Unusually Large Franz-Keldysh Oscillations at Ultraviolet Wavelengths in Single-Walled Carbon Nanotubes

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Semiconducting single-walled carbon nanotubes (SWNT) have attracted significant attention recently due to many unique properties and the potential for new nanophotonic applications [1]. They possess sharp singularities in their density of states as a consequence of one-dimensional (1D) quantum confinement leading to strong and discrete absorption maxima throughout the ultraviolet (UV), visible, and near-infrared (IR) regions of the electromagnetic spectrum [2,3]. This confinement also leads to theoretical predictions of large exciton binding energies, later confirmed using two photon photoluminescence spectroscopy [4,5]. Franz-Keldysh (FK) oscillations, in particular, are calculated [6] to be quite strong for semiconducting SWNT near the first and second band edge, a property of importance for electro-optical applications. In pioneering work several decades ago, Franz and Keldysh predicted that photo-excited electrons could tunnel into an otherwise classically forbidden energy gap under the influence of an electric field, modifying the linear optical properties of bulk semiconductors near the absorption band edge [7,8].

Modulation spectroscopy uses this effect experimentally to understand highly localized electric fields that develop at semiconductor interfaces [9,10]. Nanowires and nanotubes can amplify such fields manyfold by virtue of their geometry. Hence, there is interest in using phenomena such as the FK effect to understand how electric fields can be manipulated on the nanometer scale, although to date, no experimental observation of the effect has been reported for any of the carbon family of nanomaterials.

In this Letter, we report the first observation of FK oscillations for semiconducting SWNT films supported on fused quartz substrates, although the effect is strongest for excitonic states much higher than those near the band edge. Electroabsorption susceptibilities in the UV region are more than $10^3$ larger than the highest values reported for typical semiconductor systems, such as III-V semiconductors [9] and semiconductor-doped glasses [11]. We make use of recent progress [12] in the enrichment of metallic and semiconducting SWNT to show that the confinement energy correlates with the average band gap for semiconducting SWNT in the film. The unusually large susceptibilities arise from a subpercolated network of metallic SWNT that enhances the local electric field.

We report large electroabsorption susceptibilities in the ultraviolet region for single-walled carbon nanotubes (SWNT) supported on quartz that are approximately $10^3$ larger than the highest values reported to date for any system. The oscillatory behavior is described using a convolution of Airy functions in photon energy ascribing the effect to Franz-Keldysh oscillations. The metallic and semiconducting SWNT composition is varied, and it is shown that the confinement energy correlates with the average band gap for semiconducting SWNT in the film. The large susceptibilities arise from a subpercolated network of metallic SWNT that locally concentrates the field gradient.

Application of electric fields as low as 10 V/cm across semiconducting SWNT films supported on quartz resulted in measurable electroabsorption changes in the UV region between 3.5 and 6.5 eV as shown in Fig. 1(a) (see Ref. [13] for experimental details). The modulation consists of alternating positive and negative deviations from the absorption background clearly observed in the absorption coefficient for experimental details. The modulation consists of alternating positive and negative deviations from the absorption background clearly observed in the absorption coefficient difference using $\Delta \alpha = \alpha(V) - \alpha(0)$. In the classical description of the FK effect, the 1D carbon nanotube electronic wave functions tunnel into the forbidden energy gap at the carbon-quartz interface under the influence of the electric field, creating an absorption tail at energies below a confinement energy $E_{\text{c}, \text{FK}}$ [7,8], and a characteristic function involving the Airy function, $Ai$, and its derivative, $Ai'$ [9] according to

$$\Delta \alpha = B\left[\pi \left( Ai^2(\xi) - \xi A^i(\xi) - \sqrt{-\xi} H(-\xi) \right) \right] = F(\xi)$$

$$\xi = \left( E - E_{\text{c}, \text{FK}} \right) / h \theta,$$

where $H$ is the unit step function, $E$ is the photon energy, $E_{\text{c}, \text{FK}}$ is the FK confinement energy, and $h \theta$ is the electro-optic energy which depends on the electric field ($F$) and the carrier reduced mass ($\mu$) given by

$$(h \theta)^3 = e^2 h^2 F^2 / 2 \mu.$$

Both the period and the amplitude of the oscillations are...
quantitatively described [see Fig. 1(b)] by Eqs. (1)–(3) assuming a confinement energy of 5.35 eV, near the midpoint between the average IR band gap of the SWNT film (1 eV) and the insulating band gap of the quartz substrate (9 eV) [see Fig. 1(c)].

To confirm this interpretation, we varied the average band gap of the SWNT film using a recently developed method [12] to separate and enrich the semiconducting and metallic composition of the films (see Ref. [13]). These films are labeled according to the average band gap and the first standard deviation of the semiconducting distribution [14–17], as summarized in Table I. SF-1 films contained SWNT with an average band gap energy of 1.15 ± 0.16 eV while SF-2 contained 1.22 ± 0.10 eV. These were compared to a purely (6,5) semiconducting film SF-3 [18] and pristine (unseparated) film SF-4 control 1.08 ± 0.40 eV mean. The same sample SF-5 was completely functionalized with 4-hydroxyphenyl groups to examine how carrier scattering centers influence the modulation (no separation).

The average optical band gap energy ($\bar{E}_{11}$) of the ensemble of semiconducting SWNT in the film is calculated as

$$\bar{E}_{11} = \frac{\sum_{(n,m)} W(n,m) E_{11}^{(n,m)}}{\sum_{(n,m)} W(n,m)},$$

where $W(n,m)$ is the absorption spectral weight of the $(n, m)$ semiconducting SWNT present in the film after separation summed over all $N$ species [14–17].

The electroabsorption spectra of the ensemble film can be calculated using Eqs. (1)–(3) by assuming a linear optical response ($\Delta \alpha_{\text{tot}}$) with $f^{(n,m)}$ as the normalized abundance of species $(n, m)$ [14–17]:

$$\Delta \alpha_{\text{tot}} = C \sum_{(n,m)} F^{(n,m)} f^{(n,m)},$$

In practice, only two dominant terms in Eq. (5), for the first and second interband transitions of the most abundant SWNT, are necessary to completely describe the experimentally observed oscillations. These are characterized by two confinement energies $E_{g,\text{FK}}^{1}$ and $E_{g,\text{FK}}^{2}$. Parameters from model regression for films spanning a range in composition appear in Table I.

It is important to note that independent of the number of terms retained, the dominant confinement energy is independently estimated from the electroabsorption data itself as the energy marking the transition between the absorption tail and the start of the oscillations. Both of the confinement energy parameters ($E_{g,\text{FK}}^{1}$ and $E_{g,\text{FK}}^{2}$) clearly correlate with the average band gap energy ($E_{11}^{\text{ES}}$) of the film, as shown in Fig. 2. This proportionality implicates electronic wave functions in a higher order van Hove singularity (approximately proportional to $E_{11}^{\text{ES}}$) as tunneling into the insulating band gap of the quartz substrate ($E_{gs} \approx 9$ eV). As noted earlier, the values of $E_{g,\text{FK}}$ are approximately 5 times $E_{11}^{\text{ES}}$ but half of the band gap energy of the insulating substrate, consistent with the model depicted in Fig. 1(c) [19]. At the interface, considerable band bending is expected to occur, leading to surface states of intermediate energy and the observed confinement [20]. It is expected that SWNT possessing one or more van Hove singularities ($E_{11}^{\text{S}}, E_{22}^{\text{S}}, E_{33}^{\text{S}},$ or $E_{44}^{\text{S}}$ for the semiconducting SWNT or $E_{11}^{M}$ of the metallic SWNT) below the band gap of the quartz substrate contribute most strongly to the electroabsorption effect. The oscillations are most visible in the UV region, while theory predicts that lower-energy transitions should exist [6]. The effect may be most prominent at higher energies due to the relatively small energy

<table>
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<tr>
<th>Sample</th>
<th>Average band gap energy (eV)</th>
<th>$E_{11}^{\text{ES}}$ (eV)</th>
<th>$E_{g,\text{FK}}^{1}$ (eV)</th>
<th>$E_{g,\text{FK}}^{2}$ (eV)</th>
<th>$F_{\text{eff}}$ (V/cm)</th>
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<tr>
<td>SF-1</td>
<td>1.15 ± 0.16</td>
<td>1.15</td>
<td>5.37</td>
<td>5.91</td>
<td>4.5 × 10^9</td>
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<tr>
<td>SF-2</td>
<td>1.22 ± 0.10</td>
<td>1.22</td>
<td>5.39</td>
<td>5.91</td>
<td>4.2 × 10^9</td>
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<tr>
<td>SF-3</td>
<td>1.26</td>
<td>1.26</td>
<td>5.39</td>
<td>5.91</td>
<td>4.3 × 10^9</td>
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<tr>
<td>SF-4</td>
<td>1.08 ± 0.40</td>
<td>1.08</td>
<td>5.35</td>
<td>5.87</td>
<td>5.0 × 10^9</td>
</tr>
<tr>
<td>SF-5</td>
<td>1.08 ± 0.40</td>
<td>1.08</td>
<td>5.37</td>
<td>5.89</td>
<td>4.0 × 10^9</td>
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spacing between distinct SWNT in this region. The Airy function oscillations from distinct species may constructively interfere for closely spaced transitions, whereas a larger spread in energies may lead to destructive interference. It remains to be seen if such FK oscillations are apparent in the lower-energy region of the spectrum.

Several other wide band gap semiconductors such as GaN-[21,22] and ZnO-based [23] systems demonstrate modulation in the UV region described as a broadening and shifting in energy of the unconfined exciton with externally applied electric fields. The origin of the modulation is not completely understood [21–23]. Dow and Redfield [24,25] modified the classical FK effect for electron-hole interactions, although these results do not account for 1D quantum confinement in a nanotube. It is well known that the semiconducting SWNT have large exciton binding energies. In an electric field, the excitonic wave functions overlap with the band-to-band continuum transitions below the insulating band gap of the quartz substrate as they tunnel into the forbidden energy gap at the carbon-quartz interface. This mixing of excitonic wave functions causes a growth in spectral weight of the absorption, enhancing the observed FK effect [6,9]. From numerical simulations of SWNT excitons in an electric field, we assign the uniformly positive peaks at 4–4.5 eV as due to a predicted field-induced absorption at these energies [26].

Lastly, we address the origin of the unusually large susceptibility values. Surprisingly, in our experiments, the applied electric fields up to 160 V/cm are several orders of magnitude smaller than typical values (~10⁶ V/cm) employed in the literature to realize such phenomena [9,11,21–23]. Glasses containing semiconductor microcrystallites [11] and III-V semiconductors [9] reported in previous studies demonstrated FK oscillations, but large high electric fields (MV/cm) were needed to overcome typical electroabsorption susceptibility values. We find that increasing the concentration of metallic to semiconducting content increases the amplitude of peak intensities of oscillations. As a measure of this enhancement, the two highest intensity peaks at 5.7 and 6.2 eV in the modulation spectra were plotted as a function of applied electric field in Fig. 3(a). The slope of this graph yields the FK susceptibility for each oscillation [d(Δα)/dF]. We note that this quantity increases with increasing conductance [see Fig. 3(b)]. When semiconducting SWNT are enriched and large band gap semiconducting content of SWNT is higher (see Table I), the film conductance decreases due to lower content of metallic SWNT. The pristine film (SF-4) contains the highest metallic content and possesses the largest susceptibility (3.8 × 10² V⁻¹). In random networks of SWNT, the FK effect is apparently limited by the extent of connectivity between metallic pathways. The film necessarily contains a superpercolated network of such pathways which act to extend the electrodes beyond the macroscopic channel distance (dch) into the film and reduce the current path to

![FIG. 3 (color online). (a) Peak intensities of the SWNT films with different ratio of metallic to semiconducting content at the photon energies (PE) of 5.7 and 6.2 eV as a function of applied electric field. (b) Susceptibility of the SWNT films with different ratio of metallic to semiconducting content as a function of conductance. The closed and open symbols represent the susceptibility of the peak at 5.7 and 6.2 eV, respectively, of which the data fits are indicated with the solid and dashed lines, respectively. (c) Schematic illustration for interpreting the role of the metallic SWNT in the film. (d) Time response of the optical modulation of the SF-4 with turning on and off the electric field of 20 V/cm at 5.7 eV. The red dotted line is the best fit to an Arrhenius form.](https://example.com/fig3)
The switching time of a nanoscale optical modulator is limited by the quantum capacitance, \( C_q = \frac{\delta Q}{\delta V_a} \), where \( Q \) is the charge density and \( V_a \) is the local electrostatic potential \([27–29]\). Figure 3(d) plots the transient rise time of optical modulation of the pristine film (SF-4) subjected to an electric field of 20 V/cm, from which an effective capacitance can be calculated \( C/C_q = 6 \times 10^3 \). The capacitance of the system is apparently limited by the parasitic value for devices of this thickness (50 nm for carbon film and 1 mm for quartz substrate). Assuming a linear optical response, the susceptibility increases with a decrease in switching time as device thickness decreases.

In conclusion, unusually large electroabsorption susceptibilities in the UV region for SWNT films supported on fused quartz substrates are identified as FK oscillations. The 1D confined wave vectors from semiconducting SWNT tunnel into the classically forbidden band gap of the quartz substrate, creating a confined interfacial state SWNT tunnel into the classically forbidden band gap of the substrate. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

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To confirm that the observed oscillations arise from the SWNT-quartz interface, electroabsorption of SWNT films prepared on soda-lime glass substrates was also measured for comparison. Here, the band gap energy of the substrate is smaller \( (E_{g,\text{substrate}} \sim 5 \text{ eV}) \) compared to fused quartz substrates \( (E_{g,\text{quartz}} \sim 9 \text{ eV}) \). The observed confinement energy of soda-lime glass, \( E_{\text{conf}} \), is correspondingly red-shifted by about 1 eV (data not shown) and the susceptibility \( |d(\Delta\alpha)/dF| \) is higher \( (1.9 \times 10^3 \text{ V}^{-1}) \).

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[29] In 1D case, the quantum capacitance can be expressed by \( C_q = 2e^2/\hbar v_F \), where \( v_F \) is the Fermi velocity, and is calculated to be \( 4 \times 10^{-8} \text{ F/cm} \) for SWNT.