DOUBLE RESONANT RAMAN SCATTERING IN CARBON NANOTUBES

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The Raman process in solids normally excites phonons with wave vectors $q \approx 0$, since the photon momentum is small compared to the Brillouin zone. Defects in the lattice, a small size of the crystal, or a high optical absorption, however, allow the observation of phonons with large wave vectors in a Raman experiment.[1] We propose that the entire Raman spectrum of carbon nanotubes originates from such an apparent breaking of momentum conservation.[2] Our model does not only reproduce the spectra without further assumptions, but also yields, e.g., the dependence of the Raman frequencies on the excitation energy as found experimentally.

First evidence for disorder induced Raman scattering was the observation of the D-mode, which in graphite was explained by a higher-order Raman process,[3] in isolated nanotubes.[4] For a unique combination of phonon wave vector and frequency two of the intermediate transitions are real yielding a strong Raman signal [the D-mode process for nanotubes is *(2B)* in Fig. 1a]. The other possibility for a double-resonant transition – besides *(2B)* – is scattering across the conduction band minimum *(2A)*. We propose this process as the origin of the high and low-energy Raman spectra in single-walled nanotubes. The calculated cross section for the two fully symmetric optical phonons in chiral and achiral nanotubes perfectly reproduces the experimental Raman spectrum (Fig. 1b): The frequency of the main peak is above the Γ point frequency, the absolute peak positions, the splitting of the most intense peaks, and their relative intensities agree very well. Double-resonant scattering explains the local minimum at the graphite frequency in nanotubes because of the finite q required. We predict the low-energy radial-breathing mode at essentially its Γ point frequency, since the mode is almost dispersionless for small q and the wave vectors involved are much smaller.

The phonon wave vector and frequency fulfilling the double-resonant condition depend on the energy of the incoming light. The measured and calculated upshift of the peak $\approx 1590 \text{cm}^{-1}$ in Fig. 1c results from a positive dispersion for this phonon branch near Γ. At 3.41eV the next optical transition is reached, the double resonance occurs again closer to Γ and hence at lower frequency. Differences between the Stokes and anti-Stokes spectra of nanotubes – as observed experimentally[5] – follow from our explanation. The double-resonant wave vector is larger for the creation than for the annihilation of a phonon. For particular photon energies even the dominant optical transitions are different resulting in a single broad anti-Stokes peak while the Stokes
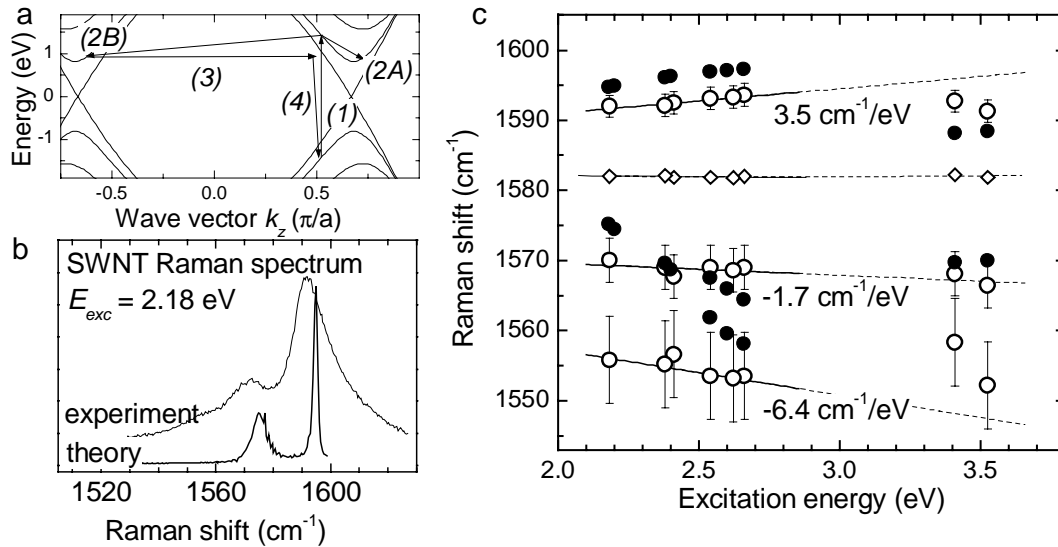
a

Energy (eV)

(2B) (3) (2A) (4) (1)

1
0
-1

-0.5   0.0   0.5
Wave vector k_z (π/a)

b

SWNT Raman spectrum
E_{exc} = 2.18 eV

experiment
theory

1520   1560   1600
Raman shift (cm^{-1})

c

Raman shift (cm^{-1})

1600
1590
1580
1570
1560
1550

3.5 cm^{-1}/eV

-1.7 cm^{-1}/eV

-6.4 cm^{-1}/eV

2.0   2.5   3.0   3.5
Excitation energy (eV)

Fig. 1. **a**: Schematic double resonant Raman process; whereas process
(2B) yields the D mode in nanotubes, the high-energy modes
originate from *(2A)*. **b** Calculated and measured Raman spectrum
of carbon nanotubes. **c** Excitation energy dependence of the high-
energy modes in carbon nanotubes. Hollow circles represent
Raman measurements on bulk nanotube samples; closed circles
were calculated from the double resonant Raman cross section.
For comparison the Raman frequency of graphite is shown by the
open diamonds.

spectrum resembles Fig. 1b. In contrast to other systems the Raman spectra of every
single nanotube thus reflect the vibrational and electronic dispersion for a wide range of
q. Both can be studied by varying excitation energies or selecting different tubes. This
is particularly promising in view of the reported monochiral tubes and single tube
experiments.[4,6]

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