

Double-Resonant Raman Scattering in an Individual Carbon Nanotube

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Abstract. Experiments on nearly individual carbon nanotubes were performed showing that double-resonance takes place even on the level of an individual tube. Important consequences for the determination of diameter, chirality and defect concentrations are discussed.

Double-resonant Raman scattering has become a well established process describing a number of features of the Raman spectra of sp^2 bonded carbon compounds such as graphite or carbon nanotubes.[1–4] Characteristic for the double resonance, which involves a photon and a phonon both being resonant in the Raman process, is the excitation-energy dependence of the observed phonon energy. For the D -mode in graphite, bundles of single-walled nanotubes and so-called bucky pearls this shift amounts to 50-60 cm^{-1}/eV excitation energy and is much larger than when observed, e.g., in GaAs quantum wells [5] or Ge [6]. The high-energy mode (HEM) at 1590 cm^{-1} ,

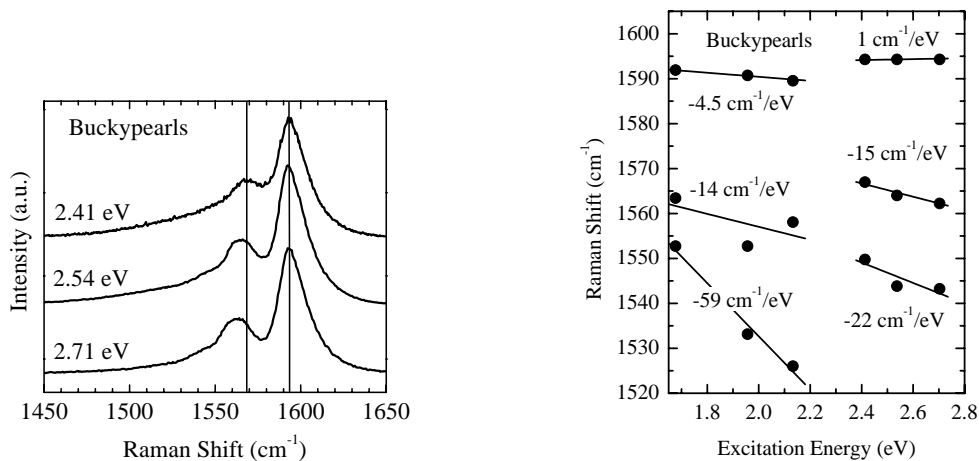


FIGURE 1. *left:* Raman spectra of bucky pearls excited at three different laser energies. Clearly seen is the downshift of the second largest peak for increasing phonon energy. *right:* Peak frequencies in the range of 1.7 to 2.7 eV excitation energy. All peaks have an excitation-energy dependence; it is due to the double-resonance process. The jump in absolute phonon energies and slopes at 2.3 eV is due to a higher electronic band involved in the double resonance as explained in Ref. [2]

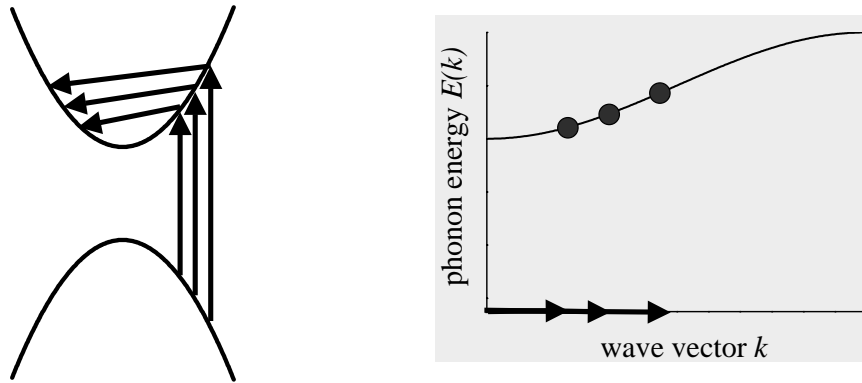


FIGURE 2. *left:* Schematic double-resonant process for a metallic carbon nanotube; different incident phonon energies imply different phonon wave vectors in the double resonance. The defect scattering process and the recombination are not shown for simplicity. *right:* The different scattering vectors correspond to different phonon frequencies.

referred to sometimes as *G*-mode, also displays excitation-energy dependent shifts;[2] they are smaller and sometimes missed in the literature when not evaluated over a large enough energy range.[7] In Fig. 1 we present the Raman frequencies of bucky pearls, which clearly show how the 2nd and 3rd largest peak in the HEM shift to lower energies when excited with increasing photon energies. In contrast to this behavior is that of the *G*-mode in graphite, which is constant in energy for excitations ranging from 1 to 4 eV [8] and thus singly resonant.

In this paper we discuss to which extent the excitation-energy dependence of the Raman spectra in carbon nanotubes is a property of an individual nanotube or whether it is an ensemble property, where specific tubes are selected by the excitation energy for the Raman process. We show with experiments on individual nanotubes that the Raman signal is indeed dominated by the band structure of an individual tube and that the ensemble interpretation may be ruled out as the dominant reason for the excitation-energy dependent shifts in nanotubes. We also discuss the consequences for the interpretation of Raman data as regards the distinction of *metallic* and *semiconducting* spectra, the use of Raman peaks to determine the radius of a nanotube, and its defect concentration.

The double-resonant process is illustrated schematically in Fig. 2. Different wavevectors of phonons corresponding to different incident phonon energies are shown, they scatter the excited electron across the band minimum. For phonons with dispersion, such as the one indicated, the different *k*-vectors correspond to different phonon energies, and hence the excitation-energy dependence of the phonon peak follows naturally. In order to fulfill momentum conservation (both incident and scattered photon momentum are very small) the electron has to be scattered back near to where it was excited. This process is usually ascribed to an elastically scattering defect (*D*-mode and high-energy mode) or a second phonon (2nd order mode scattering). Of course, in a full calculation of the Raman intensity in double resonance the single resonant process (only the photon is resonant) is automatically included; however, its contribution to the total signal is small.[2]

In an alternative attempt to explain the excitation-energy dependence some authors have been focussing on the strength of the van-Hove singularity in the electronic

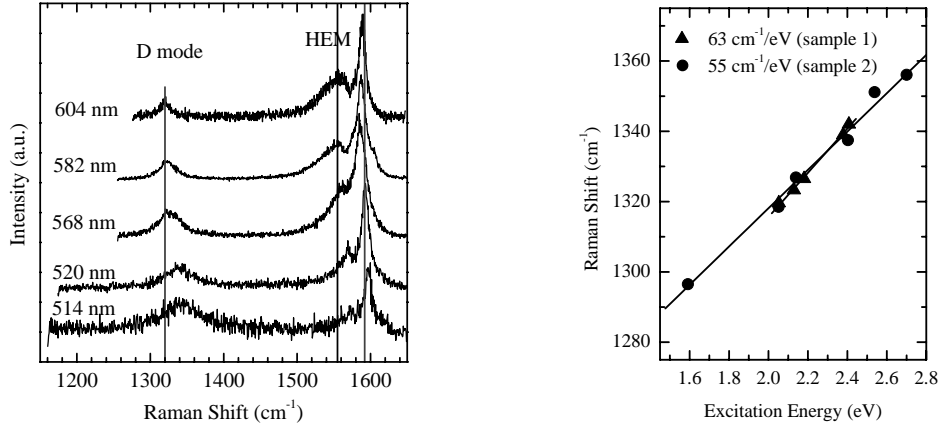


FIGURE 3. *left:* Raman spectra on an isolated or a nearly isolated nanotube; *right:* frequency-dependence of the *D*-mode for two different isolated nanotubes

transition.[3, 9] In this picture the view is taken that a nanotube contributes to the Raman signal significantly only if the optical transition occurs very close to the maximum in the density of states. Varying the excitation energy then selects a different nanotube with a different phonon energy. In this way, an ensemble of tubes with a typical diameter distribution may yield varying Γ -point phonon frequencies.

In summary, in the double-resonant process the excitation-energy dependence reflects the phonon dispersion in an individual nanotube, while in the single-resonant process it resembles a diameter and chirality distribution. Because of the important consequences for the interpretation of the Raman spectra a distinction between these two processes is vital. Obviously, experiment can decide this by measuring the excitation-energy dependence on a single isolated tube, which only in double resonance can have a varying peak frequency in the Raman spectra. In single resonance we would expect only an intensity dependence on excitation energy, but no shift in the Raman frequencies.

For the single-tube experiments we used HiPCo produced nanotubes, which were solution cast onto marked substrates. The density of tubes was ~ 0.5 tubes/ μm^2 . We used various laser lines of an Ar/Kr lasers and a number of frequencies of a dye laser for excitation. The spectra were dispersed by a Dilor XY triple spectrometer and detected by a CCD detector.

The spectra so obtained are shown in Fig. 3. On the left we show the high-energy region and make the following observations: 1) the *D*-mode, as expected for double resonance, shifts continuously to higher energies with 55-65 cm^{-1}/eV (right of Fig. 3). 2) The high-energy mode frequency varies as well, the highest peak first decreases, then increases; the second largest peak increases monotonically. 3) The lineshape of the high-energy mode changes continuously from a more metallic to a more semiconducting appearance. In the low-energy region (not shown) we find, next to the second-order acoustic peak of Si ($\sim 300 \text{ cm}^{-1}$), a strong RBM mode (250 cm^{-1}) which slightly shifts to lower energy (245 cm^{-1}) when increasing the phonon energy and then becomes weaker, disappearing for the highest photon energies shown. There is a small second RBM mode at 200 cm^{-1} which also disappears at large excitation energies. There is

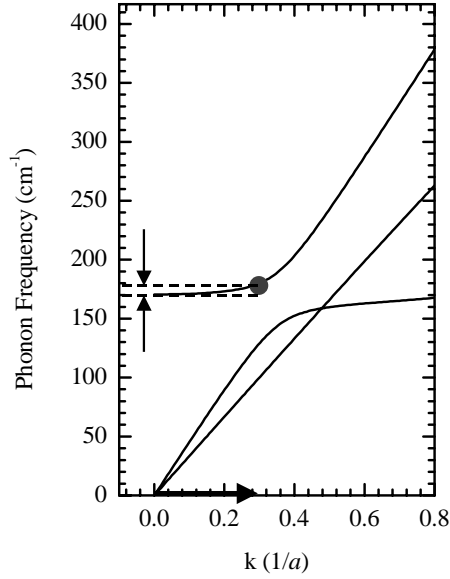


FIGURE 4. Expanded view of the radial breathing mode near the Γ -point of the Brillouin zone of a (10,10) tube. Indicated is the shift of the peak frequency observed in double-resonant Raman scattering compared to the true Γ -point frequency.

thus a single tube or possibly a very thin bundle (two or three tubes) in the experiment shown.

All observations fall naturally into the double-resonance picture and are incompatible with the single resonance interpretation. 1) The D -mode in the individual tube or thin bundle shifts at the same rate as in bulk samples; 2) The high-energy mode resembles the dispersion of a metallic tube. In such tubes the LO-like mode has been shown to soften to about 1550 cm^{-1} . [10] 3) The lineshape change from metallic-looking to semiconducting-looking occurs continuously and is due to scattering near the band minimum ($\sim 2.0 \text{ eV}$) and far away from it ($\sim 2.4 \text{ eV}$). Detailed calculations showing this lineshape dependence on excitation energy are under way. [11]

We discuss now an important implication for the radial breathing mode, which is frequently used to determine with high accuracy the diameter of a nanotube. [9, 12] While the inverse dependence of its frequency is generally accepted (for deviations at small diameter, see Ref. [13]), the Raman peak frequency, if double resonant, however, does not necessarily correspond to the Γ -point frequency of this mode. In Fig. 4 we show on an expanded scale the low-energy, low- k region of the phonon dispersion relations of a (10,10) nanotube. [14] For a typical double-resonant phonon wave vector ($\sim 0.3 \text{ 1/a}$) the dispersion-induced shift corresponds to $\sim 10 \text{ cm}^{-1}$ in this specific tube. Obviously, the shift depends on the phonon dispersion and on the incident photon energy, but it should be clear that the simple RBM frequency-tube-diameter correspondence does not hold to high accuracy when double resonance is the dominant Raman mechanism.

Finally we discuss briefly the role double resonance has for the determination of defect concentrations in nanotubes. Because the first-order scattering is a defect-induced process, both the D and the G mode intensity are a good measure for the defect con-

centration. The second-order D^* -mode, on the other hand, is Raman allowed due to the two phonons of equal and opposite momenta involved. For not too large concentrations of defects its intensity may thus be taken as constant and used to normalize the spectra which could be affected, e.g., by a change in absorption due to the defects. In this way we found a useful relative measure of the defect concentrations in nanotubes.[15]

In summary, excitation-energy dependent Raman experiments on nearly isolated tubes have established double-resonant Raman scattering as the dominant mechanism for carbon nanotubes. Diameter and chirality selective scattering, at least for the D and the high-energy mode, can be dismissed. We showed a number of important consequences for the interpretation of the RMB frequency as related to the tube diameter, for the metallic and semiconducting appearance of the high-energy mode spectra and for the determination of defect concentrations in nanotubes.

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