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UV Raman Spectroscopy of Single-Walled Carbon Nanotubes

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Deep UV Raman spectroscopy is emerging as a useful tool for the characterization of carbon materials that has many advantages over visible Raman spectroscopy. However, because of resonance enhancement and other effects, UV Raman spectra are often different from visible Raman spectra. UV Raman spectra have not been reported for even some of the most widely known carbon materials. We report Raman spectra of single-walled carbon nanotubes (SWNTs) collected with deep ultraviolet (4.8 eV) laser excitation. There are significant differences between the deep UV and the visible Raman spectrum of SWNTs for the graphitic "G" modes and "disorder-induced" "D" modes, which are common to a wide range of forms of carbon. Furthermore, only semiconducting tubes are observed in the UV Raman spectrum, which is not consistent with an expected resonance enhancement of the scattering from metallic tubes at 4.8 eV.

Introduction

Deep UV Raman spectroscopy is emerging as a powerful and convenient tool for the characterization of carbon and related covalently bonded materials.[1−4] For a wide range of carbon-based materials, it is now possible to collect Raman spectra that were formerly difficult or impossible to obtain by means of visible Raman spectroscopy.[1,3,5] This is because the visible Raman spectra of many such materials are obscured by interference from fluorescence or scattering from sp^2-bonded carbon.[3,5] In our experience the use of UV Raman spectroscopy can almost always overcome these difficulties: novel covalently bonded carbon networks synthesized from molecular precursors that fluoresce strongly in the visible spectrum can be characterized by UV Raman spectroscopy.[6] Carbonaceous deposits on catalysts for which useful visible Raman spectra cannot be collected can also now be characterized by means of UV Raman spectroscopy.[5,7] However, some issues remain to be addressed before the full potential of UV Raman spectroscopy for the characterization of carbon materials can be realized. To interpret the Raman spectrum of a novel carbon material, it is important to be able to correlate the position and intensities of the first and higher order spectral lines with the structural features of the material. For visible Raman spectroscopy, much is understood about this correlation based on years of investigation of the various forms of carbon.[8−10] However, because of resonance enhancement and other effects, UV Raman spectra are often different from visible Raman spectra and UV spectra have not been reported for even some of the most widely known carbon materials. Sample damage from the relatively high energy ∼5 eV photons used for deep UV Raman spectroscopy is another important issue. If UV Raman spectroscopy is to be useful for the characterization of carbon materials that are less stable than graphite or diamond, it is necessary to be able to collect spectra with an adequate signal-to-noise ratio below the damage threshold. Even diamond is susceptible to damage from deep UV excitation sources if suitable care is not taken.

Because of their curvature, carbon nanotubes[11] (as well as fullerenes[12]) are thermodynamically less stable than either graphite or diamond. Here we report a deep UV (257 nm, 4.8 eV) Raman spectroscopic investigation of carbon single-wall nanotubes (SWNTs).[13,14] Collection of the spectra reported here required careful optimization of the experimental apparatus and conditions to collect the Raman scattered light efficiently at low enough excitation power. We report the effect of increasing power density on the UV Raman spectra of the nanotubes and suggest potential damage mechanisms.

The most striking feature of the Raman spectra of SWNTs is the diameter selective scattering at different

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excitation frequencies[14,15] that results from the 1-D quantum confinement of the electrons in the nanotubes. Resonance Raman spectroscopy of SWNTs in the energy range of ~1−3 eV has proved to be a powerful probe of these quasi-one-dimensional materials,[14,15] although much still remains to be understood about their Raman spectra.[16] We find that much of the UV Raman spectrum of SWNTs can be understood from an examination of spectra collected at lower excitation energies, but significant differences remain.

Experimental Section

SWNTs prepared by a laser ablation technique with a Ni−Co catalyst were obtained from Carbon Nanotechnologies. The tubes are expected to be a mixture of semiconducting and metallic tubes, with a distribution of chiral vectors. The chiral vectors are specified by indices *n* and *m* that determine the diameter and type of nanotube (armchair, zigzag, or other chirality).[14] The distribution of tube diameters is in the range 1−1.4 nm, peaking about 1.2 nm. The sample powder was pressed lightly into a 400 μm diameter indentation made in a stainless steel gasket by a diamond anvil. Visible (514 nm, 2.4 eV) Raman spectra were recorded by means of a Dilor micro-Raman spectrometer equipped with a liquid-nitrogen-cooled CCD detector (Princeton Instruments). Laser powers ranging from 100 W/cm^2 to 2 kW/cm^2 were used. UV Raman spectra were recorded with separate micro-Raman spectrometer in a single-monochromator configuration, also equipped with a UV sensitive (~40% quantum efficiency) liquid-nitrogen-cooled CCD detector. A 257 nm (4.8 eV) Coherent FRED intracavity frequency-doubled argon ion laser was used for excitation. UV laser power densities from about 125 W/cm^2 to 2.5 kW/cm^2 were used to investigate the damage threshold of the nanotubes. The sample was illuminated with either a spot or a line focused by a cylindrical lens at various power densities. Because the line configuration illuminates a larger area of the sample, which can be still imaged into the monochromator, it gives better signal-to-noise ratio for the same incident laser power density. The backscattered Raman and Rayleigh light was collected using a high numerical aperture (0.5) reflecting objective. Two custom-made (Omega Optical Inc.) dielectric stack filters were employed to filter out the Rayleigh scattered light.[17] This single-monochromator configuration with dielectric filters is more efficient than a triple monochromator configuration, making it possible to collect UV Raman spectra of nanotubes with adequate signal-to-noise ratio.

Results and Discussion

Visible (514.5 nm, 2.4 eV) Raman spectra (Table 1, Figure 1) were used to characterize the nanotubes and were similar to those reported previously.[14] There is a low-frequency radial breathing mode characteristic of nanotubes that can be used to determine the diameter of the tubes probed by a particular excitation frequency.[14] The radial breathing mode for the present sample is at 186 cm^{-1}, indicating that diameter of the tubes probed by 2.4 eV radiation is about 1.2 nm, consistent with the value expected from the method of synthesis.[18]

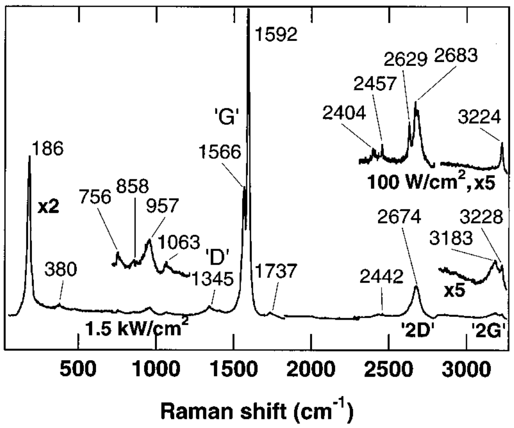

Figure 1. Raman spectrum of SWNT with 2.4 eV excitation. Features in the vicinity of "G" peaks are typical of semiconducting tubes.

Table 1

vis Raman ω (cm^{-1})	UV Raman ω (cm^{-1})	assgnt
186		RBM A_{1g} (armchair and zigzag)[16] and A_1 (chiral)[16]
380		2nd order RBM
	711	
756		E_{1g}[15]
858		E_{2g}[15]
957		
1063		
1345	1434	D A_{1g}/E_{1g} [15]
1521		E_{1g}[15]
1548		E_2 (E_{2g})[28]
1566	1569	tangential stretch G1 $A(A_{1g}) + E_1(E_{1g})$[28]
1592	1592	tangential stretch G2 $A(A_{1g}) + E_1(E_{1g})$[28]
1737		G1 + G2 + RBM
	2330	N_2
2442		
2674	~2868	2nd order D (G′)
3168	~3150	2nd order G
3224		2nd order G

Several vibrational modes are commonly observed in the visible Raman spectrum of many forms of carbon. In particular, there is a large literature regarding the behavior of the G (for "graphite") mode(s) related to the mode of E_{2g} symmetry observed at 1582 cm^{-1} for highly oriented pyrolytic graphite (HOPG) and the D (for "disordered") mode observed near 1355 cm^{-1} (with 2.4 eV excitation) for microcrystalline graphite and glassy carbon but not in pristine HOPG or single-crystal graphite.[8−10] There are also various combination and overtone bands resulting from the G and D modes. The positions and relative intensities of all of these modes can give much information about the structure and domain size of a carbon material. For the nanotubes, with visible excitation we observed two intense G peaks at 1566 and 1592 cm^{-1} (Table 1, Figure 1), characteristic of semiconducting nanotubes because there is no intense mode at 1540 cm^{-1}. As in graphite, these are tangential stretching modes.[14] The splitting results from curvature of the nanotube graphene sheet. The D peak in the visible Raman spectrum of the nanotubes is at 1345 cm^{-1}, and its overtone (2D) is at 2674 cm^{-1} (Table 1).

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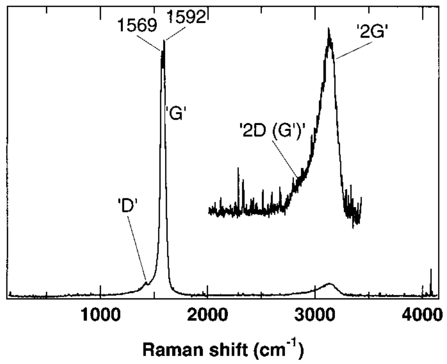

Figure 2. Raman spectrum of SWNT with 4.8 eV excitation. The tangential stretch mode is split as in the visible Raman spectra. Note the low-intensity D peak at 1434 cm^{-1} and the second-order modes (also magnified 12×) around 3100 cm^{-1}. The second order 2D peak is sometimes called G′.

Furthermore, there is a peak at 2442 cm^{-1},[19] the origin of which remains uncertain. Other assignments are in Table 1.

We note a previously unreported dependence on laser power for both the 2D (2674 cm^{-1}) peak and the 2442 cm^{-1} peak. At a low incident power of 100 W/cm^2 the 2D peak reproducibly splits into two distinct peaks and a shoulder and the peak at 2442 cm^{-1} splits into two peaks at 2457 and 2404 cm^{-1} (Figure 1). There is a peak at 3224 cm^{-1} when 100 W/cm^2 of incident power is used, and an additional peak appears at 3183 cm^{-1} when the power is increased to 1.5 kW/cm^2. The peaks at 3183 and 3224 cm^{-1} are close to that expected for the second-order tangential stretching modes of SWNT.[20,21] Further theoretical and experimental investigation of the visible Raman spectrum of SWNTs is warranted.

The UV Raman spectrum of the nanotubes (Figure 2) exhibited excellent signal-to-noise ratio. Thus, although nanotubes might be expected to be more sensitive to damage from UV radiation than the more stable diamond and graphitic forms of carbon, UV Raman spectra can still be collected if low enough power densities are used and the collection efficiency of the spectrometer is sufficiently high. The G tangential stretching modes in the UV Raman spectrum are split into a doublet at 1569 and 1592 cm^{-1}. These two modes have nearly equal intensities (Figure 2, Table 1), in contrast to the stretching modes in the visible Raman spectra of semiconducting nanotubes (Figure 1, Table 1). These two peaks could be fit by a Lorentzian line shape when a third much weaker peak at 1608 cm^{-1} (another tangential mode) was included. The absence of the mode observed near 1540 cm^{-1} for metallic nanotubes as well as the lack of a Breit−Wigner−Fano line shape also characteristic of metallic nanotubes indicates that semiconducting tubes are probed with 4.8 eV excitation.[14] Furthermore, the splitting observed indicates that the tubes remain intact upon illumination with UV excitation: disordered or damaged carbon would likely not exhibit this splitting. Visible Raman spectra collected on nanotube samples after UV illumination at the same power density used for the UV Raman experiments were still characteristic of nanotubes (including the tube radial breathing mode), further supporting the conclusion that the tubes remain undamaged. There is a very weak peak at 711 cm^{-1}, which does not appear in the visible Raman spectrum and could not be assigned. It is uncertain whether it is intrinsic to the nanotubes or due to a surfactant or other impurity.

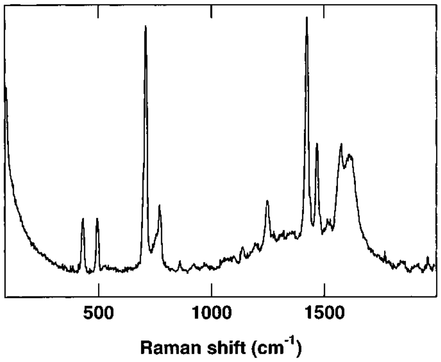

Figure 3. UV Raman spectrum of C$_{60}$. The relative intensities of the peaks are different from those of the visible Raman spectrum.

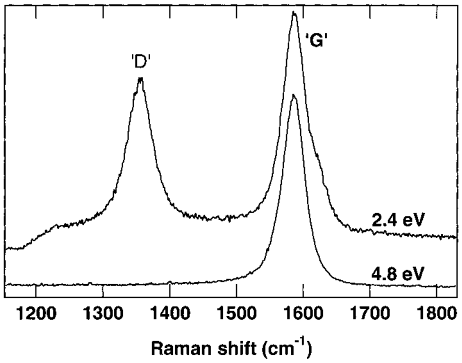

Figure 4. Visible Raman (top) and UV Raman (bottom) spectrum of glassy carbon. Note the absence of any D peak in the UV Raman spectrum.

We have also had success in collecting UV Raman spectra of C$_{60}$ fullerenes. The spectra (Figure 3) are similar to those obtained with visible excitation but with differences in peak intensities. Thus spectra can also be collected on fullerenes, which are more sensitive than nanotubes to photochemical reaction and should be more readily damaged by energetic UV radiation.[22]

The D peak observed in the Raman spectrum of sp^2-bonded carbon materials shifts to higher frequencies and decreases in intensity with increasing excitation energy (this shift in position and decrease in intensity of the D peak makes deep UV Raman particularly useful for characterizing carbon containing mixed sp^2/sp^3 bonding. In visible Raman spectra, the D peak typically obscures the spectral signal from sp^3-bonded carbon).[9,14,23] For glassy carbon, for example, with 4.8 eV excitation the D peak is too weak to be observed (Figure 4). To our knowledge there are no reports of the observation of a D peak in carbon with 4.8 eV excitation. For nanotubes, the D mode shifts by about 38 cm^{-1}/eV

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as the incident laser energy increased from 1 to 3 eV, and for its first overtone, the 2D, the shift is 90 cm^{-1}/eV.[20] With extrapolation from the observed peak positions with 2.4 eV excitation, the peak at 1434 cm^{-1} in the UV spectrum (Figure 2) can be assigned as the D mode.[20] As expected, this peak is weak in intensity.

The shift in the position of the D peak for various carbon materials with increasing excitation energy has been explained by a model involving resonance enhancement due to electronic transitions between the sp^2 carbon π and π^* levels.[14,23] There are electronic transitions near the K point in the Brillouin zone (where π and π^* cross) between the π and π^* levels that have energies in the range of 1 to 5 eV. As the energy is increased the wave vector of the electronic states in resonance with the laser excitation shifts further away from the K point. In this model, the phonons associated with the D peak have a wave vector identical to that of the wave vector of the electronic states in resonance. Thus, in contrast to most Raman scattering processes, the phonons associated with the D peak have a nonzero wave vector. The shift in the phonon wavevector with increasing laser energy causes a shift in the phonon frequency. The shift in the position of the D peak that we observe is in accord with that expected from the phonon dispersion relation. However, recently this model and the theoretical justification for the conservation of wave vector between electrons and phonons have been called into question. A double resonant Raman scattering mechanism has been proposed instead to explain the shift in the D mode frequency in graphite.[24]

We found it difficult to fit the second-order features, but there appear to be two peaks at ~2868 and ~3150 cm^{-1}. These broad peaks can reasonably be assigned as the second order of the D peak, which is often called the G′ mode (and is observed even in the Raman spectrum of pristine graphite that does not exhibit a D peak), and the G tangential modes, respectively. Just like the D peak, with 4.8 eV excitation the G′ peak has shifted so much that it begins to overlap with the tangential modes. The second-order feature likely is composed of several more peaks, but the overlap is so large that it is difficult to decompose it into individual peaks.[21] Other assignments are in Table 1.

We could not observe the radial breathing mode (at 186 cm^{-1} with visible excitation) in the UV Raman spectra. It is possible that at this excitation energy the radial breathing mode is too low in intensity[25] or it may be obscured by Rayleigh scattered light present when the dielectric filters are angle tuned to low wavenumber values. It is typically challenging to observe modes below 200 cm^{-1} with dielectric stack filters.

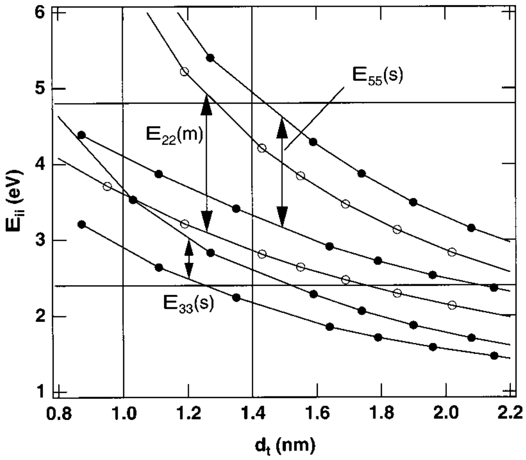

Figure 5. Energy separations ΔE_{ii} for semiconducting (closed circles) and metallic (open circles) nanotubes of various diameters d_t using $\gamma_0 = 2.9$ eV. Only the extremes of each energy band (populated by zigzag tubes) are shown. Values between the vertical lines correspond to the diameters of SWNTs in the present sample. Horizontal lines are drawn at the laser excitation energies 2.4 and 4.8 eV. The ΔE_{22} band of metallic nanotubes overlaps with the ΔE_{55} semiconducting band.

As the excitation energy is varied, most of the Raman modes observed for nanotubes shift due to a diameter selective resonance enhancement.[14,15] There are van-Hove singularities in the 1d density of states that depend on the nanotube diameter and chirality.[14,15] The singularities in the nanotube conduction and valence bands are symmetric upon reflection about the zero of energy. When the energy of the incident excitation is the same as the difference in the energy between a pair of singularities, there is a resonance enhancement of the Raman scattering. The singularities in the densities of states are sequentially labeled by an integer index. Previous tabulations of the energy separations between these singularities did not extend up to the 4.8 eV excitation energy used in the present investigation. Using the equations of reference 26, which take into account a trigonal warping effect, we performed calculations of $\Delta E_{ii}(d_t)$ where d_t is the tube diameter, ΔE is the separation between the mirror image van-Hove singularities in the valence and conduction bands, and i is the singularity index. A 20 × 20 matrix of nanotubes was considered with various values of the n and m indices of the chiral vector.[14] A total of 94 of the tubes were semiconducting and 62 were metallic, excluding tubes of diameter smaller than 0.686 nm ($n = 5$, $m = 5$), the diameter of a tube obtainable by elongating a C_{60} molecule. $\Delta E_{33}(d_t)$ and $\Delta E_{55}(d_t)$ of the semiconducting nanotubes (filled circles) and $\Delta E_{22}(d_t)$ of the metallic nanotubes (open circles) form bands in the region of interest (Figure 5). Although not plotted in Figure 5, there are many ΔE_{ii} values between the upper and lower limits of the bands. At 4.8 eV the $\Delta E_{22}(d_t)$ metallic band overlaps with the $\Delta E_{55}(d_t)$ semiconducting band. Thus, according to this calculation metallic tubes should be resonantly enhanced and observed in the UV Raman spectrum, especially since scattered photons couple strongly with various tubes.[21] However we did not observe evidence of coupling with metallic tubes. Semiconducting tubes should be resonantly enhanced as well, in accordance with our observation. With 2.4 eV excitation, only semiconducting tubes should be observed (Figure 5).

It is more challenging to accurately calculate the gaps between van-Hove singularities in the higher energy range considered here. We are extrapolating calcula-

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tions at lower energies to an energy range that appears to have not been previously considered. Thus, our failure to observe metallic nanotubes suggests that the electronic structure of nanotubes may not be fully understood at higher energies.

The only modes observed in the UV Raman spectrum of the nanotubes are those derived from the modes present in a flat graphene sheet (if we consider the D peak intrinsic to an imperfect graphene sheet). The weaker modes present in the visible Raman spectrum are not observed in the UV spectrum even though the signal-to-noise ratio was sufficient to observe these modes if they had an intensity similar to that observed with visible excitation. This could indicate that with 4.8 eV excitation larger diameter tubes are probed than with 2.4 eV excitation, because the modes not derived from a flat graphene sheet are expected to become weaker as the tube curvature decreases. However, such large tubes would not be expected to be present in our sample. An understanding of why these weaker modes are not present as well as why metallic nanotubes are not observed in the UV Raman spectra will require further theoretical and/or experimental investigation. It may be that the resonance enhancement of the non-graphene modes is considerably reduced with 4.8 eV excitation.

To investigate the damage threshold for SWNTs, we sequentially increased the laser power. When the UV laser power density is increased above 500 W/cm^2, the intensity of the 1569 cm^{-1} peak decreases relative to that of the 1592 cm^{-1} peak (Figure 6) and continues to decrease upon raising the power density to 2500 W/cm^2. After the laser power density is lowered, the UV Raman spectrum remains the same as observed at high power, indicating that the changes induced by irradiation above 500 W/cm^2 are irreversible. Visible Raman spectra of this UV-damaged sample did not exhibit the 186 cm^{-1} radial breathing mode. Only a single, weak peak was present at 1591 cm^{-1}. It is known that atmospheric oxygen binds to nanotubes.[27] Other impurities, such as surfactants used in the nanotubes synthesis or other gaseous species, may as well. These adsorbed impurities may be dissociated by the UV radiation and chemically attack the nanotubes. Thus, the presence of impurities in a carbon sample may be important to its degradation under UV laser illumination during collection of Raman spectra. It is also possible that at high intensities the UV radiation itself directly affects the nanotubes.

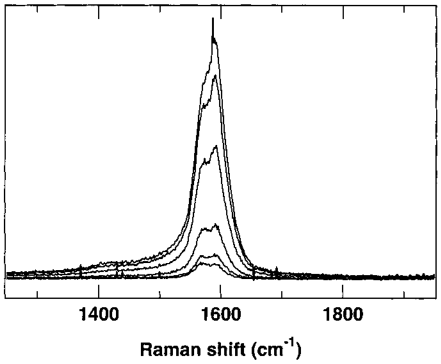

Figure 6. UV Raman spectra of SWNTs as a function of incident laser power. Spectra were recorded at 0.125, 0.25, 0.5, 1.25, 2, and 2.5 W/cm^2 (from bottom to top). The intensity of the 1564 cm^{-1} peak decreases as the incident power is increased.

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