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Nonlinear coherent magneto-optical response of a single chiral carbon nanotube

G Slavcheva^{1,3} and Ph Roussignol^{2,3}

¹ Blackett Laboratory, Imperial College London, Prince Consort Road, London SW7 2AZ, UK

² Laboratoire Pierre Aigrain, Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex 5, France

E-mail: G.Slavcheva@imperial.ac.uk and Philippe.Roussignol@lpa.ens.fr

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Abstract. We propose a theoretical framework and dynamical model for the description of the natural optical activity and Faraday rotation in an individual chiral single-wall carbon nanotube (CNT) in the highly nonlinear coherent regime. The model is based on a discrete-level representation of the optically active states near the band edge. Chirality is modelled by a system Hamiltonian in a four-level basis corresponding to energy-level configurations, specific for each handedness, that are mirror reflections of each other. The axial magnetic field is introduced through the Aharonov–Bohm and Zeeman energy-level shifts. The time evolution of the quantum system, describing a single nanotube with defined chirality, under an ultrashort polarized pulse excitation is studied using the coupled coherent vector Maxwell-pseudospin equations (Slavcheva 2008 *Phys. Rev. B* **77** 115347). We provide an estimate for the effective dielectric constant and the optical dipole matrix element for transitions excited by circularly polarized light in a single nanotube and calculate the magnitude of the circular dichroism and the specific rotatory power in the absence and in the presence of an axial magnetic field. Giant natural gyrotropy (polarization rotatory power $\sim 3000^\circ \text{ mm}^{-1}$ ($B = 0 \text{ T}$)), superior to that of the crystal birefringent materials, liquid crystals and comparable or exceeding that of the artificially made helical photonic structures, is numerically demonstrated for the specific case of a (5, 4) nanotube. A quantitative estimate of the coherent nonlinear magneto-chiral optical effect in an axial magnetic field is given

³ Authors to whom any correspondence should be addressed.

($\sim 30\,000^\circ \text{ mm}^{-1}$ at $B = 8 \text{ T}$). The model provides a framework for the investigation of the chirality and magnetic field dependence of the ultrafast nonlinear optical response of a single CNT.

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1. Introduction

The interaction of polarized light with chiral materials in the absence of magnetic fields gives rise to the phenomenon of optical (rotation) activity whereby the polarization plane is rotated continuously during the light propagation across the medium. A simple phenomenological description of this effect, without considering the actual mechanisms involved, proposed by Fresnel, is based on circular double refraction, or the difference in phase velocity of propagation for the left- and right-circularly polarized light components. This, in turn, leads to a difference in refractive indices, and/or absorption for left- and right-circularly polarized light, which manifests itself as a circular birefringence, dichroism and rotatory power. Although the phenomenon of optical activity can be treated in terms of the classical electromagnetic theory, an in-depth understanding and full description of it requires a quantum-mechanical treatment at a microscopic level. The early molecular models were of two classes: two-particle models, e.g. the models of Born, Oseen [1], Kuhn [2] and Kirkwood [3] based on a spatial distribution of coupled oscillators, and single-oscillator models, e.g. the Drude helix model [4] and the Condon, Altar and Eyring theory [5] (for a comprehensive review, consult [6]). The first consistent quantum mechanical theoretical formalism was put forward by Rosenfeld without invoking the couple oscillator model [7]. However, after Kuhn demonstrated that, when correctly treated, the Drude single-oscillator model does not exhibit rotatory power, the Drude model was forgotten. It has long been thought that the notion of coupled oscillators is a necessary condition for the explanation of the rotatory power, until the Condon, Altar and Eyring model [5] demonstrated optical activity using a quantum mechanical single-oscillator model. In the 1970s, however, it was shown [8] that the Drude model exhibits optical activity in the nonlinear regime and recently

it has been demonstrated that it leads to optical activity if the motion of the particle is treated quantum mechanically [9].

The natural optical activity in chiral media, considered above, and the Faraday effect of magnetically induced optical activity both manifest themselves as a rotation of the polarization of the transmitted light. However, the two effects are fundamentally different: while the natural optical activity is a result of a nonlocal optical response of a medium lacking mirror symmetry, the magnetic optical activity results from the breaking of the time-reversal symmetry by a magnetic field. The apparent similarity between the two effects has led to the theoretical prediction and experimental demonstration [10] of the link between the two phenomena through the so-called magneto-chiral optical effect, which occurs under conditions when both symmetries are broken simultaneously.

Formulation of a theory and model of the optical activity in chiral molecules, such as the individual single-wall carbon nanotubes (SWCNTs), in the high-intensity nonlinear coherent regime and under an axial magnetic field, which is the subject of this paper, is of special interest from a fundamental point of view. To the best of our knowledge, no such theory has been proposed and very little is known about the polarization dynamics of the nonlinear optical and magneto-optical response of a single CNT. A detailed understanding of the mechanisms underlying the optical and magneto-optical birefringence, circular dichroism and rotation in the nonlinear coherent regime opens up pathways for the development of a novel class of ultrafast polarization-sensitive optoelectronic devices, e.g. ultrafast optical switches, polarizers, etc, based on single CNTs as basic functional components of an integrated optoelectronic device.

In the quantum theory of the optical activity, one may distinguish two distinct classes of optically active molecules: a few molecules are inherently asymmetric, and the majority of the molecules owe their activity to the asymmetric juxtaposition of symmetric (inherently optically inactive) subsystems. Both mechanisms should be considered in a full treatment of the molecular optical activity model [11]. In what follows, we shall consider single objects rather than ensembles of CNTs and the chiral symmetry results from the inherent spiral alignment of the C-atoms in a single SWCNT.

Chirality is one of the main symmetries of the CNT geometry that determines the optical properties of the SWCNTs [12]. Investigation of the magneto-optical phenomena in chiral nanotubes is of considerable interest for nonlinear optical spectroscopy since it provides important information about their electronic structure [13]–[17].

Magnetic circular dichroism (MCD) and magneto-optical rotatory dispersion (MORD) techniques offer spectroscopic information that is different or impossible to obtain by other means. The magneto-optic Faraday effect and the time-resolved Faraday rotation technique in particular [18] allow the measurement of the optically driven spin dynamics in semiconductor nanostructures on an ultrafast time scale and with high spatial resolution. The study of the spin dynamics in single CNTs is of particular interest in view of the potential integration of CNTs in future spin devices.

Another motivation for the present study is that the chiral materials are of interest on their own as they exhibit negative refractive index in a given frequency range and are promising candidates for metamaterial applications. Metamaterials consisting of helical structures have long been recognized as promising candidates in the microwave range. However, for applications working in the visible range, the helical structures should be down-scaled to nanometre size and therefore natural candidates could be sought at a molecular level. In fact, it has been

demonstrated that some helical molecules show strong optical activity [19]–[24]. Recently, giant optical gyrotropy in the visible and near-infrared (IR) spectral ranges, of up to $2500^\circ \text{ mm}^{-1}$, has been demonstrated in artificial gyrotropic chiral media, in view of implementations as photonic chiral negative index metamaterials [25]. In this respect, it would be of great interest to assess the magnitude of the natural and Faraday optical rotation in single CNTs as one-dimensional (1D) helical molecules under resonant coherent optical excitation, and to compare it with one of the other candidates for metamaterials working in the visible range.

A theoretical framework for discussion of the optical activity [26] and Faraday rotation phenomena [27] in CNTs has been proposed within the tight-binding (TB) formalism. An alternative simplified TB approach was originally proposed by Romanov and Kibis [28] and developed further in [29, 30]. Within this semiclassical approach, which, in what follows, we will refer to as the Slepian *et al* approach, the lowest conduction band energy spectrum is calculated using the so-called spiral model: a phenomenological analytical method based on Wannier formulation for the Schrödinger equation in a curvilinear coordinate system for a nanotube, modelled by a chain of atoms wrapped helically around a cylinder, thereby accounting for the helicoidal symmetry. The Wannier equation, in conjunction with the Boltzmann kinetic equation, has been used to describe the nonlinear and chiral effects in the electron transport on the nanotube surface in an external rapidly oscillating (ac) and constant (dc) fields. In particular, surface wave propagation has been demonstrated and the possibility of exploiting CNTs as waveguides in the IR range has been discussed. This model, however, does not take into account the hexagonal lattice of the underlying graphene sheet and the transverse motion quantization. A full quantum-mechanical treatment, including the hexagonal lattice and the transverse quantization, is given in [31], along with a detailed comparison with the spiral model. The comparison shows that the spiral model represents an adequate description of large-radius CNTs and, due to its analytical tractability, can be useful for qualitative estimates.

It is worth noting that although chirality-induced nonlinear effects are the subject of both the present work and the above cited works, we are interested not in the electronic transport and surface plasmon effects but rather in CNT dielectric properties under resonant coherent optical pulsed excitations. To the best of our knowledge, the way the chirality affects the polarization dynamics of the ultrafast nonlinear optical response of a single nanotube and the magnitude of this effect without and in an external magnetic field have not been investigated, and this is precisely the aim of the present study. We emphasize that both our approach and the spiral model are semiclassical, but in a different way. In the case of the spiral model, the classic Boltzmann equation is coupled to the quantum Wannier equation, while within the present approach the electromagnetic wave propagation is treated classically using Maxwell's equations, whereas the quantum system dynamics are treated quantum mechanically, using the Liouville equation. Most importantly, the two approaches are similar in the following. Unlike other theories [28, 41], both approaches do not consider the interference between the axial and helical paths (or equivalently, the axial and transverse wavevectors coupling) as the origin of the chirality effects. The spiral model provides a 1D periodic (zero field) electron dispersion law with periodic energy dependence on the electromagnetic field and predicts a uniform shift of the positions of the periodic minima in the dispersion when a magnetic field is applied.

In this paper, we develop a dynamical model for the ultrafast circularly polarized light pulse interaction with single chiral SWCNTs in the absence and in the presence of an external magnetic field, which allows for assessing the magnitude and ellipticity of this rotation. In distinction with the spiral model, discussed above, the transverse quantization of motion is taken

into account within our approach through the subband structure, and the energy dispersion along the nanotube axis is approximated by a constant. This simplification is justified by the following arguments: (i) the specific CNT geometry considered, namely the CNT length (500 nm), is much greater than the unit cell length ($T = 3.32$ nm), as inferred from TB calculations (for detailed discussion, please refer to section 3 and appendix B), which allows one to approximate the periodically modulated lowest subband edges along the nanotube axis by a discrete-level system; (ii) relatively flat curvature of the lowest-lying subbands as compared to the curvature of the higher-lying subbands; in particular, the lowest-lying subbands in the (5, 4) nanotube, considered for illustration, are considerably flat (horizontal), to allow for this approximation; (iii) the resonant character of the optical excitations in the vicinity of $K(K')$ point of the Brillouin zone (BZ) (or equivalently, at the Γ point in the centre of the first one-dimensional BZ, when the zone-folding technique is applied) where the fundamental bandgap of the CNT actually occurs. It should be noted that we are interested in near-bandgap excitations, close to the energy dispersion minimum, where both the method of Slepian *et al* and ours converge, providing the level of description relevant to the resonant absorption/amplification processes considered. We thus believe that our simplified model successfully captures the most important features of the dynamics of the resonant optical excitation and interaction with the nanostructure. We should note that the model could be extended to include the full dispersion by introducing a set of four-level systems with appropriate (for each value of the wavevector along the tube axis) separation between the levels and oscillator strength for the corresponding interlevel transitions.

Another important feature of the CNT response to femtosecond laser pulses is the coherent phonon generation. The lattice dynamics of a CNT following a femtosecond optical pulse excitation has been studied by molecular dynamics simulations coupled to a TB description of the CNT [64]. The employed semiclassical technique accounts for the quantum evolution of the electronic system in an external laser field, whereas the lattice ions motion is described classically, using a thermodynamic formulation. As a result of the electronic excitation, three coherent breathing phonon modes are excited: two radial vibrations localized in the caps and the tubular body, and one longitudinal vibration coupled to the nanotube length. It has been shown that at sufficiently high (but still below graphite's ultrafast fragmentation threshold) absorbed energies, the oscillations lead to opening of the nanotube caps, while the tubular body remains intact on a picosecond time scale. Although our model does not provide a description of the lattice dynamics under a resonant ultrafast optical pulse, the discussed effects might prove quite significant. We should note that the excitation fluence assumed in our computations is of the order of $2\text{--}20\ \mu\text{J cm}^{-2}$ (corresponding to 60–150 fs pulse duration, see appendix B), which is several orders of magnitude lower than the fluences used in [64] of the order of hundreds of mJ cm^{-2} (corresponding to a 10 fs pulse duration). Taking into account the uncertainty in the fluences in the latter work, estimated using graphite data, we cannot rule out that cap opening could occur as a result of the ultrashort pulse excitation. We emphasize, however, that the numerical simulations in [64] demonstrate that the cylindrical body of the nanotube is not affected within reasonably long time intervals, of the order of the simulation times in our computations (long after the pulse passage across the nanostructure), and optical rotation in chiral nanotubes would still be possible.

Our theoretical and numerical approach follows the general Maxwell-pseudospin formalism developed in an earlier publication [38] for the description of the ultrafast coherent carrier dynamics of a discrete-level quantum system in an external dipole coupling perturbation.

The new components of the model comprise (i) the specific lowest energy-level configuration adopted for a description of the two helical forms of the nanotube; (ii) inclusion of the CNT relaxation dynamics, identifying the allowed interband dipole optical transitions and intraband relaxation and dephasing (including the specific time scales); (iii) introduction of an external magnetic field in the system Hamiltonian through the resonant transition energy and the specific energy-level configuration in an axial magnetic field, taking into account the Zeeman splitting of the energy levels and Aharonov–Bohm (AB) phase shift; (iv) provision of an estimate for the CNT dielectric response function and dipole moment matrix element for transitions excited by circularly polarized light.

The paper is organized as follows. In section 2, we formulate the problem of ultrashort circularly polarized pulse propagation and resonant coherent interactions in an isolated SWCNT. In section 3, we provide a theoretical framework for tackling the resonant nonlinear absorption/amplification in chiral CNTs based on band-edge energy-level configurations specific for left- and right-circularly polarized optical excitation. The proposed dynamical model for description of the ultrafast optically induced dynamics requires both a knowledge of the dielectric response function and the optical dipole matrix element for optical transitions excited by circularly polarized light in a single SWCNT. The calculation of these model parameters is given in appendices A and B, respectively. In section 4, we present the simulation results for the ultrafast nonlinear dynamics of the natural optical activity in a single chiral SWCNT and calculate the time- and spatially resolved circular dichroism, birefringence and specific rotatory power for a particular (5, 4) nanotube geometry. In section 5, we develop a model of the nonlinear Faraday rotation in an axial magnetic field in a chiral SWCNT, including both the energy-level shift due to the AB flux and the spin-B interaction, resulting in Zeeman splitting of the energy levels near the bandgap. We provide an estimate for the spatially resolved MCD and specific rotatory power along the tube length following the initial pulse excitation. Finally, in section 6, we give a summary of the results and outline some future model applications.

2. Problem formulation

SWCNTs are uniquely determined by the chiral vector, or equivalently by a pair of integer numbers (n, m) in the planar graphene hexagonal lattice unit vector basis. A primary classification of CNTs is the presence or absence of the chiral symmetry. Achiral nanotubes, whose mirror image is superimposable, are subdivided into two classes: zigzag ($m = 0$) and armchair ($m = n$) nanotubes. The rest of the nanotubes belong to the most general class of chiral nanotubes, whose mirror reflection is not superimposable.

Chiral molecules exist in two forms that are mirror images of each other (enantiomers). Similarly, CNTs exist in two left-(AL) and right-(AR) handed helical forms depending on the rotation of two of the three armchair (A) chains of carbon atoms counterclockwise or clockwise when looking against the nanotube z -axis. The two helical forms are shown for illustration for a (5, 4) and a (4, 5) SWCNT in figure 1, where we have adopted the following convention: $m > n$ corresponds to a left-handed (AL) nanotube, whereas $m < n$ corresponds to a right-handed (AR) nanotube.

The electronic band structure of an SWCNT [32] is described by the quantization of the wavevector along the tube circumference, perpendicular to the tube axis, resulting in a discrete spectrum of allowed k -vector states forming subbands in the valence and conduction bands labelled by the quasi-angular momentum quantum number (μ).

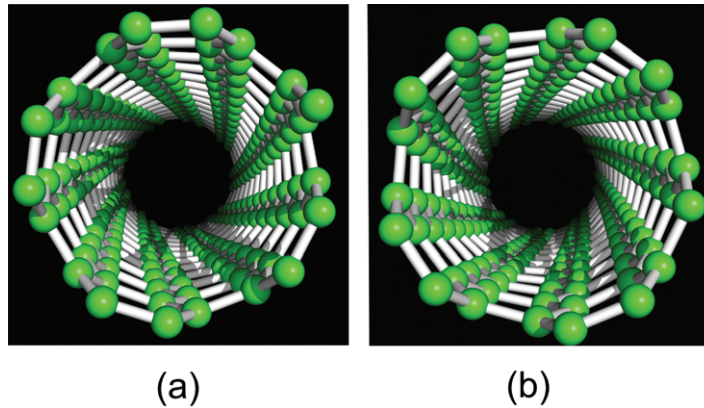


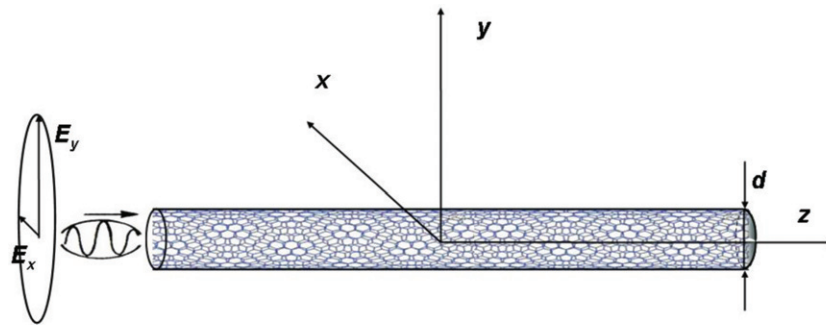
Figure 1. An illustration of the single CNT molecular structure of (a) left-handed AL (5, 4) and (b) right-handed AR (4, 5) single SWCNTs calculated using the TB method of P_z -orbitals [36]: a view along the tube axis against the z -axis direction.

In what follows, we shall consider aggregates or bundles of aligned SWCNTs [33], grown by chemical vapour deposition in an electric field [34], or aligned in a polymer matrix. When a circularly polarized (in the x - y plane) laser pulse propagates along the z -axis of an AL or AR SWCNT (figure 2(a)), only one of the two allowed transitions for a linearly polarized light (along x or y), between the quasi-angular momentum subband states $\mu \rightarrow \mu - 1$ and $\mu \rightarrow \mu + 1$, can be excited [35] (figure 2(b)). Here we adopt the following convention for optical pulse polarization: the left ($\sigma^- = x - iy$) and right ($\sigma^+ = x + iy$) helicity of light corresponds to counterclockwise and clockwise rotation of the electric field polarization vector when looking towards the light source (against the z -axis direction).

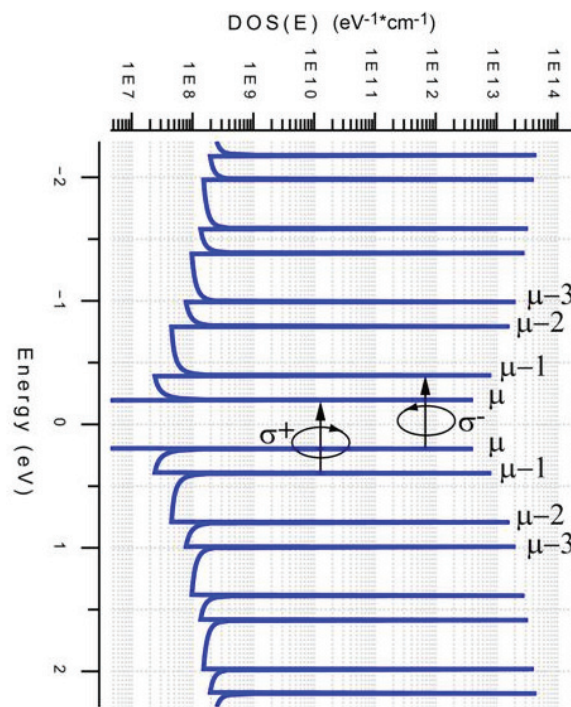
We model the single chiral nanotube band-edge structure at the K point of the BZ by an ensemble of a large number of identical four-level systems, corresponding to the dipole optically allowed transitions for AL and AR nanotube enantiomers. As has been pointed out in [35], taking into account the polarization sense convention above, absorption of right-circularly polarized light σ^+ excites the electronic transitions $\mu - 1 \rightarrow \mu$, or equivalently $\mu \rightarrow \mu + 1$ in AL-handed SWCNTs and $\mu \rightarrow \mu - 1$ transitions in AR-handed SWCNTs, whereas the absorption of left-circularly polarized σ^- light excites $\mu \rightarrow \mu - 1$ transitions in AL-handed SWCNTs and $\mu \rightarrow \mu + 1$ transitions in AR-handed SWCNTs (figure 3).

Note that the chiral symmetry of the medium is incorporated at a microscopic level through the energy-level scheme and the allowed dipole optical transitions for AL- and AR-handed SWCNTs: the mirror reflections of the two energy-level configurations cannot be superimposed. The origin of the optical activity is the difference in optical selection rules for left- and right-circularly polarized light and the specific relaxation channels involved at optical excitations with each polarization sense and their respective time scales [37].

The adopted discrete four-level system approximation of the CNT band structure is a good approximation at or in the vicinity of the $K(K')$ point of the Brillouin zone where the fundamental bandgap of the CNT actually occurs. Furthermore, since we consider only resonant, or near-resonant, laser excitations, the optically active states near the band edge are more likely to be involved in the dynamics. This is the reason why we consider the minima of two conduction and two valence subbands closest to the Fermi level. We reiterate that despite



(a)



(b)

Figure 2. (a) Geometry of an experiment with an optical excitation by a circularly polarized pulse propagating along the SWCNT axis; E_x and E_y are the Cartesian components of the E -field vector; (b) 1D electronic density of states (DOS) versus energy at the K point of the BZ ($\mu > 0$) of an AL-handed (20, 10) chiral SWCNT. The allowed dipole optical transitions for circularly polarized light are designated by arrows for left- (σ^-) and right- (σ^+) pulse helicity.

our description not including the π -electrons energy dispersion along k_z , in view of the resonant excitation considered, we select and access specifically the minima of the conduction/valence subbands closest to the band edge by tuning the optical pulse centre frequency in resonance with the circularly polarized transition frequency. In fact, although the ultrashort (60 fs) is a

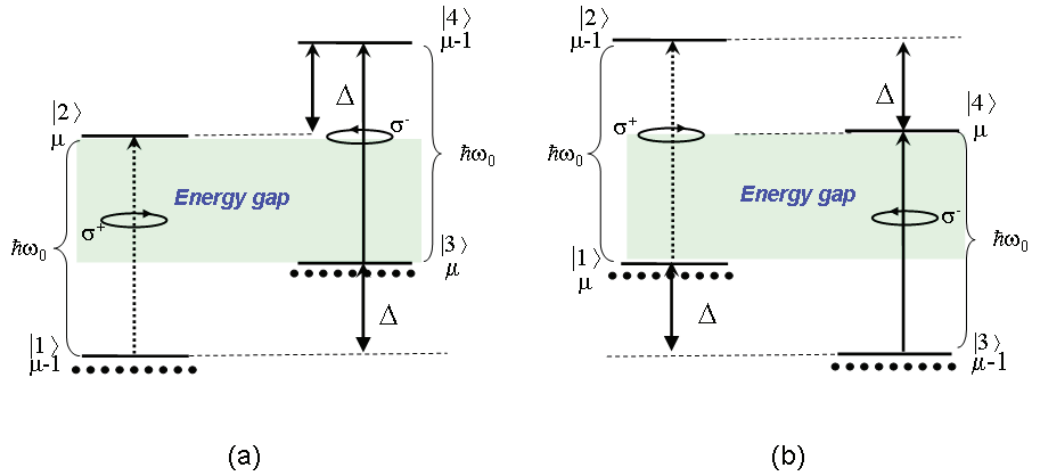


Figure 3. Energy-level structure at the $K(K')$ point of the lowest subbands labelled by the subband index μ for (a) AL-handed and (b) AR-handed SWCNTs. The fundamental energy gap is shaded. ω_0 is the resonant transition frequency and Δ is the energy separation between the lowest subband and the second lowest subband near the band gap. The dipole optical transitions excited by σ^- and σ^+ circularly polarized light are designated by arrows. Only one of the two transitions is allowed for circularly polarized light, denoted by a solid (dashed) arrow. Valence band states below the bandgap are populated.

broadband pulse, its spectral width is ~ 10 meV, which does not change the resonant character of the excitation (see figure 4). We do not expect drastic changes when the k_z -dispersion is included, primarily due to the (i) resonant excitations at the K point used and, in the specific case of a (5, 4) nanotube considered, (ii) relatively flat (horizontal) lowest-lying subbands as compared to the curvature of the higher-lying subbands (see figure 4(a)). Although this flat lowest subbands property cannot be applied to all chiral nanotubes, as is demonstrated by this particular (5, 4) nanotube, certain nanotubes exhibit these characteristics, thus enabling engineering of chirality with the aim of achieving larger rotation angles and stronger optical activity. This is the purpose of the specific case considered for illustration.

3. Theoretical framework for description of the natural optical activity in a chiral single-wall carbon nanotube (SWCNT)

The proposed theoretical model is based on the self-consistent solution of Maxwell's equations in vectorial form for the polarized optical pulse propagation and the time-evolution pseudospin equations of the discrete multi-level quantum system in the external time-dependent perturbation [38]. This is a semiclassical approach that treats the optical wave propagation classically through Maxwell's equations and therefore requires knowledge of the effective dielectric constant of the medium. On the other hand, the quantum evolution equations require knowledge of the dipole optical transition matrix element for transitions excited by circularly polarized light in a single CNT. We give an estimate of these important model parameters in appendices A and B for the specific case of a chiral AL-handed (5, 4) SWCNT, which is chosen for illustration of the general method valid for an arbitrary chirality.

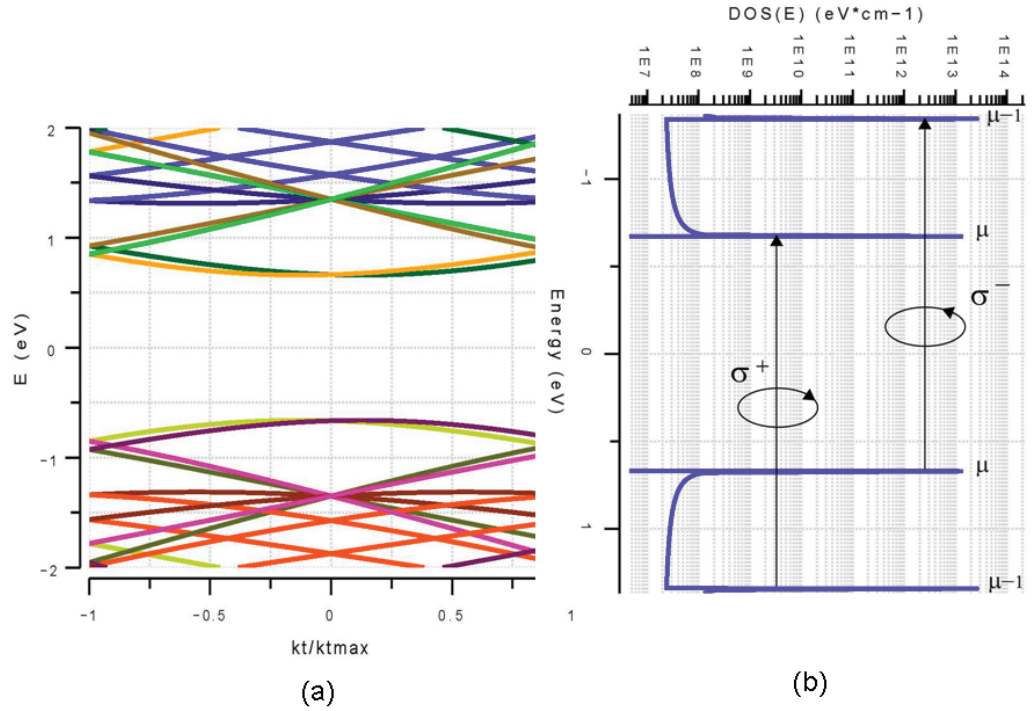


Figure 4. (a) Energy dispersion versus longitudinal (along the tube axis) wavevector k_t , normalized with respect to the wavevector at the boundary of the BZ $k_{t\max}$ of a (5, 4) SWCNT; (b) 1D-DOS versus energy showing the lowest energy subbands near the band edge involved in dipole optical transitions induced by circularly polarized light. Only one transition can be excited at any one time by each helicity (σ^- or σ^+).

We shall assume a nanotube of length $L_n = 500$ nm. In what follows, the finite-size edge diffraction effects are ignored since our model is quasi-1D and it is unrealistic to implement edge diffraction or capped CNT geometries in 1D. The main goal of the study is to provide a theoretical estimate for the rotatory power per unit length, due to the specific helical arrangement of the atoms, and to demonstrate the possibility of manipulating the optical rotation through the nanotube geometry. On the other hand, recent studies [64] of the response of CNTs to femtosecond laser pulses point out the possibility of the fragmentation, release and opening of the nanotube caps, due to the generation of coherent breathing phonons. Therefore, it is realistic to ignore the edge effects under ultrashort pulsed excitations. We should note that at least a 2D model is required to account for the edge diffraction effects.

TB calculations [36] provide the electronic band structure (figure 4), namely the fundamental bandgap $E_g = E_{\mu,\mu} = 1.321$ eV, corresponding to a wavelength $\lambda = 939$ nm, nanotube diameter $d = 0.611$ nm and chiral angle $\theta = 26.33^\circ$. The resonant transition energy for circularly polarized excitations is $E_{\mu,\mu\pm 1} = 1.982$ eV, corresponding to a resonant wavelength $\lambda_0 = 626.5$ nm.

Consider an ultrashort circularly polarized pulse in the (x - y) plane propagating along the nanotube z -axis, resonantly coupled to an ensemble of identical homogeneously broadened four-level systems describing the resonant absorption/amplification in a single CNT (figure 5).

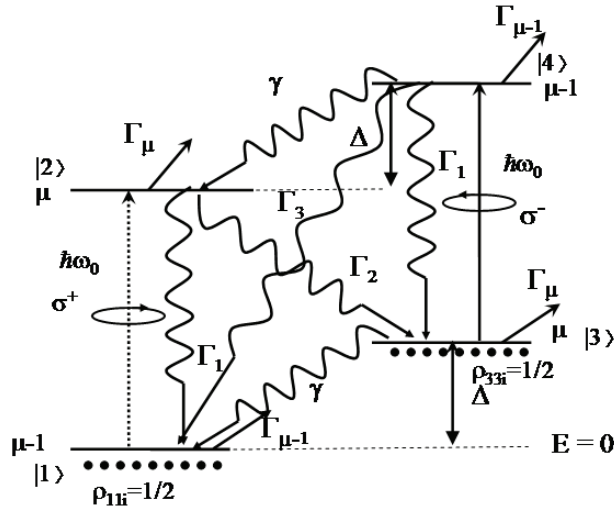


Figure 5. Energy-level diagram in the general case of a resonant optical excitation of $\mu \rightarrow \mu + 1$ and $\mu \rightarrow \mu - 1$ interband transitions by σ^+ and σ^- polarized pulses, respectively. The resonant transition energy is $\hbar\omega_0$. Δ is the energy separation between the first and second lowest conduction (valence) band states. The initial population of the lowest valence states below the bandgap, ρ_{11i} and ρ_{33i} , is equally distributed between levels $|1\rangle$ and $|3\rangle$. All allowed longitudinal relaxation processes between the levels, associated with population transfer, are designated by wavy lines. Γ_1 is the spontaneous emission (radiative decay) rate of the interband transition $|2\rangle \rightarrow |1\rangle$, which, owing to the symmetry, is assumed equal to the spontaneous emission rate of $|4\rangle \rightarrow |3\rangle$; Γ_2 is the spontaneous emission rate for the $\mu \rightarrow \mu$ transition allowed for linearly polarized light; Γ_3 is the decay rate of the $\mu - 1 \rightarrow \mu - 1$ linearly polarized transition and γ is the intraband relaxation rate. The transverse relaxation (dephasing) rates Γ_μ and $\Gamma_{\mu-1}$ are designated by arrows.

Following the coherent Maxwell-pseudospin formalism developed in [38], the generic system Hamiltonian in the four-level basis that applies to an excitation with either σ^- or σ^+ light helicity is written, at resonance, as

$$\hat{H} = \hbar \begin{pmatrix} 0 & -\frac{1}{2}(\Omega_x + i\Omega_y) & 0 & 0 \\ -\frac{1}{2}(\Omega_x - i\Omega_y) & \omega_0 & 0 & 0 \\ 0 & 0 & \Delta & -\frac{1}{2}(\Omega_x - i\Omega_y) \\ 0 & 0 & -\frac{1}{2}(\Omega_x + i\Omega_y) & \Delta + \omega_0 \end{pmatrix}, \quad (1)$$

where $\Omega_x = \wp(E_x/\hbar)$ and $\Omega_y = \wp(E_y/\hbar)$ are the time-dependent Rabi frequencies associated with E_x and E_y electric field components and $\wp$ is the optical dipole matrix element for $\mu \rightarrow \mu \pm 1$ transitions excited by circularly polarized light (calculated in appendix B).

The time evolution of the quantum system under an external dipole-coupling perturbation in the presence of relaxation processes (figure 5) is governed by a set of pseudospin master

equations for the real state 15-dimensional vector S derived in [38],

$$\frac{\partial S_j}{\partial t} = \begin{cases} f_{jkl}\gamma_k S_l + \frac{1}{2}\text{Tr}(\hat{\sigma}\hat{\lambda}_j) - \frac{1}{T_j}(S_j - S_{je}), & j = 1, 2, \dots, 12, \\ f_{jkl}\gamma_k S_l + \frac{1}{2}\text{Tr}(\hat{\sigma}\hat{\lambda}_j), & j = 13, 14, 15, \end{cases} \quad (2)$$

where γ is the torque vector, f is the fully antisymmetric tensor of the structure constants of SU(4) group, and T_j are the phenomenologically introduced non-uniform spin decoherence times describing the relaxation of the real state vector components S_j toward their equilibrium values S_{je} . Using the generators of the SU(4) Lie algebra, the following expression for the torque vector is obtained,

$$\gamma = \left(-\Omega_x, 0, 0, 0, 0, -\Omega_x, \Omega_y, 0, 0, 0, 0, -\Omega_y, \omega_0, \frac{2\Delta - \omega_0}{\sqrt{3}}, \sqrt{\frac{2}{3}}(\Delta + \omega_0) \right). \quad (3)$$

In equation (2), similar to [39], we have introduced a diagonal matrix $\hat{\sigma} = \text{diag}(\text{Tr}(\hat{\Gamma}_i \hat{\rho}))$, $i = 1, \dots, 4$, where $\hat{\rho}$ is the density matrix of the system, accounting for the longitudinal relaxation accompanied by population transfer between the levels. Defining the matrices $\hat{\Gamma}_i$,

$$\begin{aligned} \hat{\Gamma}_1 &= \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \Gamma_1 & 0 & 0 \\ 0 & 0 & \gamma & 0 \\ 0 & 0 & 0 & \Gamma_3 \end{pmatrix}, & \hat{\Gamma}_2 &= \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -(\Gamma_1 + \Gamma_2) & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma \end{pmatrix}, \\ \hat{\Gamma}_3 &= \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \Gamma_2 & 0 & 0 \\ 0 & 0 & -\gamma & 0 \\ 0 & 0 & 0 & \Gamma_1 \end{pmatrix}, & \hat{\Gamma}_4 &= \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -(\Gamma_1 + \Gamma_3 + \gamma) \end{pmatrix}, \end{aligned} \quad (4)$$

$\hat{\sigma}$ -matrix components can be expressed in terms of the real state vector as

$$\begin{aligned} \sigma_{11} &= \frac{1}{12} \left(2\sqrt{3}S_{14}(2\gamma - \Gamma_1) - \sqrt{6}S_{15}(\gamma + \Gamma_1 - 3\Gamma_3) + 3(\gamma + \Gamma_1 + 2S_{13}\Gamma_1 + \Gamma_3) \right), \\ \sigma_{22} &= \frac{1}{12} \left(3\gamma(1 + \sqrt{6}S_{15}) + (-3 - 6S_{13} + 2\sqrt{3}S_{14} + \sqrt{6}S_{15})(\Gamma_1 + \Gamma_2) \right), \\ \sigma_{33} &= \frac{1}{12} \left(\sqrt{6}S_{15}(\gamma + 3\Gamma_1 - \Gamma_2) - 2\sqrt{3}S_{14}(2\gamma + \Gamma_2) + 3(-\gamma + \Gamma_1 + \Gamma_2 + 2S_{13}\Gamma_2) \right), \\ \sigma_{44} &= -\frac{1}{4} \left(1 + \sqrt{6}S_{15} \right) (\gamma + \Gamma_1 + \Gamma_3). \end{aligned} \quad (5)$$

The introduction of a dephasing matrix $\hat{\Gamma}_t$, accounting for the dissipation in the system due to polarization relaxation,

$$\hat{\Gamma}_t = \begin{pmatrix} 0 & \Gamma_\mu & \Gamma_\mu & \Gamma_{\mu-1} \\ \Gamma_\mu & 0 & \Gamma_\mu & \Gamma_{\mu-1} \\ \Gamma_\mu & \Gamma_\mu & 0 & \Gamma_{\mu-1} \\ \Gamma_{\mu-1} & \Gamma_{\mu-1} & \Gamma_{\mu-1} & 0 \end{pmatrix}, \quad (6)$$

implies transverse relaxation (dephasing) times in the first term of equation (2) given by $T_1 = T_2 = T_3 = T_7 = T_8 = T_9 = 1/\Gamma_\mu$ and $T_4 = T_5 = T_6 = T_{10} = T_{11} = T_{12} = 1/\Gamma_{\mu-1}$.

Expressions for the longitudinal population relaxation times T_{13} , T_{14} and T_{15} are derived through the second term in equation (2), giving

$$T_{13} = \frac{4}{2\Gamma_1 + \Gamma_2}, \quad T_{14} = \frac{4}{2\gamma + \Gamma_2}, \quad T_{15} = \frac{2}{\gamma + \Gamma_1 + \Gamma_3}. \quad (7)$$

Within the coherent master Maxwell-pseudospin equations approach [38], the 1D Maxwell's curl equations for the circularly polarized laser pulse propagating in an isotropic medium with effective dielectric constant ϵ (calculated in appendix A),

$$\begin{aligned} \frac{\partial H_x(z, t)}{\partial t} &= \frac{1}{\mu} \frac{\partial E_y(z, t)}{\partial z}, \\ \frac{\partial H_y(z, t)}{\partial t} &= -\frac{1}{\mu} \frac{\partial E_x(z, t)}{\partial z}, \\ \frac{\partial E_x(z, t)}{\partial t} &= -\frac{1}{\epsilon} \frac{\partial H_y(z, t)}{\partial z} - \frac{1}{\epsilon} \frac{\partial P_x(z, t)}{\partial t}, \\ \frac{\partial E_y(z, t)}{\partial t} &= \frac{1}{\epsilon} \frac{\partial H_x(z, t)}{\partial z} - \frac{1}{\epsilon} \frac{\partial P_y(z, t)}{\partial t}, \end{aligned} \quad (8)$$

are solved self-consistently with the pseudospin equations (2). The two sets of equations are coupled through the macroscopic polarization induced in the medium by the circularly polarized electromagnetic wave. We derive the following relations between the medium polarization vector and the real state vector components,

$$\begin{aligned} P_x &= -\wp N_a (S_1 + S_6), \\ P_y &= -\wp N_a (-S_7 + S_{12}), \end{aligned} \quad (9)$$

where N_a is the density of the ensemble of resonantly absorbing/amplifying four-level systems. These polarizations act as source terms in the vector Maxwell's equation for the optical wave propagation equation (8).

The above set of equations (8), (2) and (9) is solved numerically for the fields and the real-vector components in the time domain employing the finite-difference time-domain (FDTD) technique without invoking any approximations, such as slowly varying wave approximation (SVEA) and rotating wave approximation (RWA).

The initial circularly polarized optical pulsed excitation, applied at the left boundary of the simulation domain $z = 0$ (figure 6), is modelled by two orthogonal linearly polarized optical waves, phase-shifted by $\pi/2$,

$$\begin{aligned} \sigma^- \begin{cases} E_x(z=0, t) = E_0 e^{-(t-t_0)^2/t_d^2} \cos(\omega_0 t), \\ E_y(z=0, t) = -E_0 e^{-(t-t_0)^2/t_d^2} \sin(\omega_0 t), \end{cases} \\ \sigma^+ \begin{cases} E_x(z=0, t) = E_0 e^{-(t-t_0)^2/t_d^2} \cos(\omega_0 t), \\ E_y(z=0, t) = E_0 e^{-(t-t_0)^2/t_d^2} \sin(\omega_0 t), \end{cases} \end{aligned} \quad (10)$$

where E_0 is the initial field amplitude; the pulse carrier frequency is tuned in resonance with the dipole optical transition frequency ω_0 and is modulated by a Gaussian, centred at t_0 with characteristic decay time t_d , which determines the pulse duration. A linearly polarized pulse

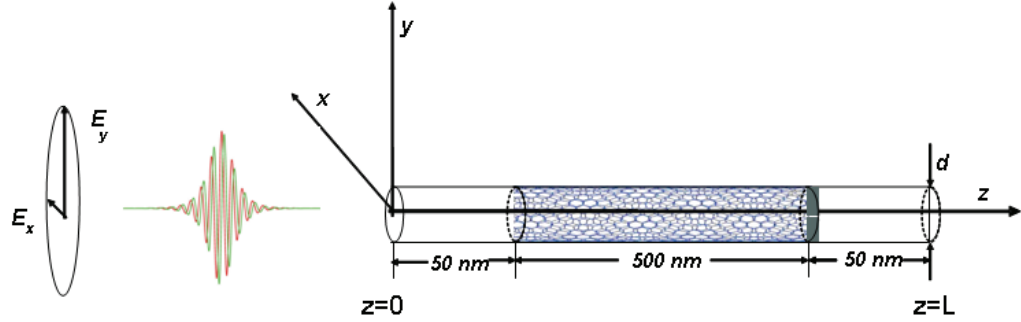


Figure 6. Simulation domain: the isolated SWCNT with length $L_n = 500$ nm is placed between two free space regions, each 50 nm long. The source pulse starts to propagate from the left boundary $z = 0$.

along the x (y) direction is modelled by

$$\begin{aligned}
 X \begin{cases} E_x(z=0, t) = E_0 e^{-(t-t_0)^2/t_d^2} \cos(\omega_0 t), \\ E_y(z=0, t) = 0, \end{cases} \\
 Y \begin{cases} E_x(z=0, t) = 0, \\ E_y(z=0, t) = E_0 e^{-(t-t_0)^2/t_d^2} \sin(\omega_0 t). \end{cases}
 \end{aligned} \tag{11}$$

4. Simulation results for the natural optical activity of an isolated SWCNT

The simulated semiconducting (5, 4) AL-handed SWCNT structure with effective refractive index $n = 2.3$ (see appendix A) is shown in figure 6 embedded between two free space (air) regions with refractive index $n = 1$. The simulation domain is finely discretized in space with $\Delta z = 1$ nm, which, through the Courant numerical stability criterion, corresponds to a time step of $\Delta t = 3.34 \times 10^{-18}$ s.

The ultrashort optical pulse with pulse duration $\tau = 60$ fs (selected to match the experimental conditions in [37]) and Gaussian envelope is injected from the left boundary ($z = 0$). The pulse centre frequency $\omega_0 = 3.01 \times 10^{15}$ rad s $^{-1}$ is tuned in resonance with the energy splitting between $\mu \rightarrow \mu \pm 1$ subband states of $E_{\mu, \mu \pm 1} \sim 1.982$ eV, corresponding to a wavelength $\lambda = 626.5$ nm. Since we are interested in the high-intensity nonlinear regime, throughout the simulations the pulse area below the pulse envelope is chosen to be π , giving an initial electric field amplitude $E_0 = 6.098 \times 10^8$ V m $^{-1}$ (see equation (10)). A π -pulse is of particular interest since it completely inverts the population in a two-level system.

In order to ensure that our ensemble approach describes properly the single nano-object, we select the density of the coupled oscillators, described by four-level systems, in such a way that the simulated nanotube volume (with diameter $d = 0.611$ nm and length $L_n = 500$ nm) contains, on average, only one carbon nanotube [38]. This yields an average density $N_a = 6.811 \times 10^{24}$ m $^{-3}$ of resonant absorbers.

The ultrafast optically induced polarization dynamics depend very strongly on the phenomenological relaxation rates. Assuming the value $\wp = 3.613 \times 10^{-29}$ Cm for the optical dipole matrix element calculated in appendix B, we use the expression for the spontaneous emission rate [40], taking into account the corresponding energy separation for each transition,

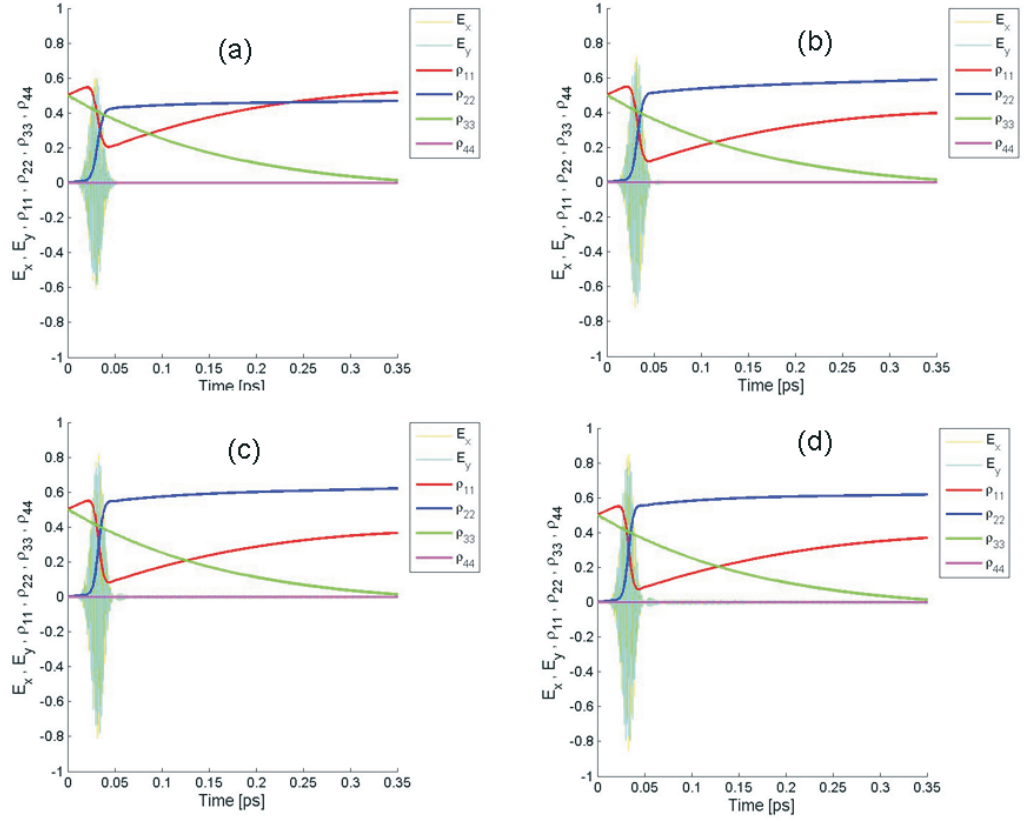


Figure 7. Time evolution of the electric field vector components E_x , E_y and the populations of all four levels in figure 5 under right-circularly polarized optical pulse excitation σ^+ at four different locations along the nanotube axis ((a) $z = 175$ nm; (b) $z = 300$ nm; (c) $z = 425$ nm; (d) $z = 550$ nm) measured from the left boundary $z = 0$ in figure 6. The initial population is assumed equally distributed between the lower-lying levels $|1\rangle$ and $|3\rangle$: $\rho_{11i} = \rho_{33i} = 1/2$. Level $|4\rangle$ is not involved in the dynamics.

to obtain an estimate for the relaxation rates. Thus, we obtain the following parameters: $\Gamma_1 = 2.907 \text{ ns}^{-1}$, $\Gamma_2 = 9.812 \text{ ns}^{-1}$, $\Gamma_3 = 1.227 \text{ ns}^{-1}$. We take the experimental value obtained in [37] for the intraband optical transitions, namely $\gamma = 130 \text{ fs}^{-1}$. Since the dephasing rates for the states involved are largely unknown, we treat them as phenomenological parameters, adopting the following values: $\Gamma_\mu = 800 \text{ fs}^{-1}$ and $\Gamma_{\mu-1} = 1.6 \text{ ps}^{-1}$. We should note that we have performed a number of simulations with different values of dephasing times varying within a fairly wide range (from fs to hundreds of ps), which confirmed that the spatio-temporal dynamics, and consequently the model predictions concerning the circular dichroism and optical rotation, are to a great extent insensitive to the choice of Γ_μ and $\Gamma_{\mu-1}$.

Throughout the simulations, the population density of all four levels is conserved ($\rho_{11} + \rho_{22} + \rho_{33} + \rho_{44} = 1$). We consider separately the two cases of an ultrafast resonant optical excitation of the $|1\rangle \rightarrow |2\rangle$ transition with σ^+ helicity and of the $|3\rangle \rightarrow |4\rangle$ transition with σ^- helicity (figure 5). Note that in the former case, level $|4\rangle$ does not participate in the relaxation dynamics and the system is effectively a three-level Λ -system, rather than a four-level system.

The ultrashort circularly polarized source pulse is injected into the medium and the temporal dynamics of the electric field vector components and population of all four levels are sampled at four different locations along the nanotube z -axis. The time evolution of the pulse E -field components, normalized with respect to E_0 , or the pulse reshaping, and the level populations are shown in figure 7 for times immediately after the excitation. The initial population is assumed equally distributed between the lower-lying levels ($\rho_{11i} = \rho_{33i} = 1/2$). The population of the lowest level $|1\rangle$, initially slightly increases due to the ultrafast population transfer from level $|3\rangle$ which is initially populated. The optical pulse excites the population to level $|2\rangle$: the population of level $|1\rangle$ sharply decreases while at the same time the population of level $|2\rangle$ increases. The population of level $|3\rangle$ decays almost exponentially, since the pumping of this level through population relaxation from $|2\rangle$ is at a much slower rate (by three orders of magnitude) than the intraband relaxation rate. The pulse trailing edge is slightly distorted due to the dipole formed between levels $|3\rangle$ and $|2\rangle$ (at the intersection point between ρ_{22} and ρ_{33} , figure 7), re-radiating back to the field. It is obvious that the final population after very long simulation times will relax to the equilibrium value $\rho_{11e} = 1$ into level $|1\rangle$ (not shown on this time scale). During the pulse propagation along the nanotube, the pulse is undergoing resonant absorption and emission, resulting in pulse amplitude amplification, increasing from ~ 0.6 near the left boundary to ~ 0.8 at the right structure boundary (figure 7(a) and (d)). This implies that the CNT behaves as a laser gain medium under an ultrashort circularly polarized pulsed optical excitation.

The system dynamics under σ^- polarized optical excitation is quite distinct, since all four levels are involved in it (figure 8). As in the previous case, the initial population is assumed equally distributed between the lower-lying levels. The population residing in level $|3\rangle$ is partly resonantly excited into level $|4\rangle$ by the passage of the pulse, shown by the sharp increase of ρ_{44} and a corresponding decrease of ρ_{33} . The population of level $|1\rangle$ slowly increases, rather than sharply dropping (cf figure 7), due to population transfer by spontaneous emission, interband ($\mu - 1 \rightarrow \mu - 1$) and intraband relaxation processes (figure 5). The population of level $|2\rangle$ increases at a slower rate during the passage of the pulse, due to depletion by the competing relaxation channels, reaching a maximum at later times (not shown) and subsequently decreasing. Eventually, the whole population relaxes into the lowest-lying state $|1\rangle$. As in the previous case considered, a slight pulse trailing edge distortion is observed, due to the forming of a dipole between levels $|4\rangle$ and $|2\rangle$ and between $|3\rangle$ and $|2\rangle$. Similar to the previous case, the pulse amplitude is amplified during the pulse propagation along the nanotube axis.

It is obvious that the different dynamics involved in the two cases of ultrafast optical excitation by σ^+ and σ^- polarized pulses would lead to asymmetry of the optical properties and therefore to a circular dichroism, birefringence and optical rotation. In what follows, we shall evaluate quantitatively the magnitude of these chirality effects.

From an experimental point of view, it would be of particular interest to be able to distinguish between the spectra of the transmitted pulses at the output facet of the simulated domain for each helicity of the ultrashort excitation pulse. The time traces of the E_x and E_y electric field components of the input and transmitted pulses (at the output facet of the simulated structure, figure 6) and their respective Fourier spectra are shown in figure 9 for the case of an ultrashort σ^+ polarized excitation. The transmission spectra exhibit a sharp peak at the resonant wavelength, which is an indication of resonant amplification. The corresponding time traces and Fourier spectra for σ^- polarized excitation are shown in figure 10. Similar to the previous case, the transmission spectrum exhibits a sharp resonant peak at the resonant wavelength. However, a comparison between figures 9 and 10 reveals nearly an order of magnitude higher intensity of

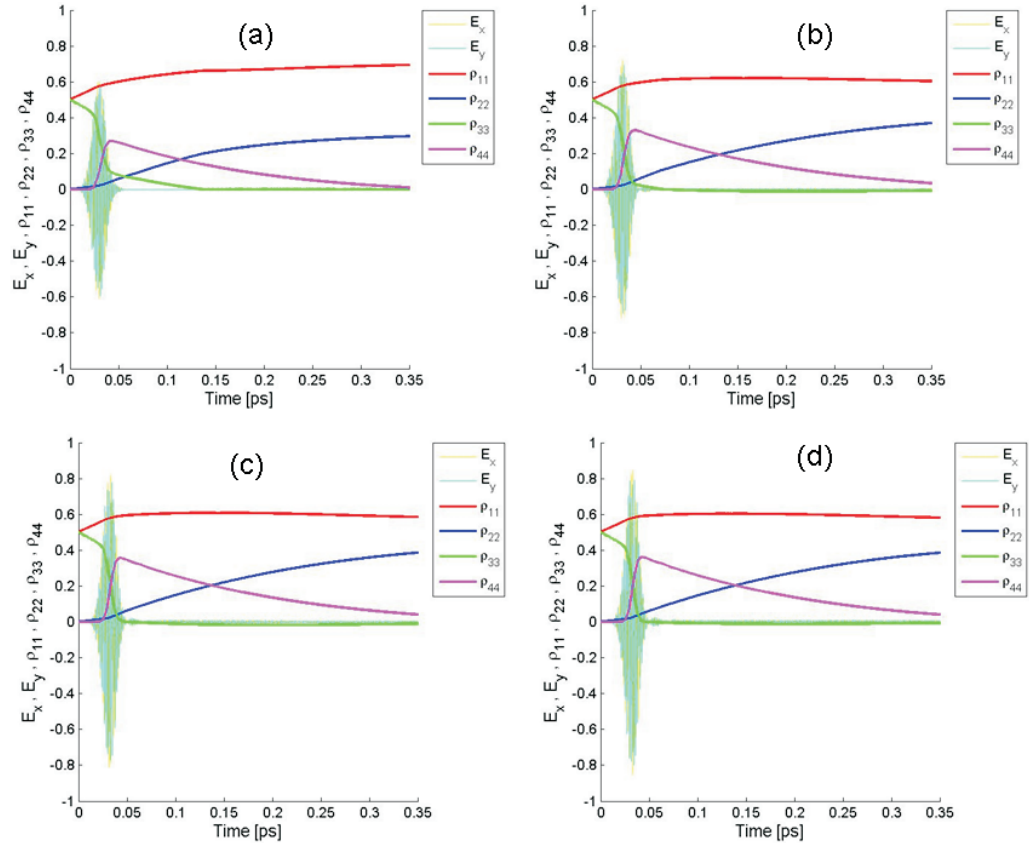


Figure 8. Time evolution of the electric field vector components E_x , E_y and the populations of all four levels in figure 5 under left-circularly polarized optical pulse excitation σ^- at four different locations along the nanotube axis ((a) $z = 175$ nm; (b) $z = 300$ nm; (c) $z = 425$ nm; (d) $z = 550$ nm) measured from the left boundary $z = 0$ in figure 6.

the peak, corresponding to the σ^+ excitation. The difference in the ultrafast transient response can be exploited in an experiment aiming to unambiguously determine the chirality of a single CNT by using ultrafast circularly polarized pulses of both helicities. In what follows, we shall demonstrate that the difference in the polarization-resolved (along x and y) transmission spectra of a linearly polarized excitation is much more pronounced and permits the identification of the precise helical form of the SWCNT.

In order to numerically demonstrate the rotation of the polarization plane during the pulse propagation across the medium, a linearly polarized (along x) pulse (equation (11), first line) is injected. The system temporal dynamics induced by the ultrashort linearly polarized pulse is shown in figure 11. Note that on this scale a non-vanishing E_y component is not apparent; however, on an expanded scale (figure 12), the appearance of a second E_y component (cyan line), and therefore the optical rotation of the E -field vector polarization, is clearly visible. The amplitude of the E_y component continuously increases as the pulse propagates along the nanotube structure. We should therefore expect a maximum optical rotation angle at the output facet, as shown in figures 13(a) and (b). The transmitted pulse is elliptically polarized. The optical transmission spectra of the x -polarized and y -polarized electric field vector components

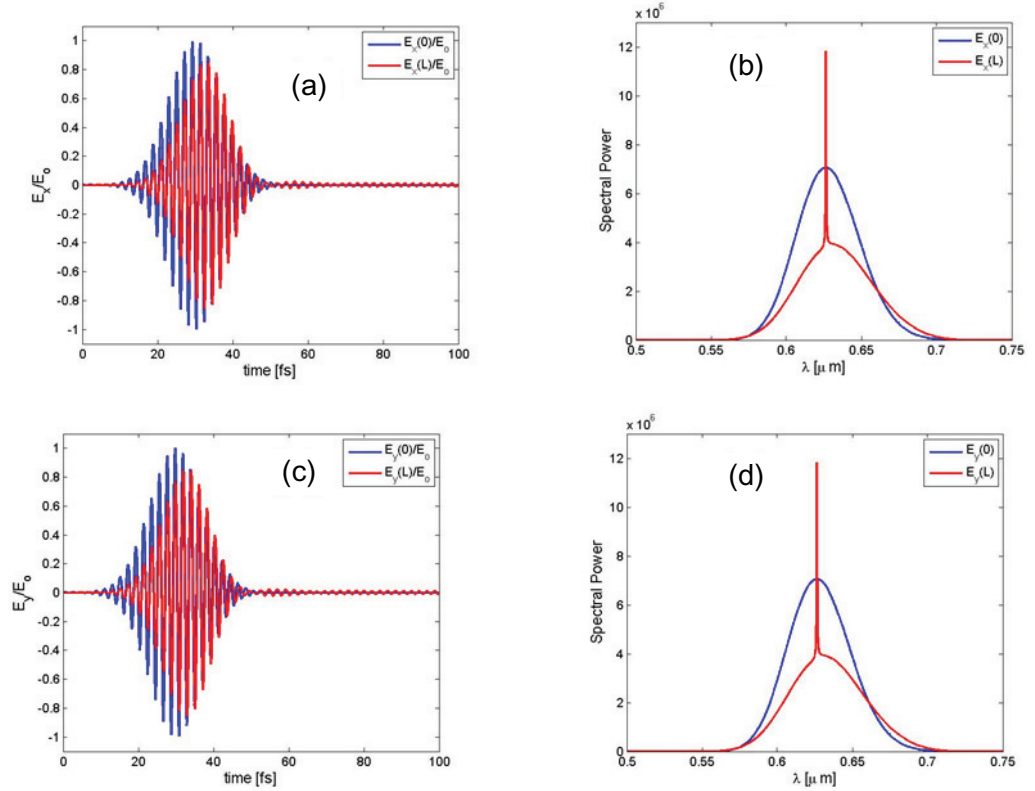


Figure 9. (a) Time trace of the E_x component of the input $E_x(0)$ (solid blue line) and output $E_x(L)$ (solid red line) σ^+ polarized pulse. (b) Transmission (Fourier) spectra versus wavelength of the input (blue line) and output (red line) σ^+ pulses. (c) Time trace of the E_y component of the input $E_y(0)$ (blue line) and output $E_y(L)$ (red line) σ^+ polarized pulse. (d) Transmission spectra versus wavelength of the input (blue line) and output (red line) pulses.

are quite distinct: while the former exhibits a sharp resonant peak superimposed on a broader line, the latter exhibits a single spectral line centred at the resonant wavelength.

In order to obtain a quantitative estimate of the natural optical activity in a single chiral CNT, we calculate the average absorption/gain coefficient and phase shift induced by the resonant medium from the real and imaginary parts of the complex propagation factor $e^{ik_c(z_2-z_1)}$ for the E_x and E_y electric field components, over a distance of one dielectric wavelength $l = z_2 - z_1 = \lambda_0/n$, where λ_0 is the resonant wavelength. The wavevector $k_c = \beta + i\gamma$, where β is the phase shift per unit length in the optical pulse induced by the interaction with the resonant medium and γ is the absorption/gain coefficient. The absorption/gain coefficient allows us to calculate the magnitude of the circular dichroism and the phase shift represents a measure of the rotation angle.

We select four pairs of points z along the nanotube length with staggered distances from the left boundary ($z = 0$) within the CNT structure, separated by one dielectric wavelength, and calculate the above quantities for each pair. The plots in figure 14 show a comparison between the gain coefficients for σ^+ excitation, corresponding to pumping $|1\rangle \rightarrow |2\rangle$ transition, and for σ^- excitation, corresponding to pumping $|3\rangle \rightarrow |4\rangle$ transition in figure 5. The theoretical

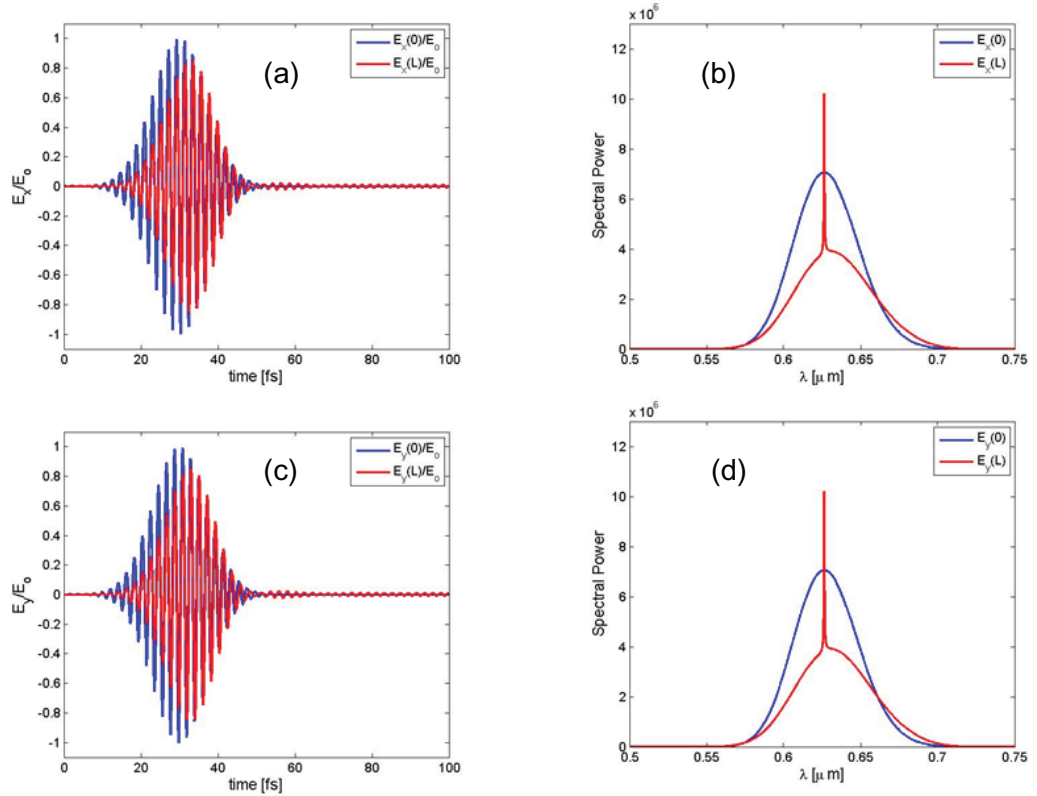


Figure 10. (a) Time trace of the E_x component of the input $E_x(0)$ (solid blue line) and output $E_x(L)$ (solid red line) σ^- polarized pulses. (b) Transmission (Fourier) spectra versus wavelength of the input (blue line) and output (red line) σ^- pulses. (c) Time trace of the E_y component of the input $E_y(0)$ (blue line) and output $E_y(L)$ (red line) σ^- polarized pulses. (d) Transmission spectra versus wavelength of the input (blue line) and output (red line) pulses.

gain coefficient of a homogeneously broadened two-level system is shown on the same plot for reference. The difference between the two plots at the resonant wavelength gives us an estimate of the magnitude of the natural circular dichroism in the (5, 4) CNT. The spatially resolved circular dichroism along the nanotube axis is calculated from the difference between the maxima of the gain coefficients at the resonant wavelength, corresponding to excitation with the two helicities (R or σ^+) and (L or σ^-): $\Delta A = G_R - G_L$ at each location (see figure 14), giving an average of $0.083 \mu\text{m}^{-1}$.

An estimate for the circular dichroism of a (5, 4) nanotube can be calculated from [41], equation (44), giving a value of 1.03 for the relative difference between σ^+ and σ^- absorption probability rates. This value, however, cannot be directly compared with the obtained result since the nanotube length does not enter the model in [41], and thus can only serve as a guide. We should stress that our analysis applies to the high-intensity nonlinear ultrafast regime, in which, to the best of our knowledge, no theory or experiments have been published. Therefore, we could expect deviations from the linear case. By comparison, the absolute value of the circular dichroism of an artificial helicoidal bilayered structure varies in the range of 5–9 dB, which is equivalent to a linear amplitude absorption/gain coefficient range of 0.58 – $1.04 \mu\text{m}^{-1}$.

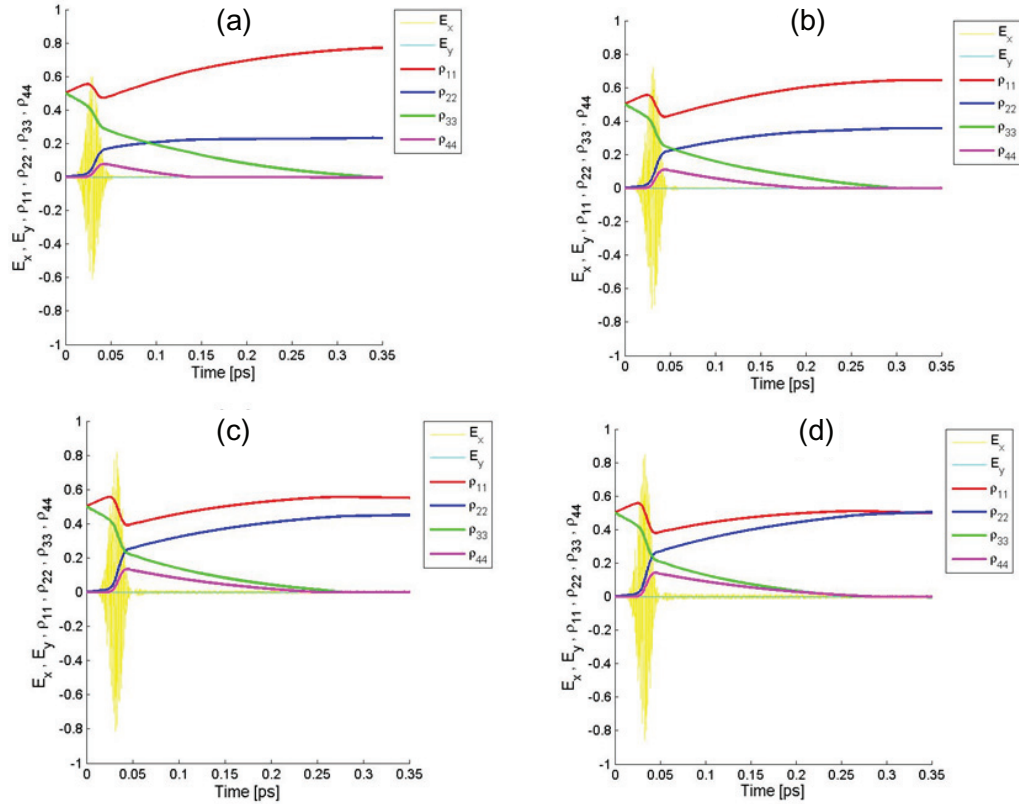


Figure 11. Time evolution of the electric field vector components E_x and E_y and the populations of all four levels in figure 5 under linearly polarized optical pulse excitation at four different locations along the nanotube axis ((a) $z = 175$ nm; (b) $z = 300$ nm; (c) $z = 425$ nm; (d) $z = 550$ nm) measured from the left boundary $z = 0$ in figure 6. The initial population is assumed equally distributed between the lower-lying levels $|1\rangle$ and $|3\rangle$: $\rho_{11i} = \rho_{33i} = 1/2$.

The phase shift difference $\Delta\phi = \Delta\phi_R - \Delta\phi_L$ introduced by the non-symmetric system response under σ^+ (transition $|1\rangle \rightarrow |2\rangle$) and σ^- (transition $|3\rangle \rightarrow |4\rangle$) circularly polarized pulse excitation represents a measure for the rotation angle. The result of the polarization is to change the phase delay per unit length from $\beta_{R(L)}$ to $\beta_{R(L)} + \Delta\beta_{R(L)}$. The atomic phase shift ($\beta_{R(L),x(y)}l$) for the four cases described above is plotted in figure 15 and the rotation angle and the specific rotatory power per unit length, $\rho = \pi(n_L - n_R)/\lambda_0$, where n_L and n_R are the refractive indices for left- and right-circularly polarized light, respectively, are given for each case. The specific rotatory power varies in the interval $\rho = 2.46\text{--}3.7^\circ \mu\text{m}^{-1}$, giving an average value of $\sim 2962.24^\circ \text{mm}^{-1}$. The corresponding anisotropy of the refractive indices for left- and right-circularly polarized light is of the order of $\Delta n = n_L - n_R = 0.0103$. The calculated natural polarization rotatory power, for the special case of a (5, 4) nanotube considered, exceeds the giant gyrotropy reported in the artificial photonic metamaterials of up to $2500^\circ \text{mm}^{-1}$ [25]. We should note, however, that the complexity of the CNT molecular structure allows for engineering the optical activity in a wide range. By comparison, the optical activity of e.g. quartz illuminated by the D line of sodium light ($\lambda = 589.3$ nm), is $21.7^\circ \text{mm}^{-1}$, implying refractive indices difference $|n_L - n_R| \sim 7.1 \times 10^{-5}$; $\rho = 32.5^\circ \text{mm}^{-1}$ for cinnabar (HgS). A comparison

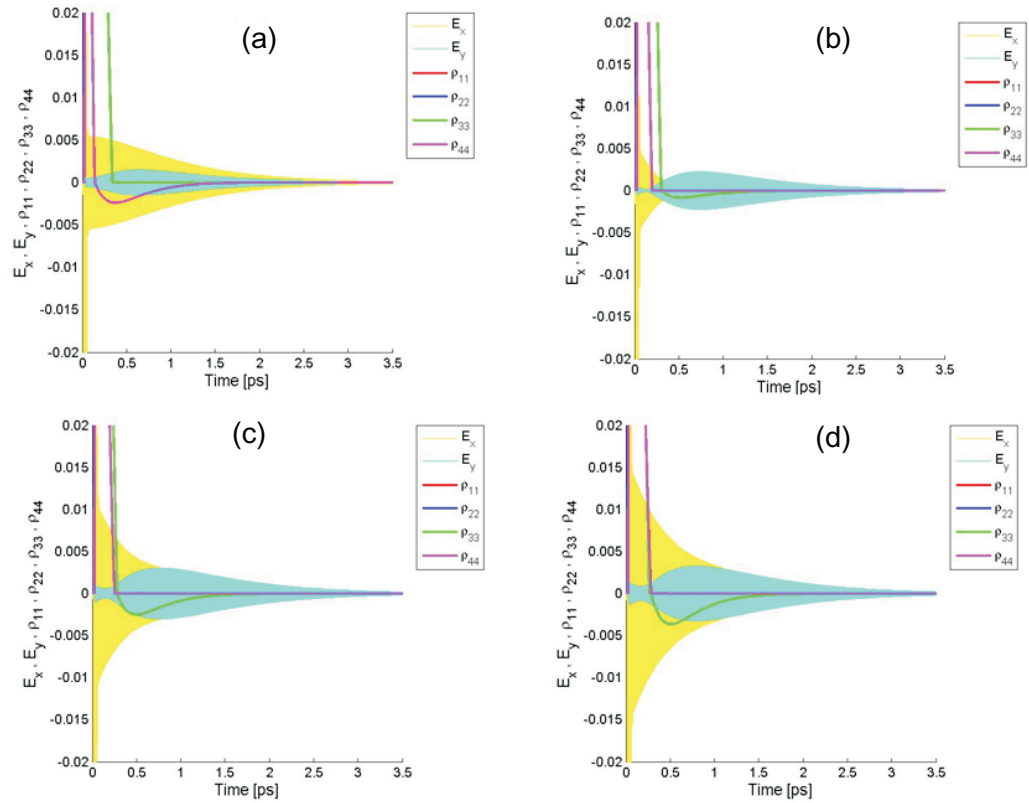


Figure 12. Expanded view of figure 11 showing the time evolution of the electric field vector components E_x and E_y and the populations of all four levels under linearly polarized optical pulse excitation at four different locations along the nanotube axis ((a) $z = 175$ nm; (b) $z = 300$ nm; (c) $z = 425$ nm; (d) $z = 550$ nm) measured from the left boundary $z = 0$ in figure 6.

of the specific rotatory power for a group of crystals is given in [43] (table), showing a wide range of variation from $2.24^\circ \text{ mm}^{-1}$ for NaBrO_3 to $522^\circ \text{ mm}^{-1}$ for AgGaS_2 .

Liquid substances exhibit much lower values of specific rotatory power, e.g. $\rho = -0.37^\circ \text{ mm}^{-1}$ for turpentine ($T = 10^\circ$, $\lambda = 589.3$ nm); $\rho = 1.18^\circ \text{ mm}^{-1}$ for corn syrup, etc. Cholesteric liquid crystals and sculptured thin films exhibit large rotatory power in the visible spectrum, $\sim 1000^\circ \text{ mm}^{-1}$ [44] and $\sim 6000^\circ \text{ mm}^{-1}$ [45], respectively.

5. Magneto-optical activity of a chiral SWCNT in an axial magnetic field

5.1. Theoretical model

We shall now focus on the theoretical description of the resonant coherent nonlinear optical activity when a static magnetic field $B_{\parallel}$ is threading the nanotube (figure 16). The rotation of the polarization of a plane-polarized electromagnetic wave propagating in a substance under a static magnetic field along the direction of propagation is known as Faraday rotation. In the presence of an axial magnetic field, the electronic band structure of a single CNT, and the electronic states near the bandgap edge in particular, significantly changes, owing to the

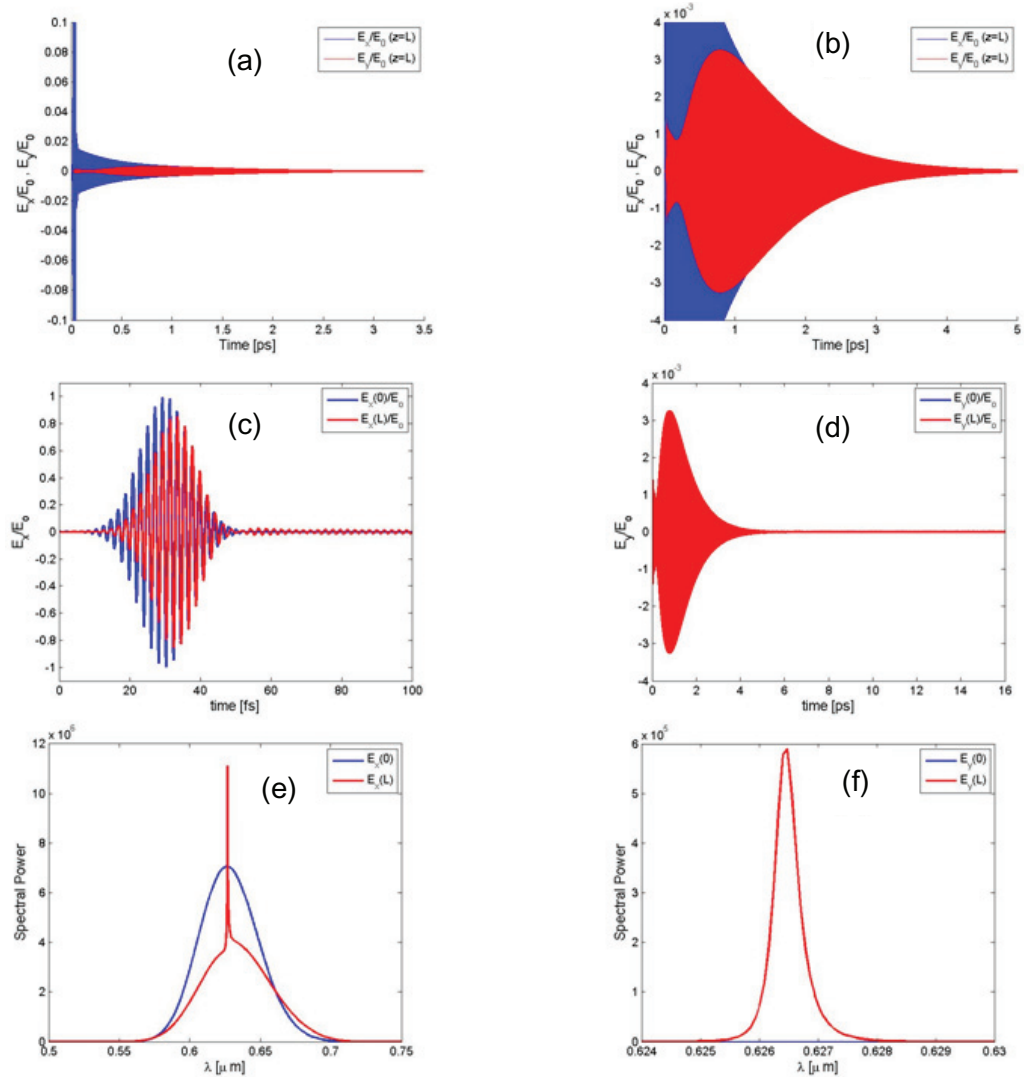


Figure 13. (a) Time evolution of the E_x (blue line) and E_y (red line) components at the output facet of the simulated domain (E_y is initially set to 0 to model the linearly polarized pulse). (b) Expanded view of (a) clearly showing the build-up with time of the electric field vector E_y component amplitude at the output facet. (c) Time trace of the E_x component at the input facet ($z = 0$) and at the output facet ($z = L$). (d) Time trace of the E_y component at the input ($E_y = 0$) and at the output ($z = L$) facet. (e) Fourier (transmission) spectra of the time traces in (c). (f) Fourier spectrum of $E_y(z = L)$ at the output facet.

combined action of two effects: the spin-B interaction resulting in Zeeman splitting of the energy levels [14, 16, 46] and the appearance of the AB phase in the wave function [15, 17, 32, 47, 48], resulting in an additional energy level shift. The two symmetric subbands at K (K') point of the BZ are degenerate at $B_{\parallel} = 0$. An applied magnetic field along the nanotube axis lifts this degeneracy and shifts the energy levels. As a result, the energy gap of one of the subbands (K') becomes larger, while the energy gap of the other subband (K) becomes smaller [46].

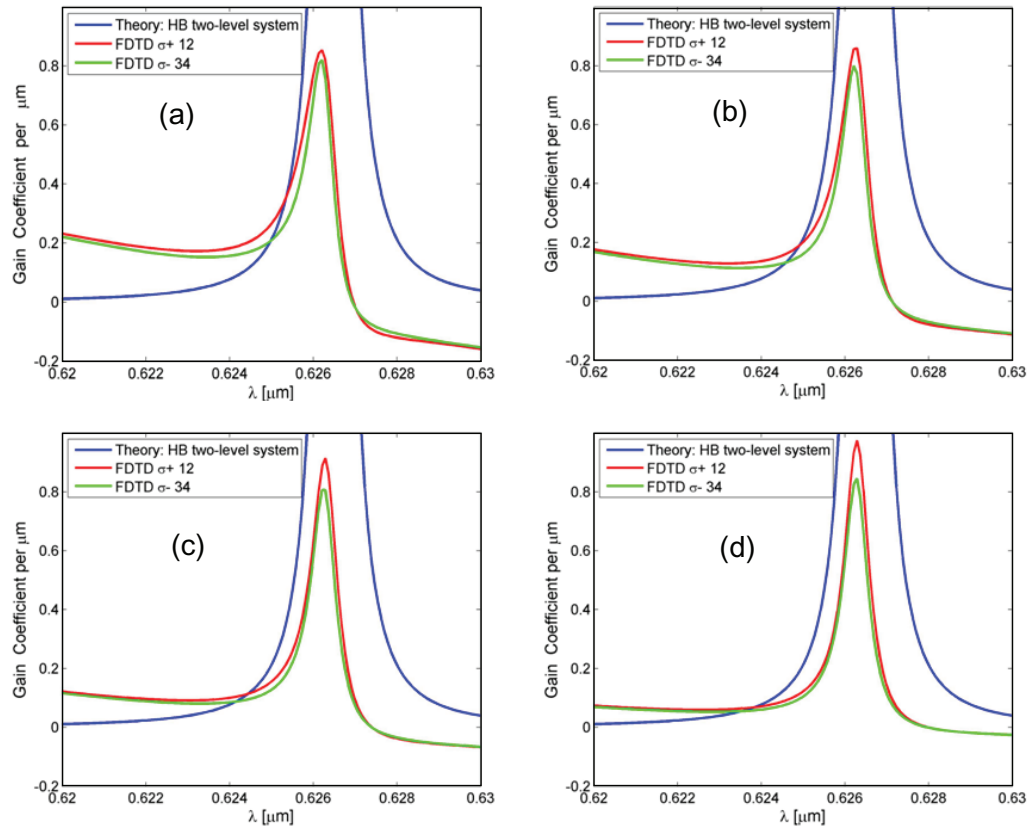


Figure 14. Spatially resolved calculated gain coefficient per micron versus wavelength for $E_x(E_y)$ electric field vector component of a σ^+ (red line) and σ^- (green line) circularly polarized ultrashort optical excitation and the theoretical gain coefficient of a homogeneously broadened resonant two-level system (blue line) for (a) a pair of points z_1 and z_2 within the CNT separated by one dielectric resonant wavelength. The offset of the first point z_1 is 5 nm from the beginning of the nanotube structure modeled as an absorption/gain medium: $\Delta A = 0.033785 \mu\text{m}^{-1}$. (b) A pair of points z_3 and z_4 within the CNT, one dielectric length apart; z_3 is shifted to the right by 1 nm with respect to z_1 : $\Delta A = 0.060104 \mu\text{m}^{-1}$. (c) A pair of points z_5 and z_6 within the active medium, separated by one dielectric wavelength; z_5 is shifted by 1 nm to the right of z_3 : $\Delta A = 0.107539 \mu\text{m}^{-1}$. (d) A pair of points z_7 and z_8 within the active medium, separated by one dielectric wavelength; z_7 is shifted by 1 nm to the right of z_5 : $\Delta A = 0.1291 \mu\text{m}^{-1}$.

Furthermore, the possibility of a magnetic field-induced metal–insulator transition has been put forward [49]. It has been theoretically predicted that the effect of the AB flux on the energy gap is to induce oscillations between zero and a fixed value with a period of the flux quantum $\Phi_0 = h/e$ [16, 32, 50], resulting in periodical oscillations of the magneto-optical absorption spectra.

At a fixed value of the static magnetic field, however, the orbital AB effect leads to a uniform shift in the energy levels. Without loss of generality, we shall consider the electronic

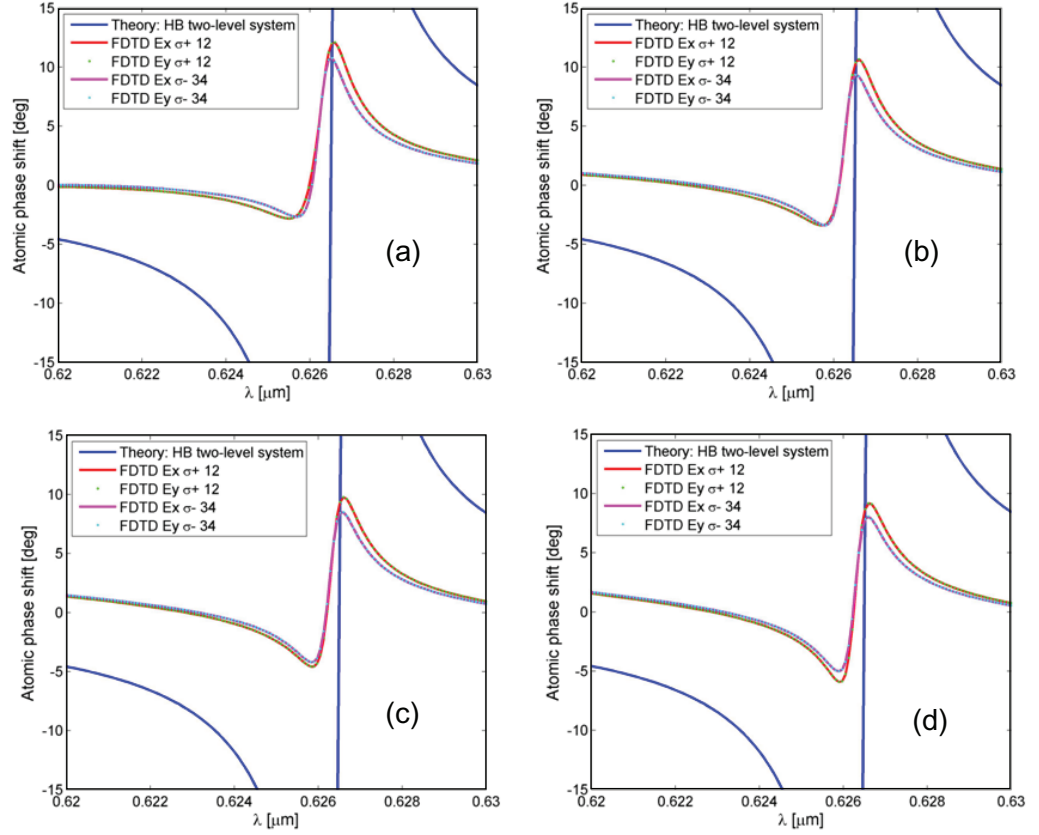


Figure 15. Spatially resolved calculated phase shift versus wavelength for E_x (red line) and E_y (green dot) components under σ^+ excitation and for E_x (magenta line) and E_y (cyan dot) under σ^- circularly polarized ultrashort optical excitation and the theoretical phase shift of a homogeneously broadened resonant two-level system (blue line) for the cases in figure 14: (a) $\Delta\phi = \beta l = 1.457076^\circ$, $\rho = 2.6746^\circ \mu\text{m}^{-1}$; (b) $\Delta\phi = 1.3388^\circ$, $\rho = 2.4574^\circ \mu\text{m}^{-1}$; (c) $\Delta\phi = 1.64222^\circ$, $\rho = 3.0145^\circ \mu\text{m}^{-1}$; (d) $\Delta\phi = 2.016985^\circ$, $\rho = 3.7024^\circ \mu\text{m}^{-1}$.

states near the band gap at the K point in the BZ. Therefore, the overall effect of the two mechanisms described above will be a bandgap reduction. We consider and calculate separately the contributions to the bandgap in respect of the Zeeman splitting and the AB effect. The Zeeman splitting or the spin-B interaction energy is given by

$$E_z = \mu_B g_e \sigma B_{\parallel}, \quad (12)$$

where $\mu_B = e\hbar/2m_e$ is the Bohr magneton, the electron g -factor, g_e is taken to be the same as that of pure graphite (~ 2), $\sigma = \pm 1/2$ is the z -axis projection of the electron spin (spin-up/spin-down state), and m_e is the free electron mass.

The model described below is valid for arbitrary magnitude of the magnetic field. We have performed simulations with magnetic fields in the range 2–100 T and found for the considered (5, 4) tube a nonmonotonous dependence of the optical rotation angle on the magnitude of B with maximum rotation reached for magnetic fields in the range 8–10 T. We should note that the magnetic field dependence of the optical rotation angle is the subject of a separate ongoing study and is beyond the scope of the present study. The specific value $B_{\parallel} = 8$ T for the magnetic

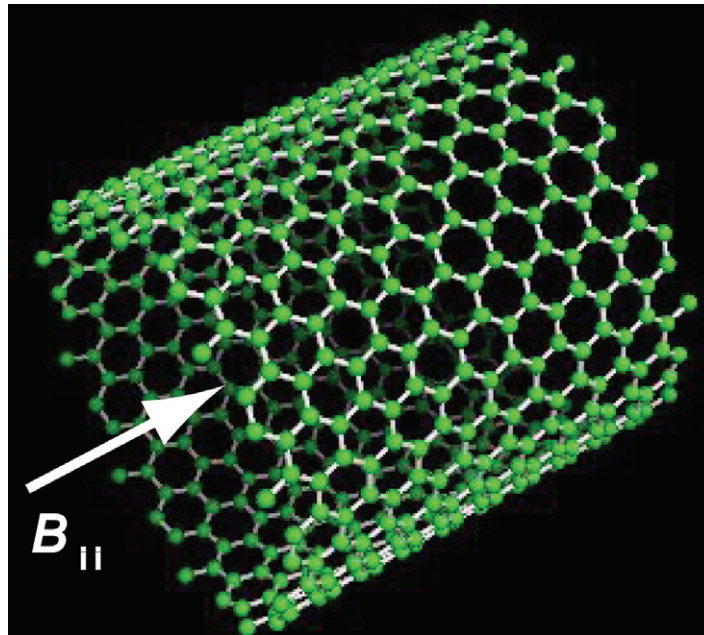


Figure 16. Scheme of a single chiral nanotube (20, 10) threaded by an axial magnetic field.

field selected is to demonstrate the maximum angle of Faraday rotation and, at the same time, was the maximum magnetic field of the static magnet available in the laboratory (in view of comparison with experiments at a later stage).

For a magnetic field $B_{||} = 8$ T, the above equation gives an energy shift of $E_z \approx 0.46$ meV, which corresponds to a resonant frequency $\omega_z = 7.026 \times 10^{11}$ rad s⁻¹.

The predicted oscillatory magnetic field dependence of the energy gap of a semiconducting nanotube [14, 51] is of the form

$$E_G(\Phi) = \begin{cases} 3E_G(0) \left| \frac{1}{3} - \frac{\Phi}{\Phi_0} \right|, & 0 \leq \Phi/\Phi_0 \leq 1/2, \\ 3E_G(0) \left| \frac{2}{3} - \frac{\Phi}{\Phi_0} \right|, & 1/2 \leq \Phi/\Phi_0 \leq 1, \end{cases} \quad (13)$$

where $E_G(0) = \hbar\omega_0$ is the energy gap at zero magnetic field ($B = 0$) and ω_0 is the resonant transition frequency.

For the case of a magnetic field $B = 8$ T with a flux Φ threading the (5, 4) nanotube cross-section with a diameter $d = 0.61145$ nm, the ratio $\Phi/\Phi_0 = 0.00057$, and therefore the first of the above equations holds. This leads to an energy-level shift, or bandgap renormalization due to the orbital AB effect of $E_{AB} = 3.37$ meV, corresponding to a resonant angular frequency $\omega_{AB} = 5.12 \times 10^{12}$ rad s⁻¹. In an external magnetic field, the energy levels near the bandgap of figure 5 split and the spin degeneracy is lifted (see figure 17). The energy-level system can be split into two reduced systems of levels, each of which represents a mirror image of the other. However, the symmetry is broken by the allowed optical transitions in each case. For simplicity, the AB uniform shift ($\hbar\omega_{AB}$) is not shown in figure 17. Another reason for selecting the magnetic field $B = 8$ T is that at this value the energy-level shift due to both AB and Zeeman splitting results in a substantial change in the pumping resonant frequency ($\omega_{\text{pump}} = \omega_0 - \omega_{AB} - 2\omega_z$)

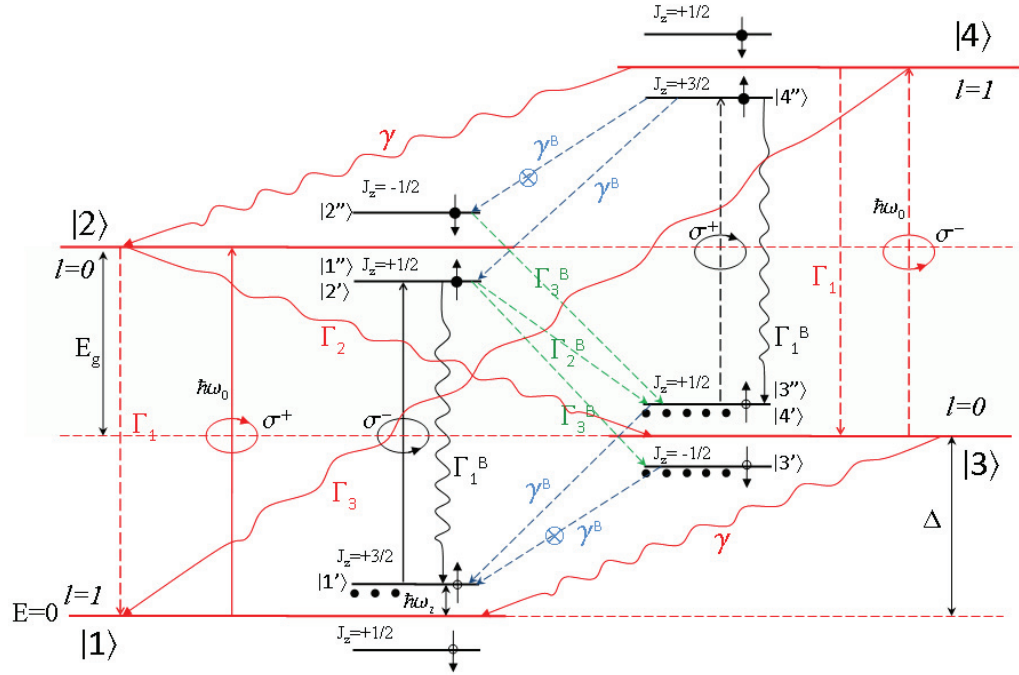


Figure 17. Zeeman splitting ($\hbar\omega_z$) of the energy levels near the bandgap of a (5, 4) nanotube in an external axial magnetic field. The original set of levels ($|1\rangle$ – $|4\rangle$) is labelled by the (quasi-angular) orbital momentum quantum number $l = 0, 1$; the resulting energy levels are labelled by the projection of the total angular momentum $J = l + s$ along the nanotube axis (z). Two reduced sets of levels, where energetically they are closest to the band edge, can be identified, namely $|1'\rangle$ – $|4'\rangle$ and $|1''\rangle$ – $|4''\rangle$ (note that levels $|4'\rangle$ and $|3''\rangle$ are common to the two systems). The energy bandgap E_g is shaded; Δ is the energy separation between the $l = 0$ and $l = 1$ states (assumed, for simplicity, equal for the valence and conduction band states). The original system of levels, the stimulated optically pumped transitions by $\sigma^{+(-)}$ light and relaxation processes are plotted in red. The black solid (dashed) arrows denote the resonant excitation of $|1'\rangle \rightarrow |2'\rangle$ ($|3''\rangle \rightarrow |4''\rangle$) transition by σ^- (σ^+) light. Note that the initial population (small black circles) is equally distributed between levels $|1'\rangle$ and $|3'\rangle$ in the valence band for the first ($'$) reduced system of levels, whereas the total population is residing in level $|3''\rangle$ in the valence band of the second ($''$) reduced system of levels. The spontaneous emission rates, designated by wavy lines, and the relaxation rates are modified in a magnetic field, which is reflected by the superscript B . The small black arrows denote the spin-up and spin-down states; note that the spin-up state is energetically higher than the spin-down state in the conduction band, whereas the opposite is valid for the valence band states. The forbidden transitions by the dipole optical selection rules are designated by $\otimes$.

with respect to the zero field case and therefore results in a considerable (tenfold, as will be shown below) enhancement of the optical rotation angle.

Analogously to the $B = 0$ case, the system Hamiltonian for an AL-handed SWCNT in an axial magnetic field $B \neq 0$ (for the (primed-system), excited by a σ^- pulse can be written in

the form

$$\hat{H}' = \hbar \begin{pmatrix} \omega_z & -\frac{1}{2}(\Omega_x - i\Omega_y) & 0 & 0 \\ -\frac{1}{2}(\Omega_x + i\Omega_y) & \omega_0 - \omega_z & 0 & 0 \\ 0 & 0 & \Delta - \omega_z & 0 \\ 0 & 0 & 0 & \Delta + \omega_z \end{pmatrix}, \quad (14)$$

where we have made the band gap renormalization with the AB shift, $\omega_0 \rightarrow \omega_0 - \omega_{AB}$, giving a torque vector

$$\gamma = \left(-\Omega_x, 0, 0, 0, 0, 0, -\Omega_y, 0, 0, 0, 0, 0, \omega_0 - 2\omega_z, \frac{2\Delta - \omega_0 - 2\omega_z}{\sqrt{3}}, \frac{2\Delta - \omega_0 + 4\omega_z}{\sqrt{6}} \right). \quad (15)$$

The time evolution of the four-level quantum system under an external time-dependent dipole coupling perturbation is given by equation (2). Similar to section 3, $\hat{\Gamma}_i$ matrices are introduced, according to

$$\begin{aligned} \hat{\Gamma}_1 &= \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \Gamma_1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma \end{pmatrix}, & \hat{\Gamma}_2 &= \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -(\Gamma_1 + \Gamma_2 + \Gamma_3) & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \\ \hat{\Gamma}_3 &= \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \Gamma_3 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, & \hat{\Gamma}_4 &= \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \Gamma_2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\gamma \end{pmatrix}, \end{aligned} \quad (16)$$

resulting in the following expressions for the diagonal components of the matrix $\hat{\sigma}$, expressed in terms of the real state vector components,

$$\begin{aligned} \sigma_{11} &= \frac{1}{12} \left(3\gamma + \sqrt{6}S_{15} (3\gamma - \Gamma_1) + (3 + 6S_{13} - 2\sqrt{3}S_{14}) \Gamma_1 \right), \\ \sigma_{22} &= -\frac{1}{12} \left(3 + 6S_{13} - 2\sqrt{3}S_{14} - \sqrt{6}S_{15} \right) (\Gamma_1 + \Gamma_2 + \Gamma_3), \\ \sigma_{33} &= \frac{1}{12} \left(3 + 6S_{13} - 2\sqrt{3}S_{14} - \sqrt{6}S_{15} \right) \Gamma_3, \\ \sigma_{44} &= \frac{1}{12} \left(-3\gamma + (3 + 6S_{13} - 2\sqrt{3}S_{14}) \Gamma_2 - \sqrt{6}S_{15} (3\gamma + \Gamma_2) \right). \end{aligned} \quad (17)$$

The dephasing rate matrix $\hat{\Gamma}_t$ is a traceless matrix with all off-diagonal components equal to Γ_μ , i.e. the transverse relaxation times $T_1 = T_2 = \dots = T_{12} = 1/\Gamma_\mu$. The longitudinal relaxation times appearing in the second of equation (2) are given by

$$T_{13} = \frac{4}{2\Gamma_1 + \Gamma_2 + \Gamma_3}, \quad T_{14} = \frac{12}{\Gamma_2 + 3\Gamma_3}, \quad T_{15} = \frac{6}{3\gamma + \Gamma_2}. \quad (18)$$

The macroscopic medium polarization vector components for this case are given by

$$\begin{aligned} P_x &= -\wp N_a S_1, \\ P_y &= -\wp N_a S_7 \end{aligned} \quad (19)$$

and the resulting pseudospin equations are solved self-consistently with vector Maxwell equation (8) directly in the time domain. The second (") reduced-level system (figure 17) is described by the following Hamiltonian,

$$\hat{H}'' = \hbar \begin{pmatrix} \omega_0 - \omega_z & 0 & 0 & 0 \\ 0 & \omega_0 + \omega_z & 0 & 0 \\ 0 & 0 & \Delta + \omega_z & -\frac{1}{2}(\Omega_x + i\Omega_y) \\ 0 & 0 & -\frac{1}{2}(\Omega_x - i\Omega_y) & \Delta + \omega_0 - \omega_z \end{pmatrix}, \quad (20)$$

resulting in the torque vector of the form

$$\gamma = \left(0, 0, 0, 0, 0, -\Omega_x, 0, 0, 0, 0, 0, \Omega_y, 2\omega_z, \frac{2(\Delta - \omega_0 + \omega_z)}{\sqrt{3}}, \frac{2\Delta + \omega_0 - 4\omega_z}{\sqrt{6}} \right). \quad (21)$$

The corresponding diagonal longitudinal relaxation rates matrix $\hat{\sigma}$ is given by

$$\begin{aligned} \sigma_{11} &= \frac{1}{12} \left(3\gamma + (-3 + 6S_{13} + 2\sqrt{3}S_{14})\Gamma_2 + \sqrt{6}S_{15}(3\gamma + \Gamma_2) \right), \\ \sigma_{22} &= -\frac{1}{12} \left(3 + 6S_{13} - 2\sqrt{3}S_{14} - \sqrt{6}S_{15} \right) \Gamma_3, \\ \sigma_{33} &= \frac{1}{12} \left(3\Gamma_1 + \sqrt{6}S_{15}(3\Gamma_1 - \Gamma_2) + (3 - 6S_{13} - 2\sqrt{3}S_{14})\Gamma_2 \right), \\ \sigma_{44} &= -\frac{1}{4} \left(1 + \sqrt{6}S_{15} \right) (\gamma + \Gamma_1) \end{aligned} \quad (22)$$

obtained with the introduction of the following $\hat{\Gamma}_i$ matrices,

$$\begin{aligned} \hat{\Gamma}_1 &= \begin{pmatrix} -\Gamma_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma \end{pmatrix}, \quad \hat{\Gamma}_2 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -\Gamma_3 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \\ \hat{\Gamma}_3 &= \begin{pmatrix} \Gamma_2 & 0 & 0 & 0 \\ 0 & \Gamma_3 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \Gamma_1 \end{pmatrix}, \quad \hat{\Gamma}_4 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -(\gamma + \Gamma_1) \end{pmatrix}. \end{aligned} \quad (23)$$

The transverse relaxation rate matrix is given by equation (6), giving $T_1 = T_2 = T_3 = T_7 = T_8 = T_9 = 1/\Gamma_\mu$ and $T_4 = T_5 = T_6 = T_{10} = T_{11} = T_{12} = 1/\Gamma_{\mu-1}$. The following expressions for the longitudinal relaxation rates are obtained,

$$T_{13} = T_{14} = \frac{4}{\Gamma_2 + \Gamma_3}, \quad T_{15} = \frac{2}{\gamma + \Gamma_1}. \quad (24)$$

The macroscopic polarization vector components are given by

$$\begin{aligned} P_x &= -\wp N_a S_6, \\ P_y &= -\wp N_a S_{12}. \end{aligned} \quad (25)$$

5.2. Simulation results for Faraday rotation

The simulated structure is the same as the one described in figure 6. We resonantly excite $|1'\rangle \rightarrow |2'\rangle$ ($|3''\rangle \rightarrow |4''\rangle$) transition by left (σ^-) (right (σ^+)) circularly polarized π -pulse with

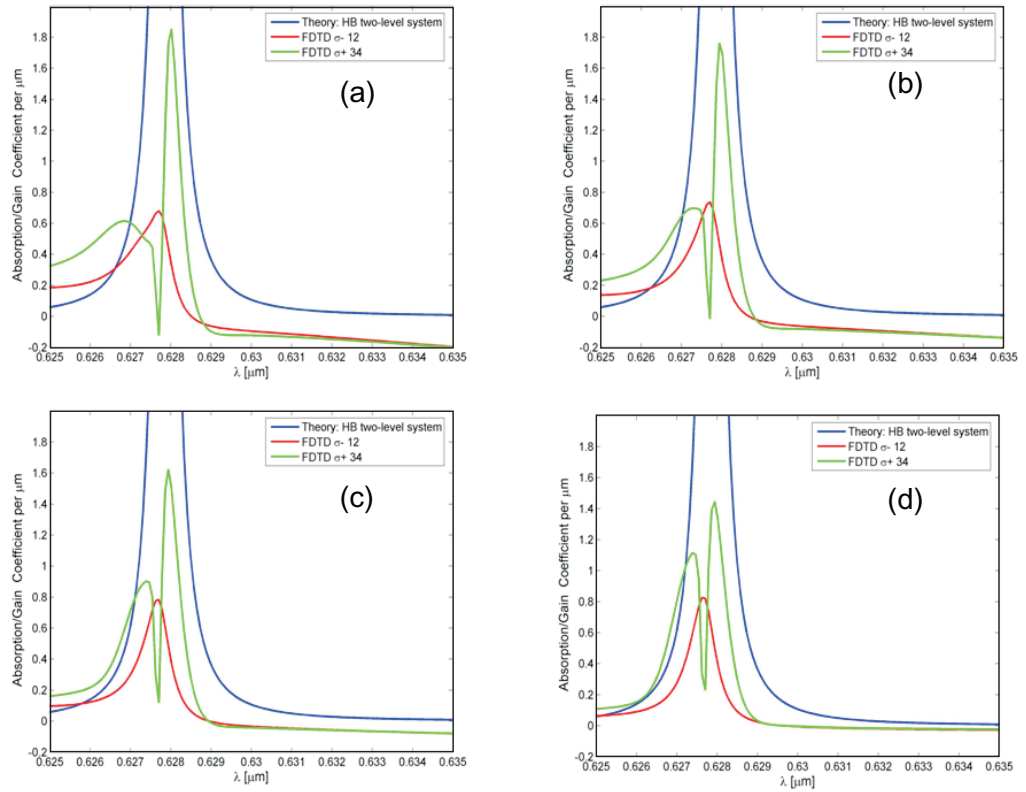


Figure 18. Spatially resolved calculated gain coefficient per micron versus wavelength for E_x (E_y) electric field vector component of a σ^+ (red line) and σ^- (green line) circularly polarized ultrashort optical excitation and the theoretical gain coefficient of a homogeneously broadened resonant two-level system (blue line) at $B = 8$ T for a pair of points (z_i, z_j) separated by one dielectric resonant wavelength within the carbon nanotube, shifted from the left boundary of the structure by offsets specified in figure 14. (a) Circular dichroism $\Delta A = 0.8048 \mu\text{m}^{-1}$; (b) $\Delta A = 0.75392 \mu\text{m}^{-1}$; (c) $\Delta A = 0.6661 \mu\text{m}^{-1}$ and (d) $\Delta A = 0.598 \mu\text{m}^{-1}$.

pulse duration $\tau = 60$ fs. The pulse central frequency is tuned in resonance with the transition frequency, $\omega_0 - \omega_{AB} - 2\omega_z$, and the pulse envelope is a Gaussian function. Owing to the combined effect of the AB and Zeeman energy levels shift, the dipole matrix element is modified. An estimate of the optical dipole matrix element in an axial magnetic field can be obtained from the theory developed in [41], taking into account the bandgap reduction at $B = 8$ T, giving $\wp = 3.6205 \times 10^{-29}$ Cm. Note that this value is slightly different from the zero magnetic field value (see appendix B). We recalculate the relaxation times using the above magnetic field dipole coupling constant, thus obtaining the following relaxation rates: $\Gamma_1 = 2.914 \text{ ns}^{-1}$, $\Gamma_2 = 9.79 \text{ ns}^{-1}$, $\Gamma_3 = 9.77 \text{ ns}^{-1}$. The intraband relaxation rate $\gamma = 130 \text{ fs}^{-1}$ and the dephasing rates $\Gamma_\mu = 800 \text{ fs}^{-1}$ and $\Gamma_{\mu-1} = 1.6 \text{ ps}^{-1}$ are taken to be the same as for the zero field case. Note that the initial boundary conditions are different for the excitation by σ^- and σ^+ pulses. Whereas in the former case the initial population is assumed equally distributed between the valence band levels ($\rho_{1'1'i} = \rho_{3'3'i} = 1/2$), closest to the band edge, in

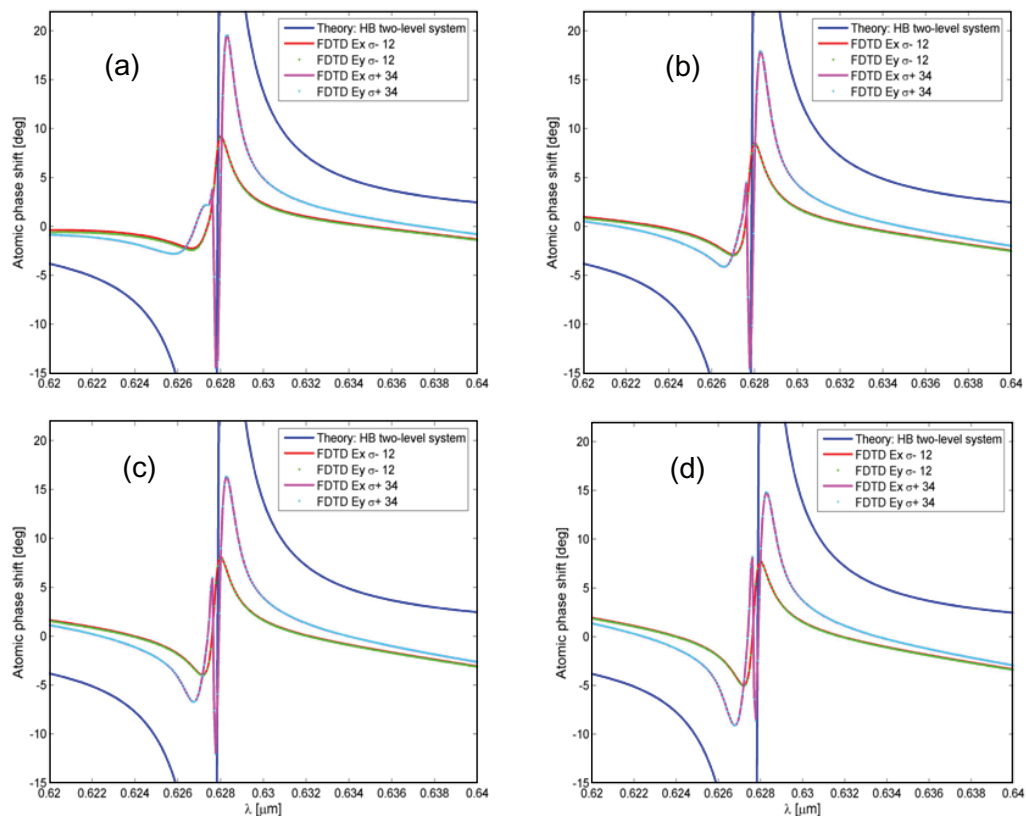


Figure 19. Spatially resolved calculated phase shift versus wavelength at $B = 8$ T for E_x (red line) and E_y (green dot) components under σ^+ excitation and for E_x (magenta line) and E_y (cyan dot) under σ^- circularly polarized ultrashort optical excitation and the theoretical phase shift of a homogeneously broadened resonant two-level system (blue line) for the cases in figure 18: (a) $\Delta\phi = \beta l = 22.011^\circ$, $\rho = -40.4033^\circ \mu\text{m}^{-1}$; (b) $\Delta\phi = 21.378^\circ$, $\rho = -39.2413^\circ \mu\text{m}^{-1}$; (c) $\Delta\phi = 16.447^\circ$, $\rho = -30.19^\circ \mu\text{m}^{-1}$; (d) $\Delta\phi = 11.161^\circ$, $\rho = -20.4871^\circ \mu\text{m}^{-1}$.

the latter case the whole population is in the single valence band state ($\rho_{4'4'i} = 1$). Similar to section 4, the time evolution of the electric field vector components and the population of all four levels is sampled at four points along the nanotube, and the real and imaginary parts of the complex propagation factor, giving the phase shift, and the absorption/gain coefficient are calculated. The absorption/gain coefficients for resonant excitation by σ^- (σ^+) pulse are plotted on the same graph (figure 18) and the theoretical gain coefficient of a homogeneously broadened two-level system is plotted for reference. Note that the resonance is shifted towards longer wavelengths due to the bandgap reduction. We should point out that the MCD spectra at $B = 8$ T shown in figure 18 are quite distinct from the zero-magnetic field spectra (figure 14) for the natural optical activity. While the σ^- polarized pulse is amplified during the pulse propagation across the nanotube, the σ^+ polarized pulse is absorbed, resulting in a much larger net circular dichroism. The average value of the MCD is $0.706 \mu\text{m}^{-1}$, an order of magnitude larger than the natural circular dichroism (cf section 4). The different behaviour of the calculated gain and absorption spectra under σ^- (σ^+) polarized optical pulse excitation is a direct consequence of the

discrete energy-level configuration describing the two cases. While the energy-level system for a σ^- excitation is a four-level system, the one corresponding to a σ^+ excitation is a three-level Λ -system, due to level $|2''\rangle$ being completely decoupled from the rest of the levels, owing to the dipole optical selection rules forbidding transitions from level $|4''\rangle \rightarrow |2''\rangle$. The calculated spectra in the latter case are reminiscent of electromagnetically induced transparency (EIT) and coherent population trapping effects in a three-level system [52, 53]. In fact, the absorption at resonance is close to zero and the shape of the spectrum is similar to the absorption dip, observed in EIT. The predicted destructive interference in an external axial magnetic field after the passage of the ultrashort pulse is a direct consequence of the specific time scales of the processes involved in the relaxation dynamics. This behaviour is confirmed by figure 19, where the induced phase shift is plotted as a function of wavelength. Whereas the phase shift spectrum for a σ^- pulse excitation is of the type of a two-level atomic phase shift, the shape of the phase shift curve is double peaked, which is characteristic of the real part of the susceptibility in a three-level system, exhibiting EIT. The calculated average specific rotatory power in a magnetic field ($B = 8$ T) is $-32.5804^\circ \mu\text{m}^{-1}$, corresponding to an average refractive index anisotropy of 6.497; the meaning of the minus sign is left rotation (counterclockwise when looking against the light source). The predicted Faraday rotation at $B = 8$ T is nearly an order of magnitude greater than the natural optical rotation. We should note that the calculated rotation is a combined effect from the chirality of the nanotube and the magnetic field-induced rotation and thus can be considered as an estimate for the magneto-chiral effect in a single nanotube. Using the developed model, an investigation of the magnetic field dependence of the optical rotation is currently under way and will be the subject of a forthcoming paper.

6. Conclusions

We have developed a theoretical formalism and dynamical model for the description of the natural optical activity and Faraday rotation in an individual chiral SWCNT in the coherent nonlinear regime under resonant ultrashort polarized pulse excitation. The model is based on a discrete-level representation of the optically active states near the band edge, whereby chirality is modelled by four-level systems, specific for each handedness, that are mirror reflections of each other and therefore non-superimposable. Thus, chirality is incorporated at a microscopic level in the model. The dynamics of the resonant coherent interaction of a polarized ultrashort laser pulse with the discrete multilevel system are treated semiclassically within the coherent vector Maxwell-pseudospin formalism. For illustration purposes, we consider the specific case of a (5, 4) SWCNT, although the model is valid for an arbitrary chiral nanotube. Furthermore, we provide an estimate of the effective dielectric constant and the optical dipole matrix element for transitions excited by circularly polarized light in a single nanotube ((5, 4) in particular). The model yields the time evolution of the optical pulse during its propagation due to the resonant coherent interactions, at each point along the nanotube, and thus enables extracting the circular dichroism and phase shift spectra. Giant natural gyrotropy for the special case of a (5, 4) nanotube considered ($3000^\circ \mu\text{m}^{-1}$ at $B = 0$), exceeding the one of birefringent crystals, liquid crystals and artificial metamaterials and thin films, is numerically demonstrated. Our results confirm the possibility to determine single nanotube handedness by time-resolved circular dichroism and magneto-optical rotatory dispersion spectroscopy. In view of the possibility of manipulating the nanotube chirality, we anticipate a much wider range of variation of the specific optical rotation. This is, however, the subject of an ongoing further study using the

proposed model and is beyond the scope of this paper. We show that the circular dichroism and specific rotatory power in an axial magnetic field for the same (5, 4) nanotube is enhanced by one order of magnitude at higher magnetic fields ($B = 8$ T). To the best of our knowledge, the way the external axial magnetic field affects the natural optical activity and the so-called magneto-chiral effect in the high-intensity nonlinear regime has not been investigated. These model studies are currently under way. We should note that although the model is developed for a resonant excitation, an off-resonant excitation, introducing detuning, can easily be implemented.

Acknowledgments

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Appendix A. Effective dielectric constant of an isolated SWCNT

We emphasize that our approach is an ensemble one. We consider a four-level atomic medium consisting of an ensemble of a large number ($N \gg 1$) of identical aligned CNTs with density $N_a = 6.8 \times 10^{24} \text{ m}^{-3}$, each replica having a dielectric constant calculated as described below. In order to obtain a single nanotube's dielectric properties, an averaging procedure over the ensemble is performed to give on average a single nanotube within the microscopic simulation domain volume. This assumption is generally valid for ergodic systems (for a detailed description of the method, see [38]).

In order to obtain an estimate of the dielectric constant of a single CNT, we use two independent approaches. Following the approach described in [54] based on the effective medium approximation, the local dielectric tensor of a cylindrical CNT can be written in cylindrical coordinates as

$$\varepsilon(\hat{r}, \hat{\phi}, \hat{z}) = \varepsilon_{\parallel} \hat{r} \hat{r} + \varepsilon_{\perp} (\hat{z} \hat{z} + \hat{\phi} \hat{\phi}), \quad (\text{A.1})$$

where $\varepsilon_{\parallel}$ ($\varepsilon_{\perp}$) are the principal components of the dielectric tensor of graphite parallel (perpendicular) to the normal axis of the graphite planes. The dielectric polarizability of a single CNT in an external potential of the form $V_m(r, \Phi) = V(r)e^{im\Phi}$, i.e. no field applied parallel to the tube z -axis, which corresponds to the considered case of a circularly polarized electromagnetic wave in a plane, perpendicular to the tube axis; an expression for the polarizability per unit length is given in [55] in terms of the inner, r , and outer, R , radii of the nanotube, described as a hollow cylinder. In the quasistatic approximation $m = 1$ and the nanotube's polarizability is anisotropic, given by

$$\alpha_1 = 4\pi\varepsilon_0\varepsilon_e R^2 \frac{(\varepsilon_{\parallel}\lambda - \varepsilon_i)(\varepsilon_{\parallel}\lambda + \varepsilon_e)\rho^{2\lambda} - (\varepsilon_{\parallel}\lambda - \varepsilon_e)(\varepsilon_{\parallel}\lambda + \varepsilon_i)}{(\varepsilon_{\parallel}\lambda - \varepsilon_i)(\varepsilon_{\parallel}\lambda - \varepsilon_e)\rho^{2\lambda} - (\varepsilon_{\parallel}\lambda + \varepsilon_e)(\varepsilon_{\parallel}\lambda + \varepsilon_i)}, \quad (\text{A.2})$$

where $\rho = r/R$, $\lambda = (\varepsilon_{\perp}/\varepsilon_{\parallel})^{1/2}$ and ε_i and ε_e are the dielectric constants of the internal and external materials; for a free standing nanotube, we shall assume $\varepsilon_i = \varepsilon_e = 1$.

An equivalent isotropic dielectric function, ε , of a solid cylinder with the nanotube's external radius, R , is introduced, according to

$$\alpha'_1 = 4\pi\varepsilon_0\varepsilon_e R^2 \frac{\varepsilon - \varepsilon_e}{\varepsilon + \varepsilon_e}. \quad (\text{A.3})$$

The principal axes of the dielectric function tensor, $\epsilon_{\parallel}$ and $\epsilon_{\perp}$, in equation (A.2) can be calculated from graphite ordinary and extraordinary ray refractive indices, $n_o = 2.64$ and $n_e = 2.03$, respectively [56]. Taking the inner radius $d = 0.61145$ nm of the (5, 4) nanotube under consideration and a typical value for the external nanotube radius of $R \sim 5$ nm [57], and equalizing equation (A.2) and (A.3), one can obtain the equivalent isotropic dielectric constant of the anisotropic nanotube, $\epsilon = 5.33$, giving a value $n \approx 2.3$ for the refractive index.

We have compared the dielectric response function of a single (5, 4) CNT, calculated by TB models with different levels of complexity from [59, 60], with the value estimated from the above effective medium approximation. Taking into account that the TB method, in general, underestimates the experimental data by 0.3 eV, the axial component of the imaginary part of the dielectric function tensor ϵ_{2zz} at the transition energy $E_{\mu,\mu\pm 1} = 1.982$ eV gives a value in the range $n = 1.835$ – 2.82 for the refractive index along the nanotube axis. Since our model is in 1D, the transverse (xx) component (which is $n \sim 1$) can be ignored. We are interested in the axial component of the dielectric function tensor, yielding the refractive index profile along the nanotube length, which is in good agreement with the value $n = 2.3$ obtained using the effective dielectric constant. We should note that a similar effective medium approach for description of the dielectric permittivity of a single nanotube within the FDTD computational method has been successfully applied in modeling the thermal radiative properties of vertical arrays of multi-walled CNTs [61].

Appendix B. Matrix element for dipole optical transitions excited by circularly polarized light in a single SWCNT

For the calculation of the optical dipole matrix element under resonant circularly polarized pulse excitation, we assume injecting a resonant ultrashort circularly-polarized pulse with pulse duration $\tau = 60$ fs and excitation fluence $S = 20$ mJ m⁻², in agreement with the experiment conducted in [37, 58].

In order to get an estimate of the dipole matrix element, we employ an extension of the effective mass method applied to chirality effects in CNTs proposed in [41]. It has been shown that chirality effects can be described by an effective Hamiltonian, in which the coupling between the electron wavevector k_z along the tube axis and the quasiangular momentum around the tube circumference is taken into account. Using this Hamiltonian, a general expression for the electron–photon matrix element between the initial state i and the final state f has been derived ([41], equation (18)) depending on the incident pulse light intensity I .

In order to obtain a value for I , we calculate first the electric field amplitude corresponding to a power of S/τ , using the expression for the intensity of a plane wave P in W m⁻² in a dielectric [40],

$$E = \sqrt{\frac{2P}{cn_{\text{refr}}\epsilon_0}}, \quad (\text{B.1})$$

where n_{refr} is the medium refractive index. The volume energy density of an electromagnetic wave in J m⁻³ in the expression for the matrix element is then given by

$$I = \frac{1}{2}\epsilon_0 n_{\text{refr}}^2 E^2. \quad (\text{B.2})$$

We substitute the chiral indices $n = 5$, $m = 4$ and all parameters (the resonant energy for the transition induced by circularly polarized light, tube diameter, refractive index (see

appendix A)) in equation (18) of [41]. Since we are considering resonant excitations, the k_z value should be taken at the point in the BZ where the band gap occurs, i.e. the value of $k_z = 0.126 \text{ m}^{-1}$ at the bandgap, when the zone-folding method is applied. Note that k_z varies within the boundaries of the first BZ, namely $-\pi/T \leq k_z < \pi/T$, where $T = 3.3272 \text{ nm}$ is the length of the unit cell. The maximum wavevector at the boundary of the BZ, $k_{z\text{max}} = 9.44 \times 10^8 \text{ m}^{-1}$. Substituting the value of the wavevector k_z at the bandgap into equation (18) yields a dipole matrix element $\wp \sim 1 \times 10^{-31} \text{ Cm}$, which varies to $1 \times 10^{-29} \text{ Cm}$ at the BZ boundary.

On the other hand, the relaxation time of a typical molecular transition in a single CNT has been measured in the range of tens of ns ($\tau_{\text{sp}} = 7\text{--}110 \text{ ns}$) [58], which for the calculated (using the same TB method of P_z -orbitals) energy gap of the circularly polarized $\mu \rightarrow \mu + 1$ transition, namely 1.982 eV , implies a value of $3 \times 10^{-29} \text{ Cm}$, which is in very good agreement with the value calculated using [41].

We have used the analytical expression for the dipole matrix elements of the interband optical transitions for arbitrary light polarization and nanotube chirality, recently given in [62, 63], to obtain an independent estimate for the dipole moment matrix element. For the specific case of a (5, 4) nanotube, the optical dipole matrix element is $\wp = 1.86 \times 10^{-30} \text{ Cm}$, which is in good agreement with the estimates previously obtained. We should note that the TB zone-folding approach of Goupalov *et al* does not take into account the curvature effects.

We assume the value $3 \times 10^{-29} \text{ Cm}$, since it is based on experimental results and is calculated by the expression for the spontaneous decay rate derived within the Weisskopf–Wigner approach, valid for both linearly and circularly polarized transitions. As it turns out, the correct prefactor of the dipole matrix element is not significant since it is within the numerical error of the method.

References

- [1] Born M 1915 *Phys. Zeits.* **16** 251
Oseen C W 1915 *Ann. d. Physik.* **48** 1
- [2] Kuhn W 1929 *Zeits. f. Physik. Chemie.* **4** 14
- [3] Kirkwood J G 1937 *J. Chem. Phys.* **5** 479
- [4] Drude P 1959 *The Theory of Optics* (New York: Dover)
- [5] Condon E U, Altar W and Eyring H 1937 *J. Chem. Phys.* **5** 753
- [6] Condon E U 1937 *Rev. Mod. Phys.* **9** 432
- [7] Rosenfeld L 1928 *Zeits. f. Physik.* **52** 161
- [8] Desorby G E and Kabir P K 1973 *Am. J. Phys.* **41** 1350
- [9] Dufey F 2006 *Chem. Phys.* **330** 326
- [10] Rikken G L A and Raupach E 1997 *Nature* **390** 493
- [11] Atkins P W and Woolley R G 1970 *Proc. R. Soc.* **314** 251
- [12] Sfeir M Y *et al* 2006 *Science* **312** 554
- [13] Bachilo S M, Strano M S, Kittrell C, Hauge R H, Smalley R E and Weisman R B 2002 *Science* **298** 2361
- [14] Jiang J, Dong J and Xing D Y 2000 *Phys. Rev. B* **62** 13209
- [15] Ajiki H 2002 *Phys. Rev. B* **65** 233409
- [16] Shyu F L, Chang C P, Chen R B, Chiu C W and Lin M F 2003 *Phys. Rev. B* **67** 045405
- [17] Mortimer I B, Li L-J, Taylor R A, Rikken G L J A, Portugall O and Nicholas R J 2007 *Phys. Rev. B* **76** 085404
- [18] Awschalom D D, Loss D and Samarth N (ed) 2002 *Semiconductor Spintronics and Quantum Computation* (Heidelberg: Springer)
- [19] Fitts D D and Kirkwood J G 1955 *J. Am. Chem. Soc.* **77** 4940

- [20] Verbiest T, Van Elshocht S, Kauranen M, Hellemans L, Snauwaert J, Nuckolls C, Katz T J and Persoons A 1998 *Science* **282** 913
- [21] Sánchez-Castillo A, Román-Velázquez C E and Noguez C 2006 *Phys. Rev. B* **73** 045401
- [22] Van Elshocht S, Verbiest T, Busson B, Kauranen M, Snauwaert J, Hellemans L, Persoons A, Nuckolls C, Phillips K E and Katz T J 2000 *Synth. Met.* **115** 201
- [23] Champagne B, André J-M, Botek E, Licandro E, Maiorana S, Bossi A, Clays K and Persoons A 2004 *ChemPhysChem* **5** 1438
- [24] Jin W, Fukushima T, Niki M, Kosaka A, Ishii N and Aida T 2005 *Proc. Natl Acad. Sci. USA* **102** 10801
- [25] Plum E, Fedorov V A, Schwanecke A S, Zheludev N I and Chen Y 2007 *Appl. Phys. Lett.* **90** 223113
- [26] Tasaki S, Maekawa K and Yamabe T 1998 *Phys. Rev. B* **57** 9301
- [27] Zarifi A and Pedersen T G 2008 *Phys. Rev. B* **77** 085409
- [28] Romanov D A and Kibis O V 1993 *Phys. Lett. A* **178** 335
- [29] Yevtushenko O M, Slepyan G Ya, Maksimenko S A, Lakhtakia A and Romanov D 1997 *Phys. Rev. Lett.* **79** 1102
- [30] Slepyan G Ya, Maksimenko S A, Lakhtakia A, Yevtushenko O M and Gusakov A V 1998 *Phys. Rev. B* **57** 9485
- [31] Slepyan G Ya, Maksimenko S A, Lakhtakia A, Yevtushenko O and Gusakov A V 1999 *Phys. Rev. B* **60** 17136
- [32] Ajiki H and Ando T 1993 *J. Phys. Soc. Japan* **62** 1255
- [33] Gommans H H, Alldredge J W, Tashiro H, Park J, Magnuson J and Rinzler A G 2000 *J. Appl. Phys.* **88** 2509
- [34] Zhang Y, Chang A, Cao J, Wang Q, Kim W, Li Y, Morris N, Yenilmez E, Kong J and Dai H 2001 *Appl. Phys. Lett.* **79** 3155
- [35] Samsonidze Ge G, Grüneis A, Saito R, Jorio A, Souza Filho A G, Dresselhaus G and Dresselhaus M S 2004 *Phys. Rev. B* **69** 205402
- [36] Yang L, Anantram M P, Han J and Lu J P 1999 *Phys. Rev. B* **60** 13874
- [37] Lauret J-S, Voisin C, Cassabois G, Delalande C, Roussignol Ph, Jost O and Capes L 2003 *Phys. Rev. Lett.* **90** 057404
- [38] Slavcheva G 2008 *Phys. Rev. B* **77** 115347
- [39] Slavcheva G 2008 *Quantum Dots: Research, Technology and Applications* ed R Knoss (New York: Nova Science Publishers) pp 373–94
- [40] Yariv A 1988 *Quantum Electronics* 3rd edn (New York: Wiley)
- [41] Ivchenko E L and Spivak B 2002 *Phys. Rev. B* **66** 155404
- [42] Rogacheva A V, Fedotov V A, Schwanecke A S and Zheludev N I 2006 *Phys. Rev. Lett.* **97** 177401
- [43] Jerphagnon J and Chemla D S 1976 *J. Chem. Phys.* **65** 1522
- [44] de Gennes P G 1974 *The Physics of Liquid Crystals* (Oxford: Clarendon)
- [45] Hodgkinson I, Wu Q W, Knight B, Lakhtakia A and Robbie K 2000 *Appl. Opt.* **39** 642
- [46] Minot E D, Yaish Y, Sazonova V and McEuen P L 2004 *Nature* **428** 536
- [47] Saito R, Dresselhaus G and Dresselhaus M S 1994 *Phys. Rev. B* **50** 14698
- [48] Zaric S, Ostojic G N, Kono J, Shaver J, Moore V C, Strano M S, Hauge R H, Smalley R E and Wei X 2004 *Science* **304** 1129
- [49] Lu J P 1995 *Phys. Rev. Lett.* **74** 1123
- [50] Roche S, Dresselhaus G, Dresselhaus M S and Saito R 2000 *Phys. Rev. B* **62** 16092
- [51] Ajiki H and Ando T 1994 *Physica B* **201** 349
- [52] Boller K J, Imamoglu A and Harris S E 1991 *Phys. Rev. Lett.* **66** 2593
- [53] Fleischhauer M, Imamoglu A and Marangos J P 2005 *Rev. Mod. Phys.* **77** 633
- [54] Lü W, Dong J and Li Z-Y 2000 *Phys. Rev. B* **63** 033401
- [55] Henrard L and Lambin Ph 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 5127, 5129 equation (4)
- [56] Palik E (ed) 1991 *Handbook of Optical Constants of Solids II* (Boston: Academic)
- [57] Garcia-Vidal F J, Pitarke J M and Pendry J B 1997 *Phys. Rev. Lett.* **78** 4289
- [58] Wang F, Dukovic G, Brus L E and Heinz T F 2004 *Phys. Rev. Lett.* **92** 177401

- [59] Popov V N and Henrard L 2004 *Phys. Rev. B* **70** 115407
- [60] Popov V N 2004 *New J. Phys.* **6** 17
- [61] Bao H, Ruan X and Fisher T S 2010 *Opt. Express* **18** 6347
- [62] Goupalov S V 2005 *Phys. Rev. B* **72** 195403
- [63] Goupalov S V, Zarifi A and Pedersen T G 2010 *Phys. Rev. B* **81** 153402
- [64] Dumitrica T, Garcia M, Jeschke H O and Yakobson B I 2006 *Phys. Rev. B* **74** 193406