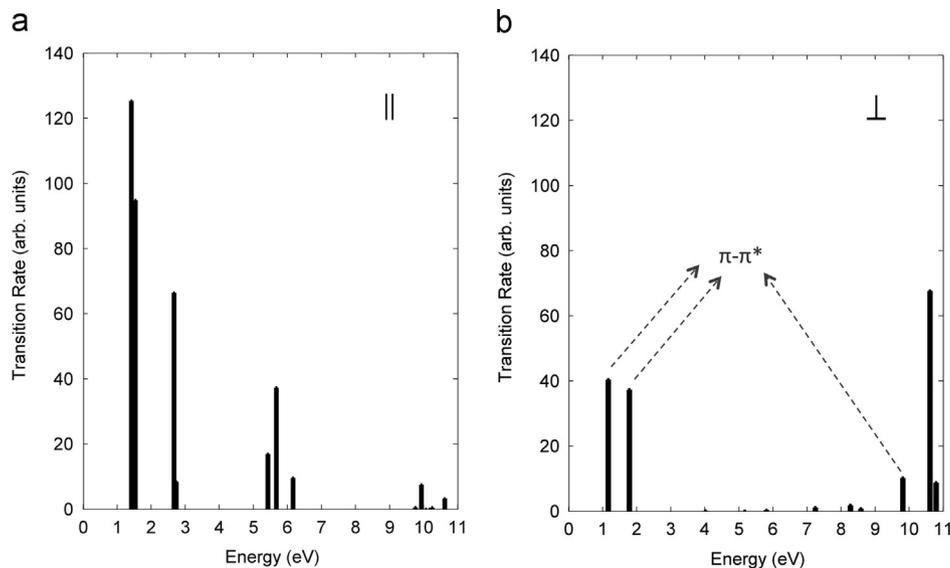
Fig. 1. Transition rate for an (8,0) nanotube (calculated with BLYP/6-31G) versus the energy of transition for parallel (a) and perpendicular (b) polarization of light. π–π* transitions with significant transition rate magnitudes in the perpendicular spectrum are pointed out.

However, at photon energies of 1.2 eV, 1.8 eV and 10.6 eV the transition probability is significant for perpendicular polarization.

According to the selection rules, light with parallel polarization, due to its $_0A_0^-$ symmetry, preserves the angular momentum quantum number, but reverses the horizontal parity, σ_h. Perpendicularly polarized light changes the angular quantum number by ± 1 while it preserves σ_h [27,28]. We define the angular momentum quantum number, m, as half of the number of nodes that a wave function carries around its circumference. We have previously shown in Ref. [26] that if a modified angular quantum number, $\widehat{m}$, is defined for an $(n,0)$ nanotube so that $\widehat{m} = m + \widehat{M}n$, all the optically allowed transitions satisfy the $\Delta\widehat{m} = 0$ condition for parallel polarization of light ($\widehat{M}$ is an integer determined such that $\widehat{m} \in (-n/2, n/2]$). For perpendicular polarization also, we note that all the allowed transitions follow the $\Delta\widehat{m} = \pm 1$ rule. For example, the first peak in the parallel absorption spectrum of an $(8,0)$ nanotube is the result of the transition between the 1st valence band (with $m=5$, $\widehat{m}=3$ and σ_h even) to the 4th conduction band (with $m=3$, $\widehat{m}=3$ and σ_h odd) while the first peak in the perpendicular polarization happens between the 1st valence and the 3rd conduction band (with $m=6$, $\widehat{m}=2$ and σ_h even). Fig. 2 depicts the molecular orbitals corresponding to each of these bands. Nodes are defined as the points where the wave function value changes sign (goes from grey to black or vice versa). The number of nodes are 10 (a), 6 (b), and 12 (c) and, therefore, the m number for these wave functions is equal to 5, 3 and 6, respectively.

According to the π-orbital tight-binding model, for semiconducting nanotubes, under the perpendicular polarization of light, there exist only two band-to-band transitions with significant dipole moments (between the first and second VHS points) [29]. Our calculations, however, show multiple $\pi-\pi^*$ transitions with considerable dipole moment values for an $(8,0)$ nanotube. Three of these transitions lead to peaks with noticeable strengths in the transition rate spectrum (at 1.2 eV, 1.8 eV and 9.8 eV) after including the JDOS and transition energies. This discrepancy originates from the fact that only transitions with $\Delta m = \pm 1$ are considered in the TB model. Based on this and the conservation of horizontal parity, only transitions between $\lfloor 2n/3 \rfloor$[1] and $\lfloor 2n/3+1 \rfloor$ subband numbers are possible for an $(n,0)$ semiconducting zigzag nanotube, which are indeed the transitions between the first and second VHS points ($2n/3$ is where the horizontal parity changes sign in zigzag nanotubes [30]).

In our calculations, however, if the $\Delta\widehat{m} = \pm 1$ rule is considered, aside from the two transitions above, other transitions will also be allowed. Some of these transitions have small dipole moment values and/or happen over large energy gaps and, therefore, their corresponding peaks are not noticeable in the transition rate spectra. On the other hand, some of them can result in strong peaks in the absorption spectra. The transition at 9.8 eV, for example, happens between the 4th valence band (with $m=8$, $\widehat{m}=0$ and σ_h odd) and 9th conduction band (with $m=1$, $\widehat{m}=1$ and σ_h odd). The other two strong peaks at 10.6 eV and 10.8 eV are the results of σ to π^* transitions, which are also not taken into account in the π-orbital tight-binding model.

3.2. Diameter dependence of the polarization effect

To study the diameter dependence of the polarization effect, we also calculated the transition rate spectra of $(4,0)$ and $(16,0)$ nanotubes for both polarizations (Fig. 3). The ratio of the transition rates for parallel and perpendicular polarizations ($W_\parallel/W_\perp$) for the $(4,0)$, $(8,0)$, and $(16,0)$ nanotubes is listed in Table 1, where W is

[1] $\lfloor \ \rfloor$ of a number is the floor of that number.
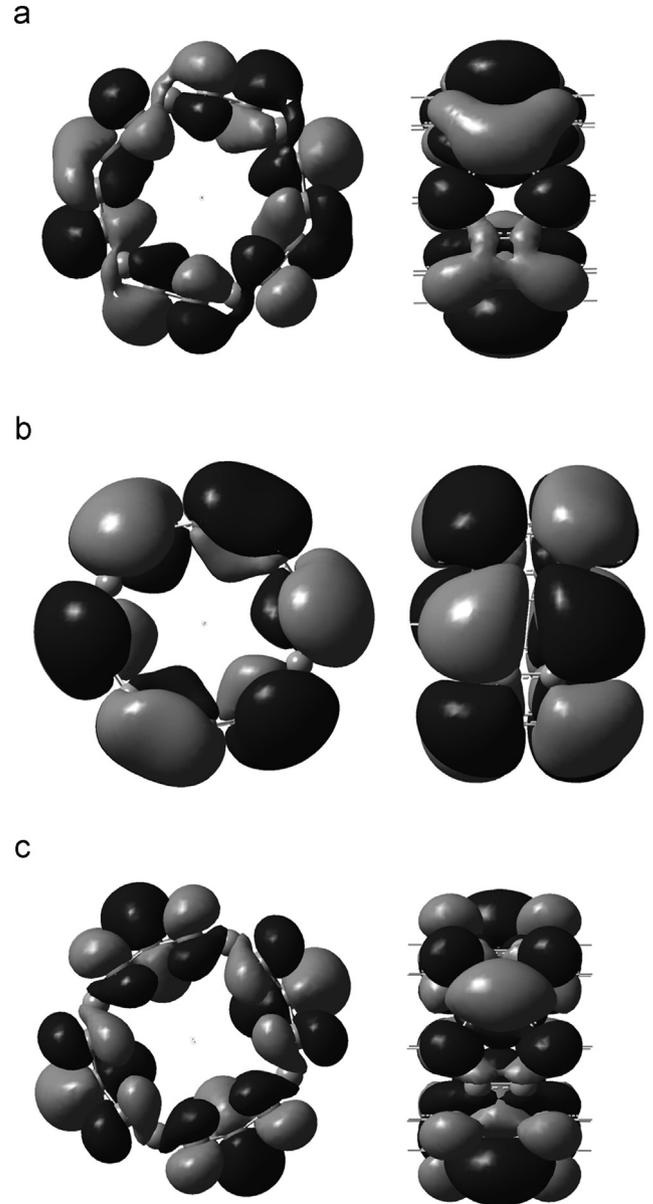
Fig. 2. Wave functions for the 1st valence (a), 4th conduction (b), and 3rd conduction (c) bands of an $(8,0)$ nanotube calculated with BLYP/6-31G. Left: view along the tube axis. Right: view perpendicular to the tube axis.

the sum of all the transition rates in the specified range. We observe that the overall spectra (0–11 eV) are suppressed for the perpendicular absorption in all three nanotubes, although this weakening does not show a monotonic diameter dependence. However, the same comparison in the infrared/visible (IR/VIS) and ultraviolet (UV) regions shows clear trends.

The overall transition rate in the IR/VIS portion of the spectrum (0–3 eV) is stronger for parallel polarization, and the $W_\parallel/W_\perp$ ratio decreases as the nanotube diameter increases. Note that the depolarization (antenna) effect is not included in these calculations. Thus, one may conclude that the antenna effect is only partially responsible for the suppression of the absorption spectra with perpendicular polarization in the IR/VIS range and part of this overall weakening can be directly due to the role of the interband transitions. For $(8,0)$ and $(4,0)$ nanotubes, in this range, the peaks are in general stronger for the parallel light compared to the perpendicular light. For a $(4,0)$ nanotube, there exists only one $\pi-\pi^*$ transition with significant magnitude in the perpendicular

Fig. 3. Transition rate (calculated with BLYP/6-31G) versus the energy of transition for a (4,0) (a), an (8,0) (b) and a (16,0) (c) nanotube. For each nanotube the spectra on the left and right correspond to the calculations with parallel and perpendicular polarization of light, respectively. $\pi-\pi*$ transitions with significant transition rate magnitudes are pointed out in the spectra.

Table 1
Ratio of the transition rates for parallel and perpendicular polarization of light ($W_{\parallel}/W_{\perp}$) in different energy ranges. For each polarization, W is the sum of all the transition rates in the specified range for the nanotube under study.

Range	(4,0)	(8,0)	(16,0)
0–11 eV	3.56	2.20	3.69
IR/VIS (0–3 eV)	10.31	3.79	2.11
UV (3–11 eV)	0.49	0.83	127.01

case. This transition happens at ~ 2 eV between the 3rd valence and the 2nd conduction bands. For a (16,0) nanotube there exist two large peaks in the perpendicular polarization spectrum, happening between the 1st and 2nd VHS points. The sharp peak

at 0.9 eV is the result of the significant dipole moment and also the small energy gap between the 1st valence and the 2nd conduction bands.

In the UV range (3–11 eV), on the other hand, the strength and the number of peaks for parallel and perpendicular polarizations become comparable for (4,0) and (8,0) nanotubes, while for a (16,0) nanotube the peaks are considerably weaker for perpendicular polarization. Therefore, while the $W_{\parallel}/W_{\perp}$ ratio is significant for a (16,0) nanotube in the UV range, for (4,0) and (8,0) nanotubes the perpendicular light seems to be absorbed more compared to the parallel light. For a (4,0) nanotube, the overall absorption of the parallel light is almost half of that of the perpendicular light in this region. Transitions with considerable magnitude in the UV region are all non-$\pi-\pi*$ ($\sigma-\pi*$, $\pi-\sigma*$, or $\sigma-\sigma*$) transitions for perpendicular polarization in a (4,0) nanotube while for parallel polarization, non-$\pi-\pi*$ transitions have small magnitudes. For a

Table 2
Ratio of the dipole moments squared for parallel and perpendicular polarization of light ($D_{\parallel}^2/D_{\perp}^2$) in different energy ranges. For each polarization, D^2 is the sum of the square of the magnitudes of the dipole moments in the specified range for the nanotube under study.

Range	(4,0)	(8,0)	(16,0)
IR/VIS (0–3 eV)	11.69	5.82	2.98
UV (3–11 eV)	0.86	0.96	15.18

(16,0) nanotube, on the other hand, $\pi-\pi^*$ and non-$\pi-\pi^*$ transitions are all of small magnitudes in the UV range for perpendicular polarization, whereas in the parallel polarization spectrum, there are a few sharp peaks in the UV region, all as a result of $\pi-\pi^*$ transitions.

To study how much of the behavior of the interband transition is due to the trends in the dipole moment, we performed a comparison similar to that of Table 1 for the squared magnitude of the dipole moment in the IR/VIS and UV regions (Table 2). We notice that the trends are similar to the trends in Table 1, implying that the dipole moment (and, therefore, the shape and interactions of the wave functions with each other) is the component mostly responsible for the trends in the transition rates in each region (as opposed to the other players in the transition rate, such as energy or JDOS).

The values of $W_{\parallel}/W_{\perp}$ combined with the depolarization effect can provide an estimate for overall weakening of the absorption spectra for perpendicular light compared to the one for parallel light. Studies of the static polarizabilities of carbon nanotubes have shown a screening factor of ~ 5 for nanotubes under a transverse field [31,32], implying that the effective field becomes approximately 5 times weaker than the applied field due to the depolarization effect. Therefore, for an (8,0) nanotube, for example, one might estimate the overall weakening of the transition spectra in the IR/VIS range to be approximately $5 \times 3.79 = \sim 19$ times after including the antenna effect. Or for instance, experimental results in Ref. [22] show an overall weakening of ~ 10 times for the maximum peak in the IR/VIS spectrum of (7,5) nanotubes. Hence, one might estimate the weakening due to the interband transitions ($W_{\parallel}/W_{\perp}$) for these peaks to be about $10/5 = \sim 2$ times. Considering the diameter of these nanotubes (~ 0.8 nm) and the values in Table 1, two times weakening of the band-to-band transition spectrum under the perpendicular light can be a reasonable prediction for (7,5) nanotubes. Obviously, these are all very rough estimations and many factors such as the frequency dependence of the screening factor or the chirality dependence of the $W_{\parallel}/W_{\perp}$ need to be taken into account for a better estimation of these values.

4. Summary

In summary, the interband optical transition rate spectra for (4,0), (8,0), and (16,0) nanotubes were calculated for both parallel and perpendicular polarizations of light in the 0–11 eV range. We observed that a modified angular quantum number, $\widehat{m}$, should be used when considering the selection rules in order to explain all the allowed transitions for perpendicular polarization, similarly to what has been shown for parallel polarization [26]. Our results showed an overall suppression of the transition rate spectra for perpendicular polarization compared to those for parallel polarization in all three nanotubes, although at certain photon energies the probability of absorption for perpendicular light turned out to be surprisingly high.

All these calculations were performed without including the depolarization effect in order to show the polarization dependence of the band-to-band transition spectra. If, after inclusion of the depolarization effect, some of the peaks in the perpendicular spectra carry a significant magnitude so as to be detectable experimentally, such as those shown in Ref. [22], there will be new opportunities for applications of nanotubes, such as in sensitive angle detection devices. Furthermore, light polarization can be used as an external parameter for tuning the optical properties of nanotube-based optoelectronic devices. This is of importance since, in this case, internal changes to the device will not be needed, and the orientation of the device with respect to the incident light can modify the wavelength of absorption or emission.

We noticed that, in the IR/VIS range, the $W_{\parallel}/W_{\perp}$ ratio increases as the nanotube diameter decreases. For UV light, not only does this trend become reversed, but also perpendicular light is absorbed with higher probability compared to the parallel light for (4,0) and (8,0) nanotubes. This can be important in UV application of small diameter nanotubes in optoelectronic devices. We observed that non-$\pi-\pi^*$ transitions play a major role in the perpendicular light absorption of a (4,0) nanotube in the UV region.

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