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Temperature dependence of the Raman spectra of carbon nanotubes

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We report on a temperature dependence of the frequency of all the major peaks in the Raman spectra of carbon nanotubes, using different excitation laser powers at the sample. The frequency decreases with increasing temperature for all peaks, and the shifts in Raman frequencies are linear in the temperature of the sample. In comparison, a similar dependence is found in active carbon, but no shift is observed for the highly ordered pyrolytic graphite within the same range of variation in laser power. A lowering of frequency at higher temperature implies an increase in the carbon–carbon distance at higher temperature. The relatively strong temperature dependence in carbon nanotubes and active carbon may be due to the enhanced increase in carbon–carbon distance. This enhancement may originate from the heavy defects and disorder in these materials. © *1998 American Institute of Physics.* [S0021-8979(98)05219-0]

The two forms of ordered carbon: graphite and diamond have been studied for a long time. More recently, discoveries of fullerenes such as C_{60} and nanoscale carbon structures such as carbon nanotubes have spurred the current interest in carbon materials. These materials have unique features that offer new potential applications. Understanding these new forms has attracted the attention of many scientists. Raman scattering has been shown to be very useful in characterizing graphite and diamond,[1,2] and more recently, fullerenes[3] and carbon nanotubes.[4–10] Frequency shifts in the Raman peak of a variety of carbon nanotubes as a function of excitation photon energy have been reported.[5,9] Temperature dependent shifts in the peaks of the Raman spectra of carbon nanotubes were reported very recently by Huong *et al.*[11] This last study was based on measurements at two laser excitation powers (and thus two temperatures). However, the accuracy of the calculation of the higher temperature is suspect. The temperature in their article was calculated using the Stokes and anti-Stokes lines at 120 cm^{-1}. These lines are strongly affected by the somewhat asymmetric Rayleigh line, thus limiting the accuracy of the calculated temperature. Using more accurate measurements of sample temperatures, we report here a systematic study of the temperature dependence of the frequencies of all the major peaks in the Raman spectra of nested carbon nanotubes, as well as active carbon.

Carbon nanotubes were prepared by the dc arc discharge method, discharge carbon nanotube (D-CNT) and by the catalytic CNT method (C-CNT) as described previously.[12] Typical transmission electron microscope images and more detailed descriptions of these samples had been presented elsewhere.[10] It was estimated that 60% and 90% of D-CNT and C-CNT are nested nanotubes with a diameter range of 10–20 nm and 30–50 nm, respectively. Grade-ZYH highly oriented pyrolytic graphite (HOPG) was purchased from Advanced Ceramics and used directly. Active carbon (A-C) was of analytical grade from Dali Active Carbon Manufacturer (Beijing, China). A-C can be considered as a mixture of amorphous carbon and microcrystalline graphite. The Raman spectra of all samples shown in this communication were measured with a Renishaw System 1000 Raman microscope at room temperature. The 632.8 nm line of a He–Ne laser was used as excitation. The typical resolution is 1.0 cm^{-1}. Laser power ranging from 0.20 to 4.0 mW at the sample was focused into a spotsize of about 25 μm in diameter, giving a power density of 32–640 $\mathrm{W/cm}^2$ at the sample. No polarizer was used and a backscattering geometry was employed to collect the Raman signal. All Raman peak parameters were obtained by least-squares fitting Lorentzian line shapes to the measured spectra.

Figure 1 shows the Raman spectrum of D-CNT between 1200 and 1700 cm^{-1} and between 2500 and 2800 cm^{-1} with different excitation powers of the 632.8 nm line of the He–Ne laser. All conditions were the same except for the difference in excitation powers. The calculated temperature is labeled next to each spectrum in Fig. 1. The intensity scales of the three spectra are identical. The D line at ~1320 cm^{-1}, the G line at ~1580 cm^{-1}, the E'_{2g} line at ~1620 cm^{-1} (not labeled), and the D^* line at ~2640 cm^{-1} all shift to lower frequencies with increasing power of the laser at the sample. Another C-CNT sample and A-C also showed similar temperature induced shifts. Furthermore, similar shifts in the frequencies of these lines were observed with different powers of 488.0 and 514.5 nm excitation for these three samples (data not shown).

The temperature at the sample can be calculated by measuring the intensities of the Stokes and corresponding anti-Stokes peaks. The difference in efficiency of the charge coupled device (CCD) detector at the different Stokes and

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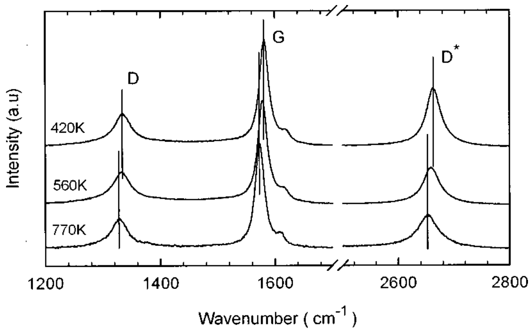

FIG. 1. Raman spectrum of carbon nanotubes (D-CNT) between 1200 and 1700 cm^{-1} and between 2500 and 2800 cm^{-1} at temperatures of 420, 560, and 770 K.

anti-Stokes lines is compensated by using the typical quantum efficiency curve for this kind of detector. Any deviation from the typical curve for the particular detector used in these measurements results in an error smaller than the uncertainty of the calculated temperature. The measured temperatures by this method for each of the observed lines (two in C-CNT and four in D-CNT) at a particular incident laser power agree reasonably well, typically within 3%–4% in the low temperature range and within 6%–8% in the high temperature range.

Figure 2 shows the frequencies of the four peaks versus the average temperature of the sample. A straight line is fit for each peak for each carbon material. Note that data points from measurements done on different days were included in the figure. Table I lists the slopes and intercepts of the fitted straight lines in Fig. 2. The slopes for each peak for different carbon materials agree to within the accuracy of the measurement. Note that the slope of the D^* peak is about twice that of the D peak (Table I), which is consistent with the assignment of the D^* peak as an overtone of the D mode. The dependence on temperature for the different peaks, however, is not the same. The slopes for the G and the E'_{2g} peaks are about the same but are different from that of the D and D^* peak in Fig. 2 (see Table I).

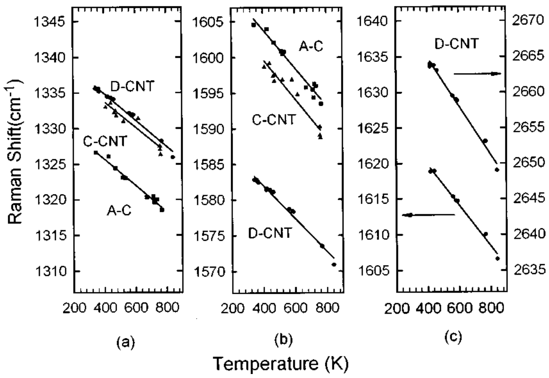

FIG. 2. The frequency dependence as a function of the calculated temperature of the sample for (a) the D peak at ~1320 cm^{-1} of carbon nanotubes made by the dc arc discharge method (D-CNT), by the catalytic method (C-CNT), and active carbon (A-C); (b) the G peak at ~1580 cm^{-1} of D-CNT, C-CNT, and A-C; and (c) the E'_{2g} peak at ~1620 cm^{-1} and the D^* line at ~2640 cm^{-1} of D-CNT.

TABLE I. The slopes and intercepts of the straight line fits in Fig. 2.

Sample	Parameter	D	G	E'_{2g}	D^*
D-CNT	slope (cm^{-1}/K)	−0.019	−0.023	−0.029	−0.034
	intercept (cm^{-1})	1342	1591	1631	2697
C-CNT	slope (cm^{-1}/K)	−0.018	−0.028	···	···
	intercept (cm^{-1})	1341	1661	···	···
A-C	slope (cm^{-1}/K)	−0.019	−0.027	···	···
	intercept (cm^{-1})	1333	1615	···	···

A similar temperature-dependent effect was observed in A-C. The slopes for each peak are in agreement with those of the carbon nanotube samples (see Fig. 2 and Table I). However, we do not find laser induced shifts in the HOPG sample. Varying the excitation power within the range available with the He–Ne laser does not change the Raman features of HOPG. The temperature calculated remains basically unchanged and no shift in frequency of any peak was observed. Likewise, changing the laser power by a factor of 5 from about 50 to 250 mW of the 514.5 nm line at the sample does not affect the frequency of the G line of HOPG.

Our results show that the dependence of the peak frequency on temperature is quite strong and is present for different excitation wavelengths (488.0, 514.5, and 632.8 nm) for CNT and A-C. Furthermore, all the major peaks exhibit this dependence. In view of this, care must be exercised when comparing the Raman frequency of any peak of carbon nanotubes measured under different conditions. For example, there are some variations in the frequencies of many peaks in published Raman spectra of nanotubes.[4–9] Different laser sources were used and laser powers at the samples were specified in only some of these reports. It is likely that different laser power densities at the sample were used which can induce different temperatures at the sample and may, therefore, account for the slightly different frequencies reported in the studies. In addition, the dependence of the frequencies of the D and D^* peaks of carbon nanotubes on excitation energies[5] and the diameter-selective resonance effect in single wall nanotubes have been reported.[9] Again, different laser power densities at the samples were likely. The effect of different sample temperatures must be corrected in these studies. It seems clear, however, that the dispersion effect is still present in carbon nanotubes[5,9] but adjustment is needed for different sample temperatures before the dispersion effect can be quantified. The results presented here provide the necessary information to correct for the different temperatures at the sample.

The lack of an observed frequency shift in HOPG in our measurements can be understood by the inability to raise the sample temperature using a laser which, in turn, is due to the high thermal conductivity of HOPG. We cannot find any published Raman spectrum of HOPG at a temperature outside of room temperature. We are thus unable to determine whether Raman peaks of HOPG have a temperature dependence comparable to that of CNT and A-C. It is interesting to note that the Raman peak of diamond has an appreciable temperature dependence.[13,14] However, the change in frequency is not linear with temperature for temperatures up to

2000 K. The magnitude of change in diamond within the temperature change in our current study (below 900 K) is significantly weaker than what we found for CNT and A-C, suggesting that different reason(s) may account for the frequency shifts observed in these carbon materials.

It is of interest to postulate the origin of the strong temperature dependence in CNT and A-C. The down shift in frequency of the Raman peaks due to C═C stretching can be correlated essentially to a lengthening of the C–C distance.[15] Thermal expansion can induce a longer C–C distance and thus a downshift in the C–C stretching frequency. However, any explanation due to simple thermal expansion has to be reconciled with the possibility of a lack of a (strong) temperature dependence in HOPG and a different dependence in diamond. Note that active carbon has a temperature effect identical to that of the nanotubes and the two materials have very different structural morphologies, suggesting that features other than the tubular structure of the nanotubes may be important for sizable temperature dependence. One possibility is that somehow nanoscale features in carbon nanotubes (and active carbon) can accommodate the elongation of the C–C bonds easily, whereas such change is not as easy in HOPG. A more likely possibility is the presence of defects and disorder in both nanotubes and active carbon. The *D* peak has been associated with defects and both materials have a significant *D* peak. It is plausible that the presence of defects gives enough flexibility to the structure to accommodate elongation of the C–C bond upon an increase in temperature, whereas such flexibility is not possible with the crystalline HOPG and diamond.

In conclusion, a temperature induced frequency shift is observed for all the major peaks in the Raman spectra of carbon nanotubes and active carbon, but not in HOPG. The frequencies of all peaks shift down linearly with increasing temperature, but by different amounts. It is plausible that defects are responsible for sizable temperature dependence in nanotubes and active carbon by allowing a significant lengthening of the C–C bond with increasing temperature.

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