RAMAN SPECTROSCOPY OF SINGLE WALL CARBON NANOTUBE BUNDLE

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Single wall nanotubes (SWNTs) were discovered in 1993 in the carbonaceous by- products from an arc discharge between carbon electrodes in an inert atmosphere [1,2]. Research on the physical properties of these quantum carbon wires have been slowed by the fact that only a few % carbon nanotubes are present in the soot produced by arc discharge methods [3]. Recently, a laser ablation technique was discovered at Rice University which produced over 70% tubes [4]. The diameter distribution for the tubes was consistent with armchair symmetry tubes ranging from (8,8), (9,9), (10,10) to (11,11) [5]. In this paper, we wish to explore the nature of these one dimensional (1D) carbon quantum wires using Raman spectroscopy.

In Fig. 1, we display the Raman spectrum (300 K) for purified, single wall nanotubes[6] obtained in the backscattering geometry using 514 nm Ar laser radiation. For comparison, the calculated Raman spectrum is shown below for n=8-11 armchair tubes. The frequencies were calculated in a phenomenological force constant model using the same C-C force constants used to fit vibrational data for a flat graphene sheet [7]. The theoretical Raman *intensities* were calculated using a bond polarizability model by Subbaswamy and co-workers [8]. It may be noticed that some of the experimental bands are narrow and some are broad. This difference is attributed to an inhomogeneous line-broadening mechanism based on the theoretical observation that particular vibrational modes exhibit a strong tube diameter dependence, while others exhibit a rather weak dependence. Thus, considering that our sample contains a distribution of tube diameters, the Raman lines can be sharp (similar to a linewidth in graphite ~ 6 cm^{-1}) or broad, depending on whether or not the mode frequency is strongly diameter-dependent. The intense line seen at 186 cm^{-1} in Fig. 1 is special. It is identified with the radial breathing mode in which all C-atoms are displaced radially outward in phase. The strong lines observed near 1600 cm^{-1} are related to the intralayer vibrations in graphite which are observed at 1582 cm^{-1}. In the nanotube, the cyclic boundary conditions around the tube waist activate new Raman and IR modes that are not observable in a well-ordered flat graphene sheet or in graphite--this is the first consequence of the one-dimensional

(1D) nature of the nanotube.

The resonant nature of the Raman scattering process is clear from Fig. 2 which shows the dramatic effect on the distribution of line intensity on the frequency (or wavelength) of the excitation laser. The data were all taken at room temperature on the same sample. Shown in the figure are spectra taken with four different lasers at the (low) power densities indicated. A closer inspection of the figure reveals that not only are the intensities changing dramatically with laser frequency, but so are the Raman line frequencies. The former effect is typical of resonant Raman scattering in many solid, gas and liquid samples, whereas the latter is a manifestation of a series of resonances each identified with different tube diameters (e.g., (n,n)). In general, resonantly enhanced Raman scattering occurs when the energy of the incident photon matches the transition energy of a strong optical absorption band [9]. Normally, with variable laser frequency and fixed incident flux the Raman line intensity can vary by several orders of magnitude, but the Raman line frequency is fixed. In the present work, large shifts in frequency are also observed which is quite unusual. The large shifts in Raman line frequency we observe are therefore identified with a diameter-dependent optical absorption which promotes resonant scattering from particular diameter tubes. The shifting frequencies are both the result of the sample being a collection of different diameter tubes and the fact that these different diameter tubes have different optical resonances. In 1D systems it is well know that $E^{-1/2}$ singularities exist in the electronic density of states (DOS). These singularities manifest themselves as spikes in the DOS calculated for n=8 - 11 armchair tubes [10]. The allowed optical transitions for these tubes can be shown to be between filled valence states in spikes (v_1, v_2) below the Fermi energy level E_F to empty conduction band states (c_1, c_2) above E_F. Raman scattering from an (n,n) tube will dominate the spectrum when the laser photon energy matches the energy difference between these $E^{-1/2}$ spikes for that (n,n) DOS. The center of gravity of each Raman band then shifts to
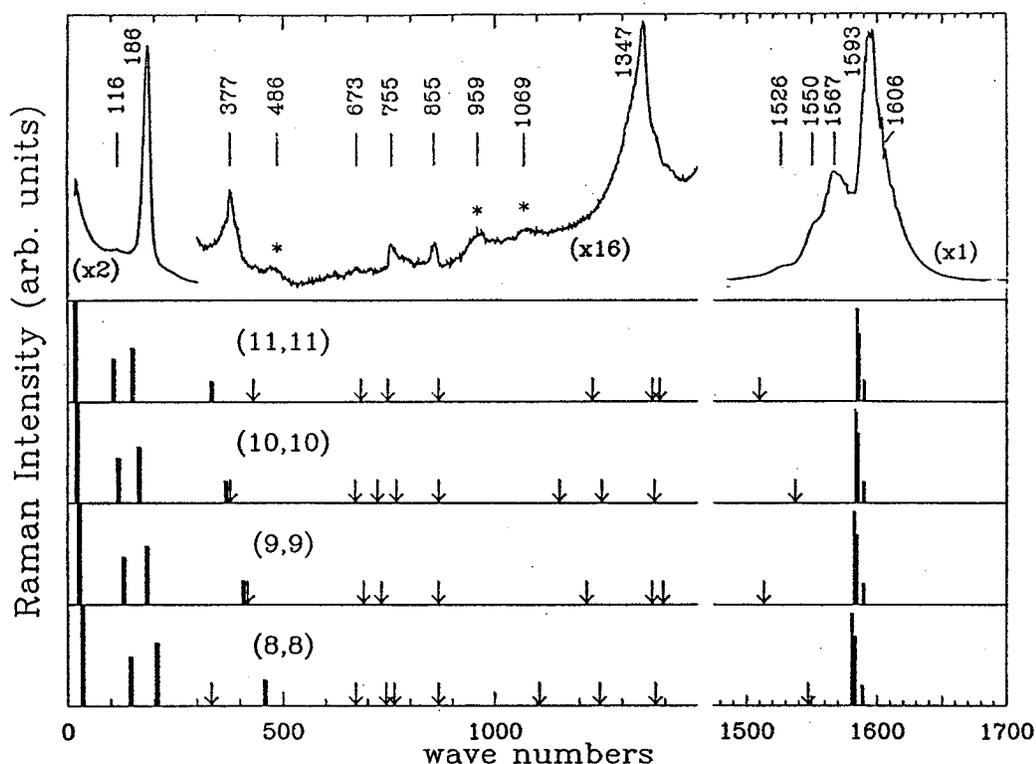
Fig. 1. Raman spectrum (top) of SWNT samples taken with 514.5-nm excitation at ~2 W/cm². The * in the spectrum indicates features that are tentatively assigned to second-order Raman scattering. The four bottom panels are the calculated Raman spectra for armchair (n, n) nanotubes, $n = 8$ to 11. The downward pointing arrows in the lower panels indicate the positions of the remaining weak, Raman-active modes.

the frequency of the (n,n) vibrational mode being resonantly driven by the laser field [10]. Thus, the unusual laser frequency dependence of the Raman spectra of carbon nanotubes shown in Fig. 2 is a direct consequence of 1D quantum confinement effects in carbon nanotubes.

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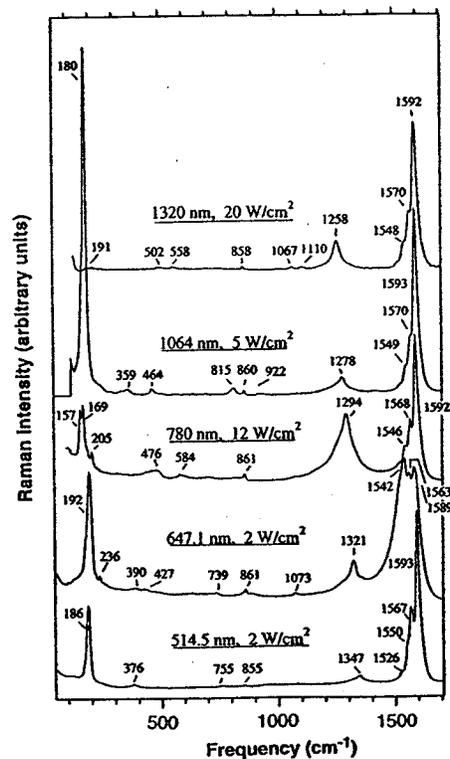
Fig. 2. Room-temperature Raman spectra for purified SWNTs excited at five different laser frequencies.