Temperature Coefficients of Raman Frequency of Individual Single-Walled Carbon Nanotubes

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In the present study, individual suspended single-walled carbon nanotubes (SWNTs) were prepared and the temperature coefficients of Raman frequency of 13 SWNTs were measured. It is found that the temperature coefficients of the G-band frequency ($\alpha_{G}$) are similar, around ($-1.67 \pm 0.20\times 10^{-5}$)K, whereas in the case of the radial breathing mode (RBM), the coefficients ($\alpha_{RBM}$) are varied from a minimum value of $-1.06 \times 10^{-6}$K to a maximum of $-2.30 \times 10^{-4}$K. Larger-diameter nanotubes tend to have larger $\alpha_{RBM}$ values; moreover, nanotubes with similar diameters may show different $\alpha_{RBM}$ values. These results reveal that the $\alpha_{RBM}$ value of individual SWNTs depends on both diameter and chirality.

Resonance Raman spectroscopy (RRS) has been demonstrated to be an effective and nondestructive technique to characterize the structures and electronic properties of single-walled carbon nanotubes (SWNTs). Because the Raman scattering process involves complicated electron–phonon interactions, the study of the temperature effects on the Raman spectra could provide important insight into the physical properties of this unique one-dimensional system. The radial breathing mode (RBM) is a unique feature in the Raman spectra of SWNTs. It involves the collective vibrational movement of carbon atoms toward and away from the central axis of a SWNT. The frequency of RBM ($\omega_{RBM}$) tightly depends on the diameter ($d_t$) of the SWNT, and the chiral angle ($\theta$) also has some influence on the $\omega_{RBM}$ value although the effect is relatively weak. Therefore, it is an interesting and important issue to investigate whether and how the temperature behaviors of $\omega_{RBM}$ depend on the $d_t$ and $\theta$ values of SWNTs. Currently, because most of the works focused on the temperature dependence of the Raman spectra of SWNTs are done on bulk SWNT samples, in which nanotubes with different $d_t$ and $\theta$ values are present, the results could not reveal the relationship between the temperature behavior of $\omega_{RBM}$ and the structure of the nanotube. Moreover, it has been proven that the surrounding environments of nanotubes may have a remarkable influence on the properties of nanotubes. So individual suspended SWNTs, being free from environmental influence, are an ideal choice for such a study.

Herein, suspended SWNTs were prepared and the temperature coefficients of the Raman frequency of 13 individual SWNTs were measured. While the temperature coefficients of $\omega_{G}$ (frequency of G-band, tangential stretching mode) of different

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A programmable hot-stage (THMS 600) was used for heating of SWNTs, as illustrated by Figure 1b. Raman spectra of suspended SWNTs at temperature of 300, 323, 348, 373, 398, 423, 448, and 473 K were collected using micro-Raman spectroscopy. To ensure that the temperatures of samples were the same as the stage, we took all spectra after the temperature of the hot stage was stable for at least 10 min. The excitation energy was 1.96 eV (632.8 nm), and the spot size was 1 μm². The laser power used was 0.16 mW at the sample place. We have checked the laser heating effect by monitoring the intensity ratio of the anti-Stokes to the Stokes of the RBM when tuning the laser power and no observable laser heating effect when the laser power was 0.16 mW. All of the Raman spectra were fitted by Lorentzian peak shape to obtain the peak frequency. The Raman peak of the anti-Stokes and Stokes of the RBM are symmetric, and the stronger one has been chosen for the fitting in order to get a more-precise value.

Figure 2. (a and b) Radial breathing mode (RBM) (a) and G mode (b) Raman frequency evolution with increased temperature (from bottom to top: 300, 323, 348, 373, 398, 423, 448, 473 K) of an individual SWNT. The left part in a is the anti-Stokes band. (c and d) Plot of the frequency of RBM (c) and G mode (d) vs temperature. Because the Stokes bands are relatively weak in part a, the anti-Stokes bands are used for the fitting in par c. The lines are linear fitting results for obtaining the temperature dependence of the frequency.

Figure 3. (a and b) Radial breathing mode (RBM) (a) and G mode (b) Raman frequency evolution with increased temperature (from bottom to top: 300, 323, 348, 373, 398, 423, 448, 473 K) of another individual SWNT, for comparison with the SWNT shown in Figure 2. (c and d) Plot of frequency of RBM (c) and G mode (d) vs temperature. The lines are linear fitting results for obtaining the temperature dependence of the frequency.
TABLE 1: Summarized Data of Raman Frequency and Corresponding Temperature Coefficients of 13 Individual SWNTs

<table>
<thead>
<tr>
<th>no.</th>
<th>$\omega_{\text{RBM}}$ (cm$^{-1}$)</th>
<th>diameter (nm)</th>
<th>$\chi_{\text{RBM}}$ (cm$^{-3}$/K)</th>
<th>$\omega_{\text{RBM}}$ (1/K)</th>
<th>$\omega_{\text{G}^+}$ (cm$^{-1}$)</th>
<th>$\chi_{\text{G}^+}$ (cm$^{-3}$/K)</th>
<th>$\omega_{\text{G}^-}$ (1/K)</th>
<th>$\omega_{\text{G}^-}$ (cm$^{-1}$)</th>
<th>$\chi_{\text{G}^-}$ (cm$^{-3}$/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>282.9</td>
<td>0.877</td>
<td>$-0.0029$</td>
<td>$-1.03 \times 10^{-5}$</td>
<td>1584.5</td>
<td>$-0.0258$</td>
<td>$-1.63 \times 10^{-5}$</td>
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<tr>
<td>2</td>
<td>222.2</td>
<td>1.116</td>
<td>$-0.0081$</td>
<td>$-3.63 \times 10^{-5}$</td>
<td>1971.3</td>
<td>$-4.92 \times 10^{-5}$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>188.0</td>
<td>1.319</td>
<td>$-0.0002$</td>
<td>$-1.06 \times 10^{-5}$</td>
<td>1591.9</td>
<td>$-0.0269$</td>
<td>$-1.69 \times 10^{-5}$</td>
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<td></td>
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<tr>
<td>4</td>
<td>186.7</td>
<td>1.328</td>
<td>$-0.0100$</td>
<td>$-5.37 \times 10^{-5}$</td>
<td>1591.9</td>
<td>$-0.0269$</td>
<td>$-1.69 \times 10^{-5}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>169.9</td>
<td>1.460</td>
<td>$-0.0006$</td>
<td>$-3.53 \times 10^{-6}$</td>
<td>1595.6</td>
<td>$-0.0207$</td>
<td>$-1.30 \times 10^{-5}$</td>
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<tr>
<td>6</td>
<td>156.8</td>
<td>1.582</td>
<td>$-0.0063$</td>
<td>$-4.02 \times 10^{-5}$</td>
<td>1579.5</td>
<td>$-0.0289$</td>
<td>$-1.83 \times 10^{-5}$</td>
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<tr>
<td>7</td>
<td>151.9</td>
<td>1.633</td>
<td>$-0.0192$</td>
<td>$-1.26 \times 10^{-4}$</td>
<td>1592.0</td>
<td>$-0.0282$</td>
<td>$-1.77 \times 10^{-3}$</td>
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<tr>
<td>8</td>
<td>147.9</td>
<td>1.677</td>
<td>$-0.0021$</td>
<td>$-1.42 \times 10^{-5}$</td>
<td>1591.9</td>
<td>$-0.0247$</td>
<td>$-1.53 \times 10^{-5}$</td>
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<tr>
<td>9</td>
<td>146.7</td>
<td>1.691</td>
<td>$-0.0184$</td>
<td>$-1.25 \times 10^{-5}$</td>
<td>1592.5</td>
<td>$-0.0289$</td>
<td>$-1.81 \times 10^{-5}$</td>
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<tr>
<td>10</td>
<td>141.1</td>
<td>1.758</td>
<td>$-0.0017$</td>
<td>$-1.20 \times 10^{-5}$</td>
<td>1587.3</td>
<td>$-0.0266$</td>
<td>$-1.68 \times 10^{-5}$</td>
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<tr>
<td>11</td>
<td>130.0</td>
<td>1.908</td>
<td>$-0.0216$</td>
<td>$-1.66 \times 10^{-5}$</td>
<td>1589.8</td>
<td>$-0.0249$</td>
<td>$-1.57 \times 10^{-5}$</td>
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<tr>
<td>12</td>
<td>115.3</td>
<td>2.151</td>
<td>$-0.0075$</td>
<td>$-6.50 \times 10^{-5}$</td>
<td>1582.9</td>
<td>$-0.0240$</td>
<td>$-1.52 \times 10^{-5}$</td>
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<td>13</td>
<td>113.3</td>
<td>2.189</td>
<td>$-0.0261$</td>
<td>$-2.30 \times 10^{-5}$</td>
<td>1590.7</td>
<td>$-0.0258$</td>
<td>$-1.62 \times 10^{-5}$</td>
<td></td>
<td></td>
</tr>
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</table>

$^a$ SWNTs are listed from top to bottom according their diameters from small to large. Each row corresponds to data of same SWNT. The “*” in the left column marks the data from references for comparison. According to the Kataura plot and resonance conditions, SWNT nos. 2–5 (marked with italic) are metallic and the others are semiconducting. $\omega_{\text{RBM}}, \omega_{\text{G}^+},$ and $\omega_{\text{G}^-}$ indicate the frequency of the corresponding Raman modes. $\chi_{\text{RBM}}, \chi_{\text{G}^+},$ and $\chi_{\text{G}^-}$ correspond to $d\omega_{\text{RBM}}/dt, d\omega_{\text{G}^+}/dt,$ and $d\omega_{\text{G}^-}/dt,$ respectively. $\alpha_{\text{RBM}}, \alpha_{\text{G}^+},$ and $\alpha_{\text{G}^-}$ are the normalized temperature coefficients of these Raman modes.

The Raman frequency downshift with temperature is due to the softening of the C–C bond. A similar $\alpha_{\text{RBM}}$ value for different nanotubes can be readily understood considering the characteristics of the G mode. The $G^+$ band is associated with in-plane C–C vibrational movement along the nanotube axis, and thus, $\omega_{\text{G}^+}$ is essentially independent of diameter. We note that the reported $\omega_{\text{G}^+}$ values of both graphite and multiwalled carbon nanotubes (MWNT) are about $1.7 \times 10^{-5}/K$, almost equal to our results of SWNTs $(-1.67 \pm 0.20) \times 10^{-5}/K$. Because carbon nanotubes can be envisioned as rolled-up graphene layers, the above results suggest that the convolution of graphene layer has no obvious influence on the temperature dependence of the G band.

In contrast to $\alpha_{\text{G}^+}$, there is a remarkable difference between the $\alpha_{\text{RBM}}$ values of different SWNTs, which indicates a distinct temperature effect on the RBM of different SWNTs. Because individual suspended nanotubes were used in the experiment, there was no environmental difference between these SWNTs. So the difference in $\alpha_{\text{RBM}}$ should originate from the specific structures of the SWNTs. SWNTs can be envisioned as rolled-up graphene layers, and, according to the rolling vector, two parameters including diameter ($d$) and chiral angle ($\theta$), define the structure of a SWNT. RBM corresponds to vibration of carbon atoms in radial directions and consequently, $\omega_{\text{RBM}}$ is tightly dependent on diameter. Chiral angle, which defines the relative directions of C–C bonds to the RBM vibration, may also influence $\omega_{\text{RBM}}$.

The downshift of $\omega_{\text{RBM}}$ with increased temperature can result from thermal expansion in the radial direction and softening of C–C bonds. The $\omega_{\text{G}^+}$ is also related to the softening of C–C bonds and similar $\alpha_{\text{G}^+}$ values (of both $G^+$ and $G^-$) of different SWNTs indicate that there is no remarkable difference in the extent of C–C softening. Therefore, the thermal expansion in the radial direction is supposed to be the main contribution to the difference in $\alpha_{\text{RBM}}$ Values. SWNTs can be envisioned as rolled-up graphene layers, and the convolution of the graphene layers will result in strain in the radial direction of the SWNTs. For SWNTs with small diameters (large curvature of the graphene layers), the strain energy due to the curvature of graphene layers is large compared to that of large-diameter
SWNTs, and that should result in smaller radial thermal expansion of small-diameter nanotubes. Therefore, larger $\alpha_{\text{RBM}}$ values are expected for nanotubes with large diameters. Additionally, as been suggested by calculational work, the chiral angle and metallicity of nanotubes also influence the softening of the RBM frequency. This is consistent with the fact that even nanotubes with similar diameters, such as the two nanotubes with $\omega_{\text{RBM}} = 115.3 \text{ cm}^{-1}$ ($d \approx 2.15 \text{ nm}$) and $\omega_{\text{RBM}} = 113.3 \text{ cm}^{-1}$ ($d \approx 2.19 \text{ nm}$), have an obvious different $\alpha_{\text{RBM}}$ values. This demonstrates the chirality dependence of $\alpha_{\text{RBM}}$. However, because definite $(n,m)$ assignments for each SWNT is difficult and there are no calculational works touching the chirality effect on $\alpha_{\text{RBM}}$, we cannot get further information on this issue. One thing that needs to be mentioned here is that it is suggested that the coupling of RBM to the other totally symmetric modes can also influence the softening of $\omega_{\text{RBM}}$, and, thus, the changes in coupling may be another explanation of the difference in $\alpha_{\text{RBM}}$ values.

In summary, the temperature dependence of the Raman spectra of 13 individual suspended SWNTs has been investigated and different SWNTs showed similar $\alpha_{\text{G}}$ values but distinct $\alpha_{\text{RBM}}$ values. The mean value of $\alpha_{\text{G}}$ is $-1.67 \times 10^{-5}/K$, which is similar to that of graphite and MWNTs, suggests that the tubular structure has no obvious influence on the temperature dependence of the G mode. In contrast, the $\alpha_{\text{RBM}}$ values of these SWNTs are found to vary from one to another, with a minimum value of $-1.06 \times 10^{-5}/K$ and a maximum of $-2.30 \times 10^{-4}/K$, which indicates the structure dependence of $\alpha_{\text{RBM}}$. SWNTs with larger diameters tend to have larger $\alpha_{\text{RBM}}$ values, and, furthermore, even SWNTs with similar diameters may show distinct $\alpha_{\text{RBM}}$ values. These results reveal the diameter and chirality influence on the behaviors of RBM. These findings demonstrate the tight relationship between the properties and structures (both diameter and chiral angle) of SWNTs. Precise $(n,m)$ assignment for individual SWNTs and calculational works may benefit further study on this issue.

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References and Notes