Optical Absorption and Thermal Transport of Individual Suspended Carbon Nanotube Bundles

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ABSTRACT

A focused laser beam is used to heat individual single-walled carbon nanotube bundles bridging two suspended microthermometers. By measurement of the temperature rise of the two thermometers, the optical absorption of 7.4–10.3 nm diameter bundles is found to be between 0.03 and 0.44% of the incident photons in the 0.4 µm diameter laser spot. The thermal conductance of the bundle is obtained with the additional measurement of the temperature rise of the nanotubes in the laser spot from shifts in the Raman G band frequency. According to the nanotube bundle diameter determined by transmission electron microscopy, the thermal conductivity is obtained.

The electronic, optical, and thermal characterization of individual carbon nanotubes (CNTs) has evolved to an unprecedented level of sophistication. In early work, bulk quantities of nanotubes were measured, yielding ensemble averages of measured properties. Because of the strong chirality dependence of the physical properties of nanotubes, new measurement techniques were developed to characterize this important material on the individual nanotube level. For example, Raman spectroscopy of individual carbon nanotubes has enabled the direct correlation between their physical structure and optical properties. Similarly, combined optical and electronic measurements of individual carbon nanotubes have revealed a striking electron scattering mechanism by nonequilibrium phonon populations. Despite these sophisticated techniques, many of the unique properties of nanotubes still elude us. For instance, their large surface-to-volume ratio strongly affects the ability to absorb and scatter light. Many aspects of this process, including surface recombination and exciton-phonon dynamics, are not well understood.

In a recent publication, an optical method for measuring thermal transport in carbon nanotubes was demonstrated. In this method, a focused laser spot is used to locally heat suspended carbon nanotubes while the resulting temperature rise in the nanotube was measured simultaneously from the Raman G band frequency shift. While this technique provides detailed information of the thermal contact resistance and diffusive/ballistic nature of phonon transport, the amount of optical absorption in the nanotube from the incident laser is unknown. As a result, no quantitative values of the thermal conductivity or the thermal contact resistance could be extracted from the measured spatial temperature profile of the nanotube. A somewhat similar method was applied to suspended, single-layer graphene. While these graphene measurements report exciting results, with thermal conductivity values exceeding those of carbon nanotubes, these results assumed 11–12% laser power absorption by the single atomic graphene layer. Recent measurements of the optical opacity of graphene show that the total optical absorption is actually much less than this value. In this paper, we present a new method for measuring the optical heating in suspended nanostructures directly, without any assumptions on the optical absorption or electron transport.

As a demonstration of this method, we directly measure the optical absorption in individual suspended single-walled carbon nanotube (SWNT) bundles bringing two suspended microthermometers. It was found that between 3.07 × 10⁻⁴ and 4.38 × 10⁻³ of the incident photons were absorbed by 7.4–10.3 nm diameter nanotube bundles in the 0.4 µm diameter laser spot. This measurement also gives the thermal conductance of the bundle from the temperature rise of the
nanotubes in the laser spot, determined from shifts in the G band Raman frequency.

In the experiment, a laser beam is focused on an individual carbon nanotube bundle suspended between two microfabricated thermometers, as shown in Figure 1a. The microfabricated platinum resistance thermometers (PRTs) consist of two adjacent 20 µm × 20 µm low-stress silicon nitride (SiNₓ) membranes, each suspended by six 420 µm long and 2 µm wide SiNₓ beams.3 CNTs are grown by chemical vapor deposition across the two microfabricated thermometers. Details of the fabrication process of the microfabricated thermometers and CNTs are described in a previous publication.3 The temperature dependence of the PRT devices are calibrated in a Linkam THMS temperature controlled stage. A 532 nm Spectra-Physics solid state laser is focused through a 100× objective lens with a numerical aperture of 0.9, producing a beam diameter of 0.4 µm full width at half-maximum (FWHM). A PRIOR ProScan II high-precision microscope stage is used to control the position of the incident laser spot. We focus the laser spot on the center of the carbon nanotube to reduce the unintentional heating of the microfabricated thermometers. The CNTs are aligned with the polarization of the incident laser. The laser power is varied from 300 to 1400 µW.

When the suspended carbon nanotube is irradiated with the focused laser, heat generated at the position of the laser spot will flow toward the two ends of the nanotube at lower temperature. On the basis of the thermal resistance circuit in Figure 1b, the power absorbed in the region of the incident laser spot (\(Q_{\text{CNT}}\)) is equal to the sum of the power detected in both PRTs (\(Q_{\text{PRT,L}} + Q_{\text{PRT,R}}\)). This heat is detected by a small change in the resistance of the PRT with temperature (\(\Delta R(T)\)). The temperature coefficient of resistance of each PRT is calibrated by measuring its four-point resistance in a temperature-controlled stage. Once calibrated, we can convert any changes in the resistance of the PRTs to temperature changes due to heat conduction through the CNT bundles during laser exposure. Figure 1b shows a schematic diagram of the experimental configuration, together with a thermal circuit of the system. Two SR830 DSP lock-in amplifiers are connected to the outer two leads of each PRT with a sinusoidal current of 0.5 µA at a frequency of 200 Hz. The resolution in the resistance is around 1 Ω for a total resistance of approximately 30 kΩ. This corresponds to a heat flow of approximately 0.32 µW, which is much smaller than that created when the laser is incident on the carbon nanotube.

The power absorbed in the nanotube from the incident laser light depends on nanotube chirality, defect density, whether the CNT is an individual nanotube or in a bundle, and whether it has an electronic transition that is resonant with the incident laser energy. We can obtain the temperature of the CNT induced by laser heating from analysis of the Raman spectra, either from the anti-Stokes to Stokes Raman intensity ratio or from the downshift of the phonon bands.24,25 Using the two microfabricated platinum thermometers (PRTs), supporting the suspended CNT at both ends, the temperature gradient can be determined from the temperatures observed in the CNT and the PRTs. Heat losses along the length of the nanotube due to radiation and air molecules are estimated to be 1 order of magnitude smaller than that due to conduction through the bundle.26–29 Hence, the total power generated in the CNT by the incident laser is equal to the sum of the power detected in both PRTs.

Figure 2a shows a CNT bundle suspended across an 11 µm trench. The resistance of the thermometers is measured when the laser is both on and off the CNT in order to subtract any unintentional heating of the PRTs from the Gaussian tail of the incident laser spot hitting the SiNₓ membrane. Accurate values of the resistance changes of both PRTs, solely due to the heat generated in the nanotube, can be obtained by subtracting the change in the resistance of the PRT with the laser spot on and off the CNT, as shown in Figures 2b and 2c. The relation between resistance change
and laser power is obtained from linear fits of these data, yielding values of $5.83 \times 10^3$ and $1.32 \times 10^3 \, \Omega/W$ for left and right thermometers, respectively. This factor of 4 difference in the heat conduction to the two thermometers is likely due to asymmetric thermal contact resistance.

In calibrating the PRTs, Joule heating is used to obtain the thermometer’s resistance-power relation by applying a DC current. This is shown schematically in Figure 3a. In this calibration, heat is also generated in the two leads that supply current to the PRT device. Therefore, we must take into account the Joule heating in each lead ($Q_{\text{lead}}$) and the heat dissipated in the PRT ($Q_{\text{PRT}}$), observed by a four-point measurement. The power dissipated through one of the two leads can be obtained by subtracting the electric power measured by the two-point and four-point measurements of the PRT at elevated direct currents, $Q_{\text{lead}} = (IV_{2p} - IV_{4p})/2$.

Since only half of the Joule heat generated in the leads causes heating in the PRTs and the other half is conducted to the substrate directly, we can write $Q_{\text{PRT}} = IV_{2p} + Q_{\text{lead}}$ for the heat flux into the PRT during this calibration. This relation is derived in detail elsewhere.\textsuperscript{3} Figures 3d and 3e show the change in resistance with heating of the PRT ($\Delta R(Q_{\text{PRT}})$), corrected for the effects of Joule heating in the leads.

The heat generated in a nanotube bundle at a given laser power can be obtained by dividing the change in resistance $\Delta R$ under laser irradiation (Figures 2b and 2c) by the slopes in Figures 3d and 3e. The probability of laser photon absorption in a CNT is revealed by taking the ratio of the slopes in Figures 2b and 2c to the slopes of Figures 3d and 3e. It was found from this procedure that $2.05 \times 10^{-3}$ and $3.92 \times 10^{-4}$ of incident photon energy were conducted to the left and right thermometers, respectively. The total probability of nonradiative photon absorption in the CNT bundle is found by adding these two quantities, which yields $2.44 \times 10^{-3}$. Other samples measured, with diameters between 7.4 and 10.3 nm, exhibited absorption

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**Figure 2.** (a) Scanning electron microscopy image of a SWNT bundle suspended across an 11 µm trench. The circle and square represent the location of laser spot on and off the SWNT, respectively. (b, c) Resistance change with increasing laser power on and off the SWNT for the left and right thermometer, respectively.

**Figure 3.** (a) Schematic diagram of the experimental setup for the PRT’s electrical self-heating calibration. (b, c) Calibration data of the self-heating power plotted as a function of direct current for two-point and four-point measurements of the left and right PRTs. (d, e) Resistance of the left and right thermometers as a function of electric power, corrected for the effects of Joule heating in the leads.

**Table 1.** Data Summary of Four Measured CNT Bundles

<table>
<thead>
<tr>
<th>sample</th>
<th>length of bundle (µm)</th>
<th>bundle diameter (nm)</th>
<th>no. of nanotubes in bundle</th>
<th>absorption probability</th>
<th>resonant Raman intensity (meas at 400 µW, 60 s)</th>
<th>thermal conductance (nW/K)</th>
<th>thermal conductivity (W/(m K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.7</td>
<td>N/A</td>
<td>N/A</td>
<td>$2.4 \times 10^{-3}$</td>
<td>913</td>
<td>1.07</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>14.3</td>
<td>10.3</td>
<td>4</td>
<td>$4.4 \times 10^{-3}$</td>
<td>3521</td>
<td>1.47</td>
<td>253</td>
</tr>
<tr>
<td>3</td>
<td>12.9</td>
<td>7.4</td>
<td>4</td>
<td>$3.1 \times 10^{-4}$</td>
<td>928</td>
<td>2.28</td>
<td>683</td>
</tr>
<tr>
<td>4</td>
<td>12.3</td>
<td>8.2</td>
<td>5</td>
<td>$1.6 \times 10^{-3}$</td>
<td>1050</td>
<td>0.51</td>
<td>118</td>
</tr>
</tbody>
</table>
due to the thermal expansion of the carbon particular, the G band Raman mode downshifts in frequency Raman spectra taken from the scattered laser light. In absorption. The total thermal resistance of the carbon to the end of the CNT per unit laser power by the optical

temperature gradient between the incident laser spot and the measurement device. The experimental results on optical

determination of the heat generated by the nonradiative absorption of light for suspended carbon nanotube bundles. Values for this absorption probability lie in the range from $3.07 \times 10^{-4}$ to $4.38 \times 10^{-3}$ for 7.4–10.3 nm diameter nanotube bundles. This is a direct measurement of the optical absorption of carbon nanotubes, in contrast to recent work on graphene, which measures the transmission but not the absorption.23 Furthermore, this measurement gives the thermal conductance of the suspended nanostructures, based on the
temperature gradient between the incident laser spot and the microthermometers. Upper and lower bounds of the thermal conductance are observed to be 0.51 and 2.28 nW/K, which is comparable to previous reports of Shi et al.3 On the basis of the nanotube bundle diameters determined by HRTEM, the thermal conductivity varies from 118 to 683 W/m K. This low thermal conductivity can be attributed to internanotube coupling, defects, and thermal contact resistance between the nanotubes and the SiN membrane.

In conclusion, we demonstrate a technique that uses both Raman spectroscopy and microfabricated thermometers to
determine the heat generated by the nonradiative absorption of
light for suspended carbon nanotube bundles. Values for this absorption probability lie in the range from $3.07 \times 10^{-4}$ to
$4.38 \times 10^{-3}$ for 7.4–10.3 nm diameter nanotube bundles. This is a direct measurement of the optical absorption of
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Supporting Information Available: High-resolution tunneling electron microscopy images of carbon nanotube bundles measured in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

References


(26) The Rayleigh number for this geometry is calculated to be on the order of 10⁻⁶ to 10⁻³ which is much smaller than the typical range between 10⁻¹ and 10¹² for natural convection to occur. For such a small Rayleigh number approaching zero, free convection is negligible and the heat loss to air is dominated by heat conduction. Because the carbon nanotube diameter is much smaller than the mean free path of air molecules, molecular gas conduction should be calculated using detailed gas dynamics instead of Fourier’s law. When the molecule accommodation coefficient is 1, the molecular thermal conductance per unit nanotube length reaches the upper bound of g = (υₔ/₉kB)(dΔT) ≈ 0.2 mW/(mK) for a 10 nm diameter (d) nanotube bundle, where and are the number density and mean velocity of air molecules, respectively, and is the Boltzmann constant. The average temperature rise in the nanotube is about half of the temperature at the laser spot, or ΔT ≈ 100 K. For a nanotube of length L = 10 μm, the heat loss to air molecules is q ≈ gΔT ≈ 0.2 μW, which is 1 order of magnitude smaller than the absorbed laser power transferred by conduction along the nanotube to the two membranes. On the other hand, radiation heat loss from the nanotube is estimated to be 3 orders of magnitude smaller than the absorbed laser power.


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**High Resolution Transmission Electron Microscopy (HRTEM)**

High Resolution Transmission Electron Microscopy (HRTEM) was performed on the nanotube bundles measured in this study. Figures (a)-(c) show these images below.

![HRTEM images](attachment:image.jpg)

**Figure 5.** HRTEM images of carbon nanotube bundles measured in this study.