Induced electro-optic effects in single-walled carbon nanotubes. I. Polarizability of metallic nanotubes

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The polarizability of single-walled carbon nanotubes (SWNTs) results in an *induced* dipole moment which in turn allows their alignment, when in suspension, in an applied electric field. The consequent introduction of anisotropy into what was a previously isotropic suspension of SWNTs gives rise to induced optical effects such as birefringence and linear dichroism. In this paper the induced linear dichroism is studied by application of a pulsed electric field. The results demonstrate that the effect is due to metallic SWNTs whose polarizability is found to be in close agreement with the classical result predicted for metallic cylinders. Electric-field-induced birefringence has been the subject of previous studies and it is frequently the case that linear dichroism interferes with measurements of birefringence, both producing similar effects. The induced linear dichroism and birefringence of SWNTs are compared here, and it is demonstrated that the linear dichroism has minimal influence on the measurement of birefringence in SWNTs.

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I. INTRODUCTION

An allotrope of carbon first identified by Iijima,[1] the single-walled carbon nanotube (SWNT), described at its most basic as a rolled-up graphene sheet, has some remarkable physical properties. Among the better known are those related to its electronic transport,[2,3] where it has been demonstrated to have very high carrier mobility,[4] and to its high tensile strength.[5]

SWNTs are one of the most frequently cited routes toward nanoscale electronics, and single SWNTs have been used to act as part of an active component such as the channel of a field-effect transistor (FET).[6] With a length-to-diameter ratio of order 10^3 and molecular scale dimension represented by the nanotube diameter, the SWNT may also be viewed as a prototype one-dimensional solid state system. For this reason among others it has been the object of a great deal of interest. The reduction in dimensionality gives rise to unique effects such as ballistic transport.[7]

Their electronic transport properties have been studied, including conductive and photoconductive properties and their very large electronic polarizability. The large electronic polarizability is of particular interest because, while both semiconducting and metallic SWNTs are polarizable, the metallic SWNTs are much more so.[8] This differential polarizability, it has been suggested, may form the basis of a means of separation of metallic from semiconducting SWNTs using the technique of dielectrophoresis.[9,10] Such separation has been demonstrated on a limited scale.

The induced dipole also causes the metallic tubes once aligned in an electric field to come together, due to the very large intertube van der Waals interactions, forming conducting filaments. Such filaments may eventually cause short circuits in dc electronic experiments.[11] Filament formation is clearly undesirable for many potential applications while for others, such as using metallic nanotubes in dispersion to render epoxies conducting,[12] it may be desirable to introduce alignment and filament formation in the loading process, thus rendering the material conducting at a lower nanotube concentration.

Field-induced optical anisotropy has been used to observe SWNT alignment in electric fields.[13,14] It has been demonstrated that the metallic SWNTs play the more important role in the Kerr effect.[15] In those measurements the Kerr coefficient was found to be even larger than that of the tobacco mosaic virus and the rate of rotational alignment was shown to depend on the electric field in a quadratic manner as predicted for the Kerr effect. It has since been appreciated that, in a typical optical setup of the type designed to measure the Kerr effect, if linear dichroism (LD) is present then its role cannot be ignored as it would give rise to an effect similar to that produced by the Kerr effect. The application of electric fields to suspensions of nanotubes has indeed been observed to produce LD,[16] and it is in part the objective of this work to measure the LD and compare and contrast it quantitatively with the Kerr effect previously measured in SWNTs in order to establish the relative importance of these two effects.

II. EXPERIMENT

The SWNTs used in these experiments were obtained commercially from Carbolex. They were synthesized by the arc discharge method and have a radius of $b = 0.7 \pm 0.1$ nm. The sample is polydisperse with a length lying typically between about 0.5 and 2 μm. The SWNTs were suspended in 1,2-dichloroethane (DCE) after dispersal with an ultrasonic probe. DCE is a suspending medium known to disperse the nanotube material well and to break up SWNT ropes into single nanotubes capable of being imaged using STM techniques.[17] Once held in suspension after ultrasonic probing, the dispersion was used for half a day before being again dispersed with the probe. Very low concentrations of the order 1.6×10^{-6} wt fraction were used in these experiments to limit tube-tube interactions. The suspension was contained in a Teflon cell with glass windows either end of the cell allowing light into and out of the cell. A HeNe laser beam passed through the cell along a path length of 3.0 cm defined by the length of parallel plate electrodes placed within the cell and separated

by $d = 2.0$ mm. The electrodes created a uniform electric field perpendicular to the propagation direction of the HeNe beam. In zero electric field the suspension is isotropic, becoming anisotropic as a voltage is applied across the electrodes. The absorbance of an isotropic suspension was measured at 633 nm in a 1 cm path length cell using a spectrophotometer and found to be 0.114. Corrected for the path length of the Kerr cell and the concentration of the suspension in the Kerr cell the absorbance used for normalization purposes in these experiments is $A = 0.547$.

Light from the HeNe laser was already initially plane polarized and had its plane of polarization further selected by a Glans prism acting as a preparation polarizer before it entered the cell to select the plane of polarization to be either parallel or perpendicular to the applied electric field. The light transmitted by the cell, as an electric field in the form of a square pulse of duration T and amplitude V applied across the cell, was measured using a silicon junction photodiode. From such measurements the changes in absorbance A for each polarization, $\Delta A_{//} = A_{//}(E) - A_{//}(E = 0)$ and $\Delta A_{\perp} = A_{\perp}(E) - A_{\perp}(E = 0)$, were found as the electric field oriented the nanotubes. The reduced dichroism defined as

$$\frac{\Delta A}{A} = \frac{\Delta A_{//} - \Delta A_{\perp}}{A} = \frac{A_{//}(E) - A_{\perp}(E)}{A} \tag{1}$$

was then determined.

III. RESULTS

Figure 1 shows the intensity (in arbitrary units), as a function of time, of the light transmitted by a sample of SWNTs suspended in DCE at a concentration of 1.6×10^{-6} wt fraction. The transmitted intensity is shown before, during, and after the application of an electric field for light polarized parallel and perpendicular to the electric field. The fact that the parallel and perpendicular polarizations appear to transmit slightly differing intensities in zero field when the sample is isotropic is because the initial plane polarization state of the HeNe is such that it is polarized at an angle of 44.46 ° to the applied electric field, differing from the desired 45°. This leaves the light intensity slightly larger when the polarizer selects for the parallel component than when selecting for the perpendicular component. Also shown in Fig. 1 is a voltage pulse of approximately 20 ms duration and 200 V amplitude. With the electric field applied the transmission of light polarized parallel to the applied field is reduced while the transmission of perpendicularly polarized light is increased as a result of the induced anisotropy of the sample.

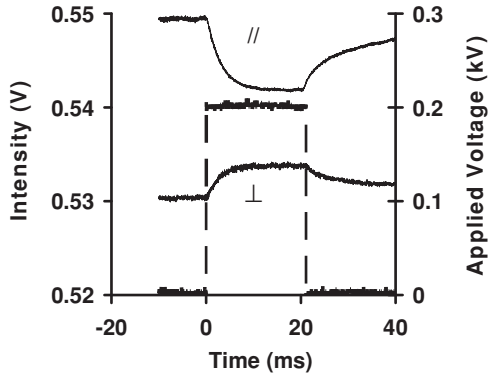

FIG. 1. The transmitted intensity for both parallel (//) and perpendicular (⊥) polarizer orientations for SWNTs suspended in DCE at a concentration of 1.6×10^{-6} wt fraction. Also shown is the applied voltage pulse amplitude 200 V and duration 20 ms.

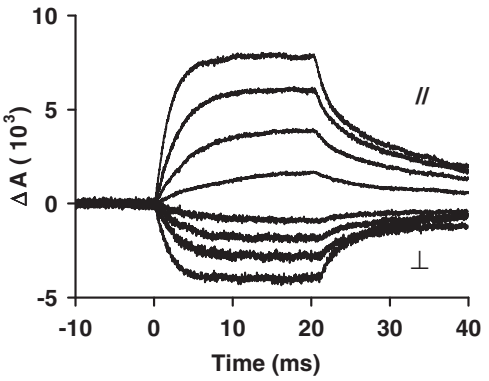

FIG. 2. The transient dichroism for parallel and perpendicular polarized light for SWNTs suspended in DCE at 1.6×10^{-6} wt fraction. Electric fields used are 50, 75, 100, and 150 kV m^{-1} in order of increasing effect.

From such data the change in transmission can be obtained for each polarization and the difference in absorption coefficient inferred.

Using the definition of absorbance:

$$A = \log_{10}\frac{I_{\text{in}}}{I_{\text{out}}} = \log_{10}\frac{1}{T}, \tag{2}$$

we may find the transient changes in absorbance following the application of an electric field,

$$\Delta A = \log_{10}\frac{T(E = 0)}{T(E)} = \log_{10}\frac{I(E = 0)}{I(E)}. \tag{3}$$

Figure 2 shows $\Delta A_{//}$ and $\Delta A_{\perp}$ inferred from data similar to those of Fig. 1 at a range of applied electric fields. The reduced dichroism $\Delta A/A = (\Delta A_{//} - \Delta A_{\perp})/A$ obtained from the data of Fig. 2 is shown in Fig. 3. Figure 4 shows how the linear dichroism is proportional to the square of the electric field at low fields before tending slowly to saturation at high electric fields as the SWNT alignment becomes more complete.

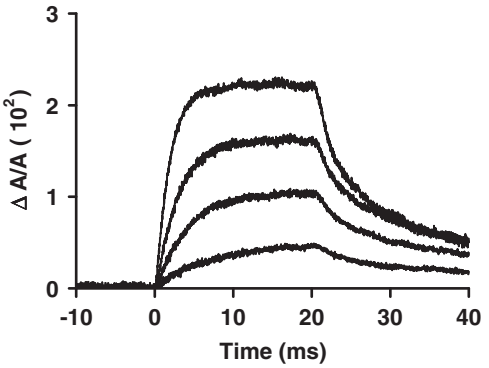

FIG. 3. The reduced dichroism for low, medium, and high electric fields for SWNTs suspended in DCE at 1.6×10^{-6} wt fraction derived from the data shown in Fig. 2.

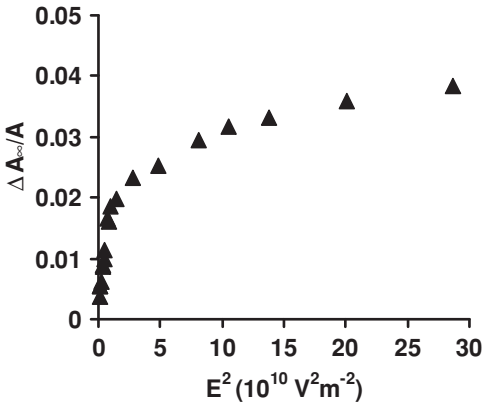

FIG. 4. The variation of the steady-state reduced dichroism with the square of the applied electric field for SWNTs suspended in DCE at 1.6×10^{-6} wt fraction.

IV. DISCUSSION

A previous experiment[15] that proposed to measure the magnitude of the induced birefringence of a suspension of SWNTs aligned in an electric field used a classical optical setup for the Kerr effect measurements. In this classical Kerr measurement[15,18] light is plane polarized by an initial polariser at 45° to the direction of the applied electric field used to align the sample. This plane-polarized light is thus the superposition of equal and orthogonal plane-polarized components with the light electric vector parallel and perpendicular to the applied field direction. A second polarizer-analyzer was set at 90° to the first. A detector then measured any light transmitted by this analyzer. The transmission through the two crossed polarizers plus suspension may be analyzed using one of two approximations:

(i) Assuming no dichroism, $A_{//} = A_{\perp}$, and a finite induced birefringence $n_{//} \neq n_{\perp}$ due to the partially aligned nanotube suspension, where $n_{//}$ and $n_{\perp}$ represent, respectively, the real components of the refractive index for light polarized parallel and perpendicular to the applied electric field.

(ii) Assuming no birefringence, $n_{//} = n_{\perp}$, and a finite induced dichroism $A_{//} \neq A_{\perp}$, where $A_{//}$ and $A_{\perp}$ are the absorbances of light polarized parallel and perpendicular to the applied electric field.

It is the first approximation which is usually used,[15,18] i.e., the absence of any dichroic effect is assumed but with birefringence induced in the aligned sample. Parallel and perpendicular components of the original plane-polarized light field will have a mutual phase shift $\Delta\varphi$ after passing through the sample. The transmitted light would now be in a state of elliptical polarization and a proportion T of the intensity originally incident upon the Kerr cell would be transmitted by the analyzer. The transmission T is a direct measure of the birefringence according to

$$\frac{I_{\text{out}}}{I_{\text{in}}} = T = \sin^2\left(\frac{\Delta\varphi}{2}\right) = \sin^2\left(\frac{\Delta n k_0 L}{2}\right), \qquad (4)$$

where the birefringence $\Delta n = n_{//} - n_{\perp}$, $k_0 = 2\pi/\lambda$ is the wave vector in free space, and L (=3 cm) is the interaction path length in the suspension (the distance over which the electric field is applied and along which the laser beam travels).

Analysis of these earlier experiments of Donovan *et al.*[15] followed this usual approximation and found the electric-field-induced birefringence of a suspension of SWNTs using Eq. (4). From the birefringence the specific Kerr coefficient was found to be $K_{\text{SP}} = 2.0 \times 10^{-12}$ m^2 V^{-2} $= 1.8 \times 10^{-3}$ esu, a value comparable to the largest known, that of the tobacco mosaic virus, $K_{\text{SP}} = 1.36 \times 10^{-3}$ esu, as found by O'Konski *et al.*[19] It needs to be noted here that in the earlier work [15] there is an error in Eq. (1a) [Eq. (4) in the current work] that is used to calculate birefringence from measured transmission: the factor 2 in the denominator of the $\sin^2$ factor was omitted. This means that all values of Δn in that paper are a factor $\times 2$ too small as are quantities derived from Δn; in particular the Kerr coefficient is undervalued and should be $K_0 = 2.8 \times 10^{-18} m^2 V^{-2}$ with a specific Kerr coefficient $K_{\text{SP}} = 4.0 \times 10^{-12} m^2 V^{-2}$.

It has since been appreciated that using this approximation was too simplistic and that the aligned nanotubes would also show a difference in absorption for the two components of the light field, $\Delta A \neq 0$. The effects of this linear dichroism would be to give rise to a transmission in the absence of any birefringence. This second effect comes about because the two initially equal components of the electric field vector of the light will now no longer be equal on exiting the cell, leading to a rotation of the plane of polarization. Such a rotation would also give a nonzero transmission through the polarizer-analyzer when the applied field aligned the SWNTs. It is now possible with the separate determination of linear dichroism in the present work to determine the transmission due to linear dichroism alone that would occur for the Kerr geometry previously used. This now requires use of the second approximation that $\Delta n = 0$, the transmission being due to linear dichroism alone. What the transmission would have been in such circumstances may be calculated from the measured values of dichroism in this work. The plane of polarization would be rotated by an angle

$$\theta = \tan^{-1}\left[\frac{10^{A_{//}}}{10^{A_{\perp}}}\right] = \tan^{-1}[10^{\Delta A}]. \qquad (5)$$

The analyzer, as a result of this rotation, is now set at an angle $\varphi = 135^{\circ} - \theta$ to the plane of polarization of the light from the cell and as a result there will be transmission through the polarizer–Kerr cell–analyzer system given by

$$T_{LD} = \frac{10^{-A_{//}}}{4}\left(10^{\Delta A/2} - 1\right)^2 = \frac{10^{-A_{//}}}{4}(\tan\theta - 1)^2. \qquad (6)$$

To cleanly separate out the effects due to the difference in birefringence and the difference in absorption as described in Eqs. (4) and (6), respectively, is not possible as the former transforms the linearly polarized input beam into an elliptically polarized beam while the latter maintains a linearly polarized beam but with a change in angle. However, intuitively one might regard the effect of linear dichroism as a perturbation on the overall transmission when carrying out experiments using the Kerr geometry. With this in mind, to obtain an estimate of the effect of linear dichroism on the previous measurements of birefringence,[15] we have used Eq. (6) and the values for the linear dichroism reported here to find the transmission T_{LD} for the Kerr geometry due to linear dichroism alone. We have subtracted this component of the transmission

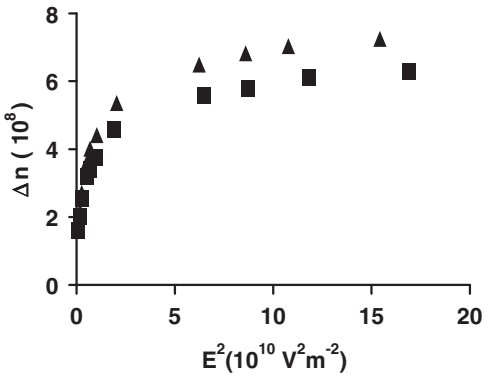

FIG. 5. A comparison of the birefringence measured in Ref. 15 (including a ×2 correction) with a crossed-polarizer geometry, ▲, with the birefringence corrected for the effects of linear dichroism found in the current work, ■.

from the overall transmission measured in the experiments reported by Donovan *et al.*[15] to obtain a corrected transmission $T_{\text{Corr}} = T_{\text{Net}} - T_{LD}$. Shown in Fig. 5 is the variation of Δn with the applied electric field calculated from Eq. (4) using the corrected transmission, as measured in the Kerr geometry.[15] Also shown in Fig. 5 is the value given previously[15] when any perturbation due to linear dichroism was ignored. It is clear from the results of Fig. 5 that the error introduced through the existence of a finite linear dichroism, in attempts to measure the birefringence of SWNTs using the standard optical setup, never accounts for more than an 18% overestimate of the Kerr effect at any electric field, and at most fields the contribution of linear dichroism is less; therefore the previous results on the magnitude of the birefringence and the conclusions remain substantially correct having taken account of the factor 2 error in the equation used to go from transmission to birefringence in that paper.

To disentangle the separate roles of linear dichroism and the Kerr effect with the results obtained using the Kerr geometry is not possible but nevertheless that optical setup is widely used to obtain information about the Kerr effect.[18–20] When doing so care must be taken to ensure that the results are not affected by the potential existence of electric-field-induced dichroism. An involved experimental method has been suggested to separate linear dichroism and birefringence in a single set of measurements and has been demonstrated on photosystem 1;[21] however, an attempt to employ this method on SWNT suspensions by the current authors has not proved successful and no presentable results have been obtained. It is important to note in passing that the method described here for measuring linear dichroism is not susceptible to any component of birefringence distorting the determined values.

The rate and degree of nanotube alignment (magnitude of the effect) are determined by the torque applied by the electric field acting on any dipole moment present on the nanotubes and on rotational friction forces that need to be overcome in order to establish alignment. A complete theory of field-induced birefringence and linear dichroism has been created[19,20] describing the rate of alignment and the magnitude of the effect in terms of the polarizability and geometry of the aligning particle and the rotational friction coefficient ς_R, which in turn depends on the viscosity of the suspending medium. This classical theory, due largely to pioneers such as Benoit[22] and O'Konski and Zimm,[23], has been developed using continuum models of hydrodynamics of particles in viscous media. The present situation deals with SWNTs which are nanoscopic particles where the cross section of the rotating cylinder is of molecular dimension comparable to the size of the suspending molecules. While in this case the continuum models developed for mesoscopic particles such as viruses may be inappropriate, it is worth using them to compare the magnitudes of the LD observed in this work with predictions of these models. A second paper, part II,[27] will compare the rate of alignment as found for SWNTs with the predictions of the classical theory.

In considering the magnitude of the reduced dichroism as established in these experiments, Fig. 4 shows that the magnitude of the reduced dichroism is proportional to the square of the electric field at low fields, tending to saturation at high electric fields where most of the SWNTs are aligned. Figure 6 shows more clearly the low-field data of Fig. 4 where the reduced dichroism varies quadratically with the electric field. The classical, established theory of linear dichroism shows that the gradient of Fig. 6 yields information that may be used to find the value of the dichroism Kerr coefficient K_D and the polarizability α of the nanotube. From the slope of Fig. 6 it is possible to find the dichroism Kerr coefficient,[19,20]

$$\lim_{E\to 0}\left(\frac{\Delta A/A}{E^2}\right) = K_D. \tag{7}$$

The dichroism Kerr coefficient from Fig. 6 is found to be $K_D = 1.58 \times 10^{-12}\ \text{m}^2\ \text{V}^{-2}$.

At high fields the effect tends to saturation as the SWNTs come into more complete alignment. The saturation behavior of Fig. 4 has no analytic expression able to describe its form according to classical theory; however, the saturated value of the dichroism is an important quantity.

In Fig. 7 the reduced dichroism is plotted against the reciprocal square of the electric field, and from the intercept of Fig. 7 the value of the saturated reduced dichroism for a fully aligned sample at infinite electric field is extrapolated. It is found to be $\Delta A_S/A = 4.11 \times 10^{-2}$.

It is possible from K_D and the saturation value of the reduced dichroism to obtain a value for the polarizability of a

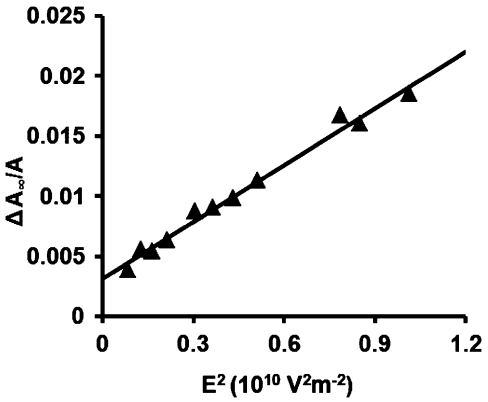

FIG. 6. The low-electric-field data of Fig. 4 showing the proportionality of the reduced dichroism to the square of the applied electric field.

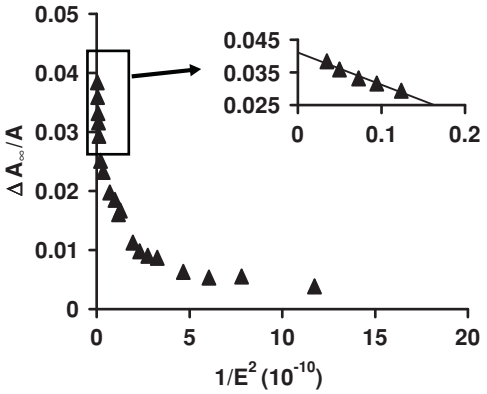

FIG. 7. The variation of the steady-state reduced dichroism with the inverse square of the applied electric field for SWNTs suspended in DCE at 1.6×10^{-6} wt fraction. The inset shows the data close to the origin, demonstrating the intercept value.

nanotube in DCE by noting that in terms of acting dipoles the Kerr dichroism coefficient is given by

$$K_D = \frac{\Delta A_S}{A}\frac{(P-Q)}{15}. \tag{8}$$

Here P is a factor set by any permanent dipole moment and Q is a factor dependent on the induced dipole alone. In fact there is no permanent dipole moment on an SWNT and

$$Q = \frac{\alpha_{//} - \alpha_{\perp}}{k_B T} = \frac{\alpha_{//}}{k_B T}, \tag{9}$$

where $\alpha_{//}$is the polarizability parallel and $\alpha_{\perp}$ the polarizability perpendicular to the nanotube axis. It has been demonstrated that $\alpha_{//} \gg \alpha_{\perp}$ for SWNTs,[24] and this has been used to simplify Eq. (9).

The Kerr dichroism coefficient for SWNTs is then related to the polarizability along the SWNT axis by

$$K_D = \frac{\Delta A_S}{A}\frac{(\alpha_{//} - \alpha_{\perp})}{15 k_B T} = \frac{\Delta A_S}{A}\frac{\alpha_{//}}{15 k_B T} \tag{10}$$

and the polarizability is given by

$$\alpha_{//} = \frac{15 k_B T K_D}{\Delta A_S / A} = 15 k_B T \left(\frac{\Delta A_S}{A}\right)^{-1}\left(\lim_{E\to 0}\frac{\Delta A/A}{E^2}\right). \tag{11}$$

The value for the polarizability is found to be $\alpha_{//} = 2.39 \times 10^{-30}\,\mathrm{m}^2$.

In general the polarizability will depend on the length of the nanotube and this dependence is hidden in the experimentally measured value of $\Delta A/A$ which represents an average over all lengths present and actively contributing to the effect; therefore the value of polarizability is also an average value.

To compare and comment further on this value of polarizability it is necessary to recognize that there are two different electronic species of SWNT present together in the samples studied. Both metallic SWNTs and semiconducting SWNTs coexist and they each have very different theoretical polarizabilities.

The polarizability of a metallic cylinder of length L in vacuum is well known and given by[8,25]

$$\alpha^M = \frac{4\pi\varepsilon_0 L^3}{24\,[\ln a - 1]}\left[1 + \frac{4/3 - \ln 2}{\ln a - 1}\right]\ \mathrm{m}^2, \tag{12}$$

where $a = L/b$ is the aspect ratio of the tube. For the semiconducting nanotubes the theoretical polarizability is given as[8,26]

$$\alpha^S = \left[\frac{8\pi\hbar^2 e^2}{mA}\right]\left(\frac{bL}{\tilde{E}_G^2}\right)\mathrm{m}^2, \tag{13}$$

where $A = 2.7 \times 10^{-20}\ \mathrm{m}^2$ is the area per carbon atom on the graphene sheet, $\tilde{E}_G = 5.4 E_G$, E_G is the band gap for the nanotube in joules, and m is the free-electron mass.

Both equations (12) and (13) are given here in SI units whereas the author of Ref. 8 has a combination of units, using SI units and esu for semiconductors and metals, respectively. The polarizability α throughout this paper is defined such that the dipole moment μ of a nanotube in an applied electric field E is given by $\mu = \alpha E$.

The present samples have, according to the manufacturers, a radius $b = 0.7 \pm 0.1$ nm and a typical length in the range $0.5 < L < 2\ \mu$m.

For the case of metallic SWNTs we may, given the slowly varying logarithmic dependence on a in (12), assume a typical $a \approx 10^3$ with $\ln a = 6.9$ and treat this as a constant, giving for the theoretical polarizability of metal SWNTs of length L in vacuum

$$\alpha^M = 8.85 \times 10^{-13} \times L^3 \mathrm{m}^2. \tag{14}$$

For metallic SWNTs suspended in a medium with static dielectric constant κ the polarizability corrected for polarization of the medium is given by

$$\alpha^M_{\mathrm{sus}} = \kappa\alpha^M = \frac{4\pi\varepsilon_0\kappa L^3}{24\,[\ln a - 1]}\left[1 + \frac{4/3 - \ln 2}{\ln a - 1}\right] m^2 \tag{15}$$

and in 1,2-DCE where κ=10.3 the polarizability is

$$\alpha^M_{\mathrm{sus}} = 9.11 \times 10^{-12} \times L^3\ \mathrm{m}^2. \tag{16}$$

For tubes of length L=1 μm in DCE the polarizability is then $\alpha_{//}^{\mathrm{theory}} = 9.11 \times 10^{-30}\ \mathrm{m}^2$ in reasonable agreement with the experimental value $\alpha_{//}^{\mathrm{expt}} = 2.39 \times 10^{-30}\ \mathrm{m}^2$ found from the data of Fig. 6.

Use of Eq. (13) to find a theoretical value for the polarizability in vacuum of a semiconductor nanotube of band gap $E_G = 1$ eV gives $\alpha^S = 2.72 \times 10^{-28} \times L\mathrm{m}^2$. For tubes of length L=1 μm the semiconductor polarizability in vacuum is then $\alpha_{//}^{\mathrm{theory}} = 2.71 \times 10^{-34}\ \mathrm{m}^2$. In order to find the polarizability for a semiconducting SWNT in a suspending medium of static dielectric constant ε_m the Clausius-Mossotti factor would need to be introduced in order to compensate for the modification of the applied electric field at the tube. The factor involves a knowledge of the dielectric constant of the nanotube and is a complication that is unnecessary in the present case where metallic nanotubes dominate. For a given length of SWNT the metals have a theoretical polarizability three orders of magnitude larger than that of semiconductors.

In view of the good agreement between the theoretical polarizability for metallic SWNTs and the experimentally established value for the sample of nanotubes measured in the present work, it is clear that the dichroic effect is brought about by the orienting metallic SWNTs. The theoretical polarizability of semiconducting SWNTs is four orders of magnitude smaller than the observed value and we conclude therefore that the semiconducting SWNTs contribute insignificantly to the effect observed in this work.

Given the predominance of metallic SWNTs as contributors to the effect, the experimental value of $\alpha_{//}$ found here may be equated to the theoretical value for metallic SWNTs:

$$\alpha_{//} = 2.39 \times 10^{-30}\ \mathrm{m}^2 = \alpha^M_{\mathrm{sus}} = 9.11 \times 10^{-12} \times \overleftarrow{L^3}, \quad (17)$$

where an average value for the length of the SWNTs contributing to the dichroism has been defined. Following this definition an average value for the length of the SWNTs contributing to the dichroism is found to be $\bar{L} \approx 0.64\ \mu$m. This is very close to the expected mean value for the nanotubes and strongly confirms the expression for polarizability of metallic rods in a medium of dielectric constant κ as given in Eq. (15).

V. CONCLUSIONS

Measurements of the magnitude of the linear dichroic effect created by alignment of SWNTs in an applied electric field have shown that the undesired effect of induced dichroism, on previous experiments intended to measure the Kerr effect,[15] is a minor influence. There was an error of a factor of 2 in the birefringence and Kerr coefficients as reported in that work, and the value for Kerr coefficient given in that work is otherwise correct within 18%. This $\times 2$ error has arisen due to an error of a factor 2 in an equation relating the transmission to the birefringence in that paper.

The dichroic Kerr coefficient has been found to be $K_D = 1.58 \times 10^{-12}\ \mathrm{m}^2\ \mathrm{V}^{-2}$ and from this the polarizability parallel to the axis of the set of nanotubes giving rise to the induced dichroism was found to be $\alpha_{//} = 2.39 \times 10^{-30}\ \mathrm{m}^2$. The polarizability will be dependent on the length of the SWNT, and this value of polarizability is an average value representing the mean length of the SWNTs responsible for the effect. By using the classical model for the polarizability of a metallic cylinder this mean length could be inferred. It was found to be $\bar{L} \approx 0.64\ \mu$m, a value eminently consistent with the SWNTs used in these experiments whose length lies between 0.5 and 2 μm.

This work has not reported on the time dependence of the growth of the dichroism after the application of the electric field, neither has it commented upon the decay of the dichroism once the electric field is terminated. The growth of the dichroism is well fitted by a single exponential in, for example, Figs. 2 and 3. The reasons for this and information on the local viscosity of the suspending medium are discussed at length in part II of this series.[27] The decay of dichroism after cessation of the electric field is more complicated because of the polydisperse nature of the sample. It will be used in future to obtain a length distribution for SWNTs after some detailed analysis.

Finally, it is clear from the magnitude of the experimental polarizability that the role of semiconducting SWNTs in the dichroic effect is negligible.

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