Bimolecular recombination on carbon nanotubes

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By using a suspension of single-walled carbon nanotubes in an applied electric field and measuring transient photoinduced currents the problem of contacting nanotubes in charge transport studies is circumvented; basic electronic transport properties are thus studied. It is observed that the peak photocurrent excited by a mode-locked laser pulse has a sublinear dependence on light intensity. Careful measurement of these phototransients has allowed a fit of the intensity dependence of the peak photocurrent to a bimolecular recombination model developed for the one-dimensional semiconductor that the nanotubes represent. Application of the model allows the determination of some microscopic transport properties. This has been done as concentration, electric field and excitation wavelength are varied.

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I. INTRODUCTION

The discovery of carbon nanotubes by Sumio Iijima[1] excited a great deal of interest in these materials in the decade that followed. Excitement has been generated by the potential to use these novel materials in the emerging field of nanoelectronics. Since the creation of single walled carbon nanotubes (SWNT's) and their reliable production in 1993, experimentalists have worked hard to verify the many novel properties of these one-dimensional (1D) materials that have been predicted by theorists such as the formation of a Luttinger liquid[2] and ballistic conduction.[3] In this study we are interested in understanding the electronic transport properties of SWNT's and use a technique previously developed and described by us[4] to study transient photocurrents induced on a suspension of such nanotubes. Such studies of photoconductivity on SWNT's are surprisingly rare. Previous work includes a study of dc photoconductivity and photoaction spectra of SWNT films[5] and pulsed photoconduction of films[6,7] along with measurements of the effect of illumination on SWNT FET's.[8]

The axial mobility, μ, of carriers on SWNT's has been inferred from measurements of transconductance on SWNT field effect transistor FET's and found to be as high as 10^5 cm^2 V^{-1} s^{-1}.[9]

We add significantly to the understanding of transient photoconductivity in the present work where we show that bimolecular recombination is an extremely effective process on these 1D SWNT's. We present results showing the dependence of the photocurrents on light intensity on suspended, comparatively isolated nanotubes (when compared to the films heretofore studied by others). We show that the peak photocurrent after a 25 ps laser pulse increases sublinearly with light intensity. This sublinearity is modeled in terms of bimolecular recombination and the experimental results are fitted to the model leading to the retrieval of a number of microscopic parameters.

II. EXPERIMENT

The nanotubes used were synthesized by the arc discharge method and were obtained from Carbolex. They have a diameter of 1.4 ± 0.2 nm. Their length is ill defined but the longest are in the order of microns in length. They are initially dispersed in water, using the surfactant sodium dodecyl sulphate (SDS) in order to break up the SWNT ropes. They are then dried and suspended in an electrically and optically inert hydrocarbon oil supplied by Brookfield as a viscosity standard (standard No. B2000) using a sonic probe to homogenize the suspension.

The experiment is performed by holding the suspension of SWNT's in a 50 Ω coaxial cell connected to a voltage supply and to a 3 or 5 GHz digitizing oscilloscope (DSO) via high frequency 50 Ω cables and a 50 Ω load resistor at the DSO. The whole system forms an integrated 50 Ω architecture which reduces signal distortion.[4] A 25 ps laser pulse at 1064 nm from a mode-locked Nd:YAG laser has been used to excite the SWNT suspension in the coaxial cell via a quartz rod introduced into the cell. Also used was a 6 ns laser pulse from an optical parametric oscillator (OPO) when wavelength variation was required. The light pulse excites electron-hole pairs across the energy gap of the semiconducting nanotubes and the carriers separate in the applied electric field. The charge separation and subsequent drift gives rise to a transient photocurrent which induces a displacement current in the external circuit displayed as a voltage across the 50 Ω input resistance of the DSO. The inner electrodes of the coaxial cell were 5.2 mm in diameter with a variable gap, D, of typically 1 mm between them that contained the nanotube suspension. The tendency of the SWNT's to align in a dc electric field forming filaments over time would lead to short circuiting of the cell. Therefore the high voltage of up to 3 kV was applied as a voltage step of 40 μs duration. The light pulse was timed to arrive 10 μs after the application of the voltage step. The geometry and experimental arrangement have been described in greater detail elsewhere.[4]

III. RESULTS

Figure 1 shows a typical transient photocurrent generated on a suspension of nanotubes of concentration $C_T = 1.12 \times 10^{-3}$ by weight fraction in oil. The dependence of the peak photocurrent on the number of photons absorbed is shown in

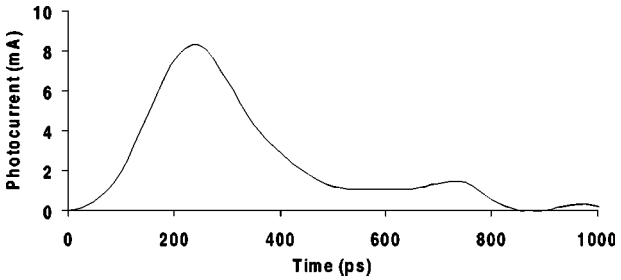

FIG. 1. A typical photocurrent transient generated in a SWNT suspension by the 25 ps, 1064 nm laser pulse from a ND:YAG laser and displayed on a 5 GHz DSO. The applied field was 2.7 MV m^{-1}.

Fig. 2 for a series of applied electric fields. The dependence is found to be sublinear at all fields. The data was obtained using a 25 ps light pulse at 1064 nm from a mode-locked Nd:YAG laser. By measuring the transmission of the laser light through a 2 mm optical cell containing nanotubes in suspension, the fraction of absorbed photons was found as a function of nanotube concentration to be

$$\frac{N_{\mathrm{ph}}}{N_0} = 1430 \times C_T, \tag{1}$$

(Ref. 4) where C_T is the nanotube concentration as a weight fraction, N_0 is the number of photons incident and N_{ph} is the number of photons absorbed. Equation (1) has been used in Fig. 2 to find the number of photons absorbed.

Similar results to those of Fig. 2 were obtained in a series of experiments where the concentration was varied, as shown in Fig. 3.

Using an OPO with a 6 ns pulse the light intensity dependence of the peak photocurrent was established at a series of wavelengths in the near-infrared. These results are shown in Fig. 4.

IV. RECOMBINATION MODEL

The sublinearity found in Figs. 2–4 strongly suggests that bimolecular recombination is playing a role in limiting the magnitude of the photocurrent. Previous workers[7] have seen this effect in nanotube films but have not attempted a serious explanation. In order to model this behavior we consider the

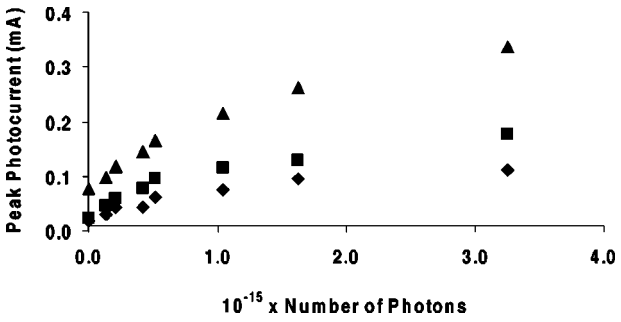

FIG. 2. Dependence of the peak photocurrent on the number of photons incident on the sample shown as the electric field is varied. ▲, $E=2.68$ MV m^{-1}; ■, $E=1.5$ MV m^{-1}; ◆, $E=1.0$ MV m^{-1}. The sample weight fraction was $\mathbf{C}_T=2.2\times10^{-4}$.

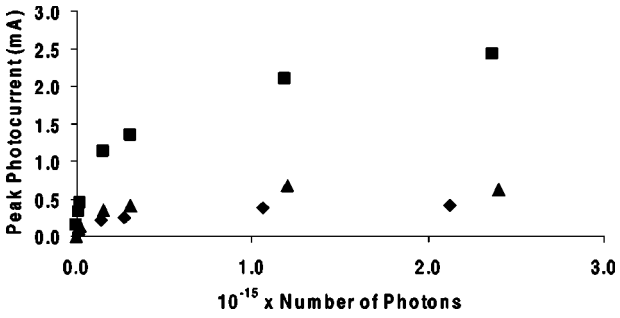

FIG. 3. Dependence of the peak photocurrent on the number of photons incident on the sample as the nanotube weight fraction is varied. ■, $C_T=3.0\times10^{-4}$; ▲, $C_T=1.61\times10^{-4}$; ◆, $C_T=0.81\times10^{-4}$. The applied field was 2.7 MV m^{-1}.

situation depicted in Fig. 5. Figure 5(a) cartoons the creation of one photogenerated electron-hole pair on a nanotube. The nanotube of length L is suspended with its axis in general making some arbitrary angle with the electric field. We assume here that the angle is 0 deg. One end of the tube is at $x=0$ and the other at $x=L$ and the pair is created at $x=x_1$. The electron moves towards $x=L$ and the hole towards $x=0$, both stopping at the nanotube ends. It is easy to show from electrostatics that the hole with charge $+e$ moving a distance x_1 induces a charge

$$Q_h = +e\frac{x_1}{D} \tag{2a}$$

and the electron induces a charge

$$Q_e = +e\frac{L-x_1}{D}, \tag{2b}$$

and, so, the total charge induced is

$$Q = Q_e + Q_h = +e\frac{L}{D}. \tag{2c}$$

In Eqs. (2a)–(2d), D is the interelectrode separation. Now consider the situation in Fig. 5(b) when a higher light intensity is used to generate two carrier pairs on one nanotube at positions x_1 and x_2. Suppose that the probability of bimolecu-

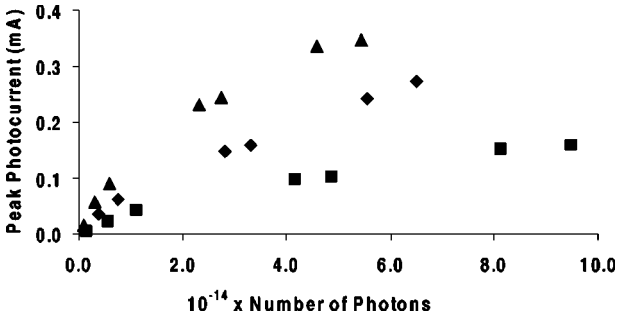

FIG. 4. Dependence of the peak photocurrent on the number of photons incident on the sample shown as the excitation wavelength is varied. ■, λ=1700 nm; ◆, λ=1600 nm; ▲, λ=1300 nm. The applied field was 2.7 MV m^{-1} and the nanotube weight fraction was $C_T=2.2\times10^{-4}$.

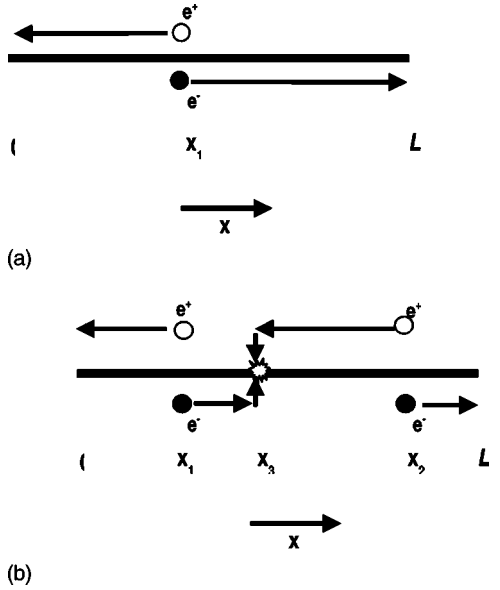

FIG. 5. (a) A cartoon of a single electron-hole pair creation and separation in a SWNT suspended in an electric field E created by two electrodes separated by a distance D. As the carriers separate to the ends of the tube a charge Q is induced in an external circuit. (b) There are now two electron-hole pairs created on a single tube but the same charge Q is measured in the external circuit.

lar recombination upon electron-hole encounter is unity and that this encounter occurs at x_3 somewhere between x_1 and x_2. We find the total induced charge by addition of the contributions of the four carriers as follows:

$$Q = +e\frac{x_1}{D} + e\frac{x_3 - x_1}{D} + e\frac{x_2 - x_3}{D} + e\frac{L - x_2}{D} = e\frac{L}{D}. \quad (2d)$$

From the point of view of an experimentalist measuring the photocharge/current induced in an external circuit as a result of these two different microscopic events, the effect of the creation of two pairs is identical to that of one pair and one of the two absorbed photons is effectively wasted if the probability of bimolecular recombination upon encounter on the tube is unity. The result of Eq. (2d) can be extended straightforwardly for the general case of n carrier pairs on a nanotube. More generally, when the tube is at an angle θ to the applied electric field, a distance L_E representing the projected length of the tube in the field direction must be used in place of L in Eqs. (2a)–(2d). For the ensemble of tubes we are using in these experiments the average projected length, $\langle L_E \rangle$, for a random distribution of angles must be used. L could equally well be the average separation between Shockley Read recombination centers or deep traps/defects on a nanotube. It is straight forward to show that $\langle L_E \rangle = L/2$ for the case of the random alignment distribution.[10]

We may make this more quantitative by considering how many tubes have one or more electron hole pairs as the light intensity is increased by considering the probability, Pdx, of carrier pair creation on any tube within a length dx,

$$Pdx = \eta\phi\rho dx, \quad (3)$$

where ρ is the probability of excitation per unit length, η is the probability of absorption leading to exciton formation, and ϕ is the probability of dissociation of that exciton into an electron-hole pair, a quantity that is often field dependent and frequently described within the Onsager framework of ion dissociation/geminate recombination.[11]

$$\rho = \frac{N_{\mathrm{ph}}}{N_T L}, \quad (4)$$

where N_{ph} is the number of absorbed photons, N_T is the number of nanotubes *within the excitation volume*, and L the average tube length or interdefect separation. The probability of no carrier pair within segment dx is then given by

$$dP^0 = 1 - \eta\phi\rho dx. \quad (5)$$

The probability of there being no excitation on a tube is therefore

$$P^0 = (1 - \eta\phi\rho dx)^{L/dx} = \exp(-\eta\phi\rho L), \quad (6)$$

and the probability that a tube has one or more excitations is given by

$$P^E = 1 - P^0 = [1 - \exp(-\eta\phi\rho L)]. \quad (7)$$

Each of these tubes with any number of free carrier pairs as demonstrated previously will contribute one unit of photocurrent i_P to the overall peak signal irrespective of the number of excitations and the current is then

$$I_p(N_{ph}) = i_P P^E, \quad (8)$$

where i_P will depend on whether the electronic response time, τ_e, of the measurement system is greater than or less than the lifetime of the photocurrent, i.e., whether we are in charge (integrating) or current measuring mode, respectively.

Bringing together Eqs. (4), (7), and (8) we have a dependence of the photocurrent on photons absorbed of the form

$$I_P(N_{ph}) = i_P N_T[1 - \exp(-\eta\phi\rho L)] = i_P N_T\left[1 - \exp\left(-\eta\phi\frac{N_{\mathrm{ph}}}{N_T}\right)\right], \quad (9)$$

It has been previously demonstrated in similar experiments[4] that the response time $\tau_e = 150$ ps (for 5 GHz DSO) and $\tau_e = 180$ ps (for 3 GHz DSO) when the effect of the 50 Ω coaxial cell is included.

We find i_P for the two modes of detection.

(i) **Current mode**. In current mode the voltage on the DSO will follow the photocurrent in real time. The photocurrent will be the ratio of charge created to the carrier lifetime. The unit of peak photocurrent *per excitation per tube* is then given by

$$i_P = \frac{e\langle L_E \rangle}{D\tau}, \quad (10)$$

and the peak signal voltage is

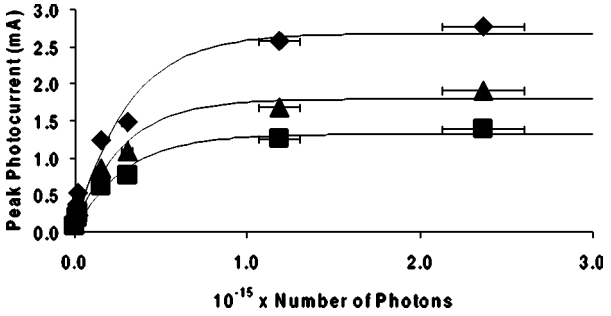

FIG. 6. Data similar to that of Fig. 2 fitted to Eq. (13) as E is varied. ◆, $E=2.68$ MV m^{-1}; ▲, $E=1.5$ MV m^{-1}; ■, $E=1.0$ MV m^{-1}.

$$\nu_P = I_P R_L = \frac{e\langle L_E\rangle R_L}{D\tau} N_T \left[1 - \exp\left(-\eta\phi \frac{N_{\rm ph}}{N_T}\right)\right], \quad (11)$$

where the load resistor $R_L=50\ \Omega$ and $\tau(>\tau_e)$ is the shorter of the laser pulse width or carrier lifetime on the tube.

(ii) **Integrating mode**. Integrating mode, where $\tau_e > \tau$, is the usual case in these experiments due to high axial electron mobilities and the consequent short lifetime. When the Nd:YAG laser is used, the laser pulse width will also ensure that this is the case. Here the photocurrent is integrated over the response time and a charge $Q=I_P\tau_e$ will determine the measured voltage

$$\nu_P = I_P R_L = \frac{Q}{\tau_e} R_L = e\frac{\langle L_E\rangle}{D}\frac{1}{\tau_e} R_L N_T \left[1 - \exp\left(-\eta\phi \frac{N_{\rm ph}}{N_T}\right)\right]. \quad (12)$$

V. DISCUSSION

Figures 6–8 show the data of Figs. 2–4 fitted to Eq. (12) recast as

$$\frac{\nu_P}{R_L} = I_P = I_\infty[1 - \exp(-kN_{ph})]. \quad (13)$$

The data show a good fit to the proposed model of bimolecular recombination. From the fits, values of the parameters

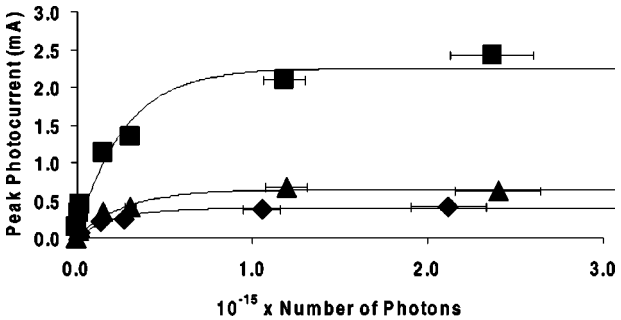

FIG. 7. Data similar to that of Fig. 3 fitted to Eq. (13) as C_T is varied. ■, $C_T=3.0\times10^{-4}$; ▲, $C_T=1.61\times10^{-4}$; ◆, $C_T=0.81\times10^{-4}$.

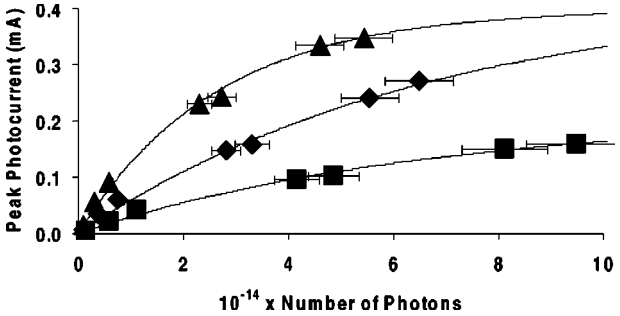

FIG. 8. Data similar to that of Fig. 4 fitted to Eq. (13) as λ is varied. ■, λ = 1700 nm; ◆, λ = 1600 nm; ▲, λ = 1300 nm.

$$I_\infty = e\frac{\langle L_E\rangle}{D}\frac{1}{\tau_e} N_T \quad (14)$$

and

$$k = \frac{\eta\phi}{N_T} \quad (15)$$

have been extracted as a function of electric field, E, and nanotube concentration C_T.

(i) The results of Fig. 9 show that I_∞, the value to which I_P tends at high light intensity, is found to be linear in electric field. By comparing Eq. (14) we see that this requires that some quantity on the rhs is linear with electric field. This is a surprising result as first examination would lead us to expect no dependence of I_∞ on electric field. Further consideration leads us to the interesting speculation that the value of the average projected length of a nanotube in the electric field direction, $\langle L_E\rangle$, increases in proportion to the electric field. Because of the nature of SWNT's it is expected that they are highly polarisable. Calculations have borne this out, metallic tubes being more so than semiconducting tubes, but both with high polarizabilities.[12] In these experiments the electric field has been on for 10 μs before the photocurrent is excited. The results presented here, within the context of the recombination model, imply that this is enough time to partially align the nanotubes in the field direction thus increasing $\langle L_E\rangle$. Such a mechanism is sufficient to explain a factor of two increase in I_∞ as the tubes go from random alignment to fully aligned. The results of Fig. 9, however, indicate that at least a factor of 3 increase is needed. To achieve a greater

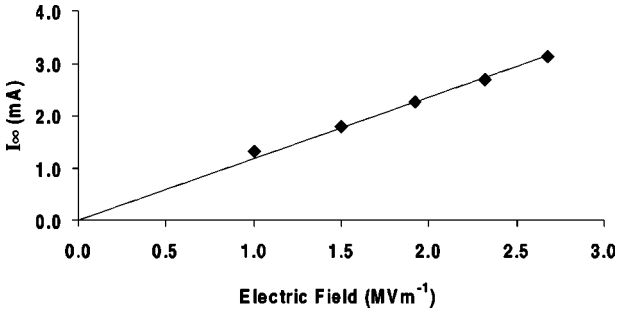

FIG. 9. The value of i_∞ as a function of electric field found from the fits of Fig. 6.

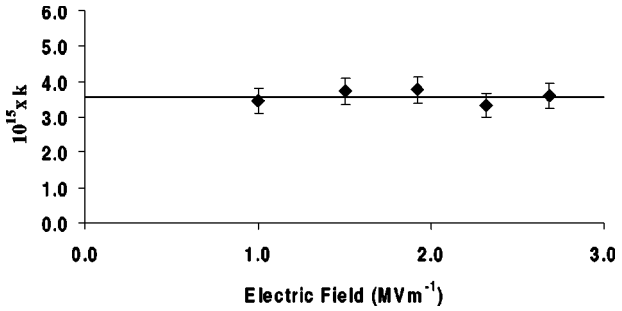

FIG. 10. The value of k as a function of electric field found from the fits of Fig. 6.

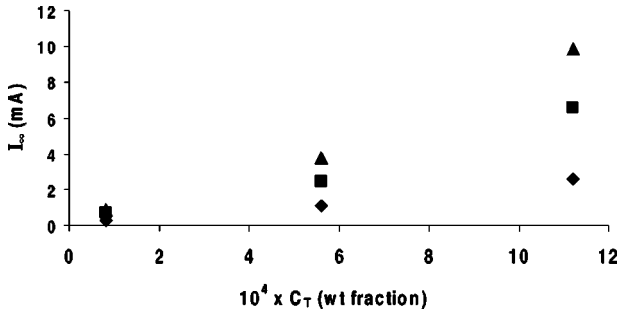

FIG. 11. The value of i_∞ as a function of nanotube concentration found from the fits of Fig. 7 ▲, $E=2.68$ MV m^{-1}; ■, $E=1.71$ MV m^{-1}; ◆, $E=0.75$ MV m^{-1}.

increase requires that light is preferentially absorbed by tubes aligned perpendicular to the field direction when the field is low, thus giving a photoelectric effect that is much smaller than for the random case (all orientations absorbing with equal probability). This would be the case if, for example, the laser light was polarized to a large degree perpendicular to the applied electric field and thus absorbed selectively by tubes that are also perpendicular to the field. These tubes having a very small $\langle L_E \rangle$ will give a negligible effect. As the tubes align with the electric field, the residual parallel polarization of the light becomes important as it is selectively absorbed by tubes aligned parallel to the field. In this way, the effect of electric-field-induced alignment of the nanotubes may allow for a mechanism for giving an electric-field-dependent I_∞. The Nd:YAG laser is originally polarized perpendicular to the electric field direction. Before reaching the sample it is coupled into the sample cell by focusing into a short 3 cm stub of a 2 mm diameter quartz rod. This procedure has been measured to have a negligible effect on the polarization of the laser light which continues to be effectively polarized perpendicular to the applied electric field.

(ii) The value of k, as shown in Fig. 10, is independent of the electric field, demonstrating that the probability of carrier pair separation, ϕ, is independent of the electric field. For organic materials such as anthracene it is well established that the value of ϕ is field dependent.[13] Indeed, for one-dimensional organic materials such as polymers, ϕ is strongly field dependent, being linear in field and tending to zero at zero applied field,[14,15] The main reason for this field dependence is that these typically low mobility organic materials form strongly bound molecular excitons that require an electric field to aid in the dissociation. That this is not found to be the case here is initially surprising but indicates that these high mobility materials have more in common with inorganic semiconductors such as silicon where strongly bound excitons are not produced as an initial photoexcitation event.

(iii) Figure 11 shows the variation of I_∞ as a function of nanotube concentration, C_T, as the electric field is varied. This may be compared with the prediction of Eq. (14) recalling that here N_T refers to the number of nanotubes in the excitation volume whose relation to C_T may not be one of exact proportionality. The expected rise of I_∞ with C_T is nevertheless found.

(iv) More interestingly, in Fig. 12, the variation of k^{-1} with C_T is shown. This shows good agreement with the prediction of Eq. (15). The accurate variation of C_T is a difficult task to achieve and great care was taken to obtain the raw data, such as that of Fig. 3, from which the data of Figs. 7, 11, and 12 are derived. We described earlier the technique used to get the nanotubes into suspension. The photoelectric experiments are then carried out within a couple of hours before the initial homogeneity of the suspensions begins to degrade. However, we feel that any very small departures from linearity as seen in Figs. 11 and 12 are explicable in terms of the difficulty in obtaining accurate concentrations and we comment on them no further.

The quantity N_T is poorly known, however it is possible to obtain some numerical information regarding these experiments and the model. Examination of Eqs. (14) and (15) indicates that the quantity N_T may be cancelled by taking the product $kI_\infty = e(\eta\phi/\tau_e)(\langle L_E \rangle / D)$. This will be linear in the electric field and at a typical field of $E=2.68$ MV m^{-1} we find $kI_\infty = 1.1 \times 10^{-17}$ A. With a knowledge of $\tau_e = 150$ ps, the quantity $\eta\phi\langle L_E \rangle = 1.03 \times 10^{-11}$ m has been determined. It is common in photoconduction experiments to find that the quantum yield, $\eta\phi$, is found in combination with the carrier range S. In these experiments, if the carriers do not separate to the ends of the tube as assumed, but some distance S until they undergo deep trapping, we must replace $\langle L_E \rangle$ in all equations with the average carrier range projected onto the field direction $\langle S_E \rangle$. The surprisingly small value for $\eta\phi\langle S_E \rangle \approx 10^{-11}$ m may be reinterpreted in two limiting cases:

(a) If we assume that $\langle S_E \rangle = \langle L_E \rangle \approx 10^{-6}$ m, then the quantum yield of 10^{-5} is extremely small. Such a small value for the yield is difficult to understand in terms of strongly

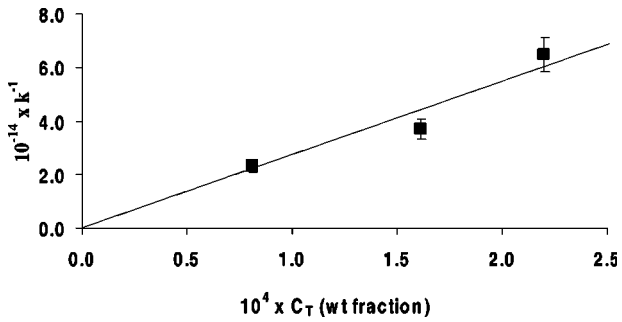

FIG. 12. The reciprocal of k as a function of nanotube concentration found from the fits of Fig. 7.

coupled electron-hole pairs in the absence of evidence of field assisted dissociation.

(b) The alternative limit would assume a quantum yield of 1 and the value of $\langle S_E \rangle$ would be 10^{-11} m. Again such a small value is unphysical and cannot be allowed. For the model that produced the number to be self-consistent there must be a possibility that electrons and holes from different pairs on the same tube meet, thus providing some constraint on how small $\langle S_E \rangle$ may be.

We are left with the conclusion that the value of $\langle S_E \rangle$ must lie somewhere between these two extremes and clearly alternative (a) must be more approximate to the truth in order for the model to work in its own terms. Unfortunately we are unable to comment further at this time..

VI. CONCLUSIONS

We have presented results on transient photoconduction on single-walled carbon nanotubes in suspension, a technique recently developed by us. The behavior of the amplitude of the photocurrent transient as light intensity is varied has led us to develop a one-dimensional bimolecular recombination model which fits the observations well.

Within this model we find an unexpectedly low carrier yield: range product suggestive of either strong geminate recombination and low concomitant quantum yield or of defective nanotubes and a consequently reduced range. To find the density of the defects requires an independent experiment to measure the carrier yield. One experiment that suggests itself is to try and cut the nanotubes, using acids and ultrasinication, into nanopipes of length $L_P < S$, when the carrier range would be identical to the pipe length. This is a nontrivial experiment to perform in particular because methods of creating nanopipes would themselves almost certainly introduce defects.

Another unexpected phenomenon that suggests itself out of the model developed is that the nanotubes must be aligning with the applied electric field and the degree of alignment is proportional to the electric field. Such alignment leads to an increase in the photoelectric effect per pair created. Given the mobility of the nanotubes within our experimental arrangement and their high polarizability this speculation is eminently plausible and is now the subject of an ongoing research effort as many experiments suggest themselves to lend support to this suggestion or otherwise. It is hoped to report on the outcome of these experiments in the future.

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