The dependence on excitation energy of the D-mode in graphite and carbon nanotubes

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Abstract. The excitation-energy dependence of the D-mode in graphite is known to originate from a double-resonance Raman process. The same process can occur in the electronic band structure of carbon nanotubes as well. The corresponding calculated D-mode shift is shown explicitely for an individual (11,11) armchair tube. It amounts to 56 cm $^{-1}$/eV and depends on the γ_0 value chosen. The D-mode peak in the nanotube is seven times narrower than in graphite as agrees with experiment.

Graphite was first investigated by Raman spectroscopy by Tuinstra and Koenig in 1970 [1]. They reported the now well known high-energy mode at 1582 cm^{-1} which is of E_{2g} symmetry and hence observed under crossed polarizations of incident and scattered light. They also reported a mode at 1350 cm^{-1} which was not predicted by group theory and which they assigned to a zone boundary mode. Although not Raman active in a perfect crystal, Tuinstra and Koenig, correlating x-ray and Raman data, could show that the signal is due to the finite crystallite size in the sample. They thus identified the mode as defect induced, and it was henceforth referred to as the D-mode, whereas the high-energy Γ-point mode at 1582 cm^{-1} is generally called G-mode.

A little over 10 years later Vidano *et al.* [2] made the surprising discovery that the energy of the D-mode in the Raman spectra depended on the wavelength of the exciting laser line. They found that the D-mode shifted at 48 cm^{-1}/eV and its second-order overtone at 96 cm^{-1}/eV, twice that of the D-mode. For nearly 20 years this experimental finding has remained not understood although it was confirmed a number of times and attempts at explaining it have been put forward. Before reviewing these attempts we mention another apparently mysterious experimental results. In 1998 Tan *et al.* [3] found that the anti-Stokes frequency was larger than the corresponding Stokes frequency by on the order of 10 cm^{-1}. In carbon nanotubes, a material which is related to graphite very much structurally, the D-mode has been observed as well, and it shifts similarly as in graphite. Kastner *et al.* reported 43 cm^{-1}/eV for the D-mode and 89 cm^{-1}/eV for its second-order overtone [4] for multiwalled nanotubes. Single-walled tubes were reported to have 38 cm^{-1}/eV (overtone 90 cm^{-1}/eV) [5] and, recently, 53 cm^{-1} (106 cm^{-1}/eV) [6]. Grüneis *et al.*, after subtracting the average shift of 53 cm^{-1}/eV, reported an oscillation of the D-mode frequency, which they related to an effect of different chiralities in their nanotube sample [6].

Attempts of explaining the energy shift have been put forward at the XVI Conference on Raman spectroscopy by Pócsik *et al.* [7] and by Sood *et al.* [8]. The former base the Raman process on the idea of an incoming resonance which is followed by the

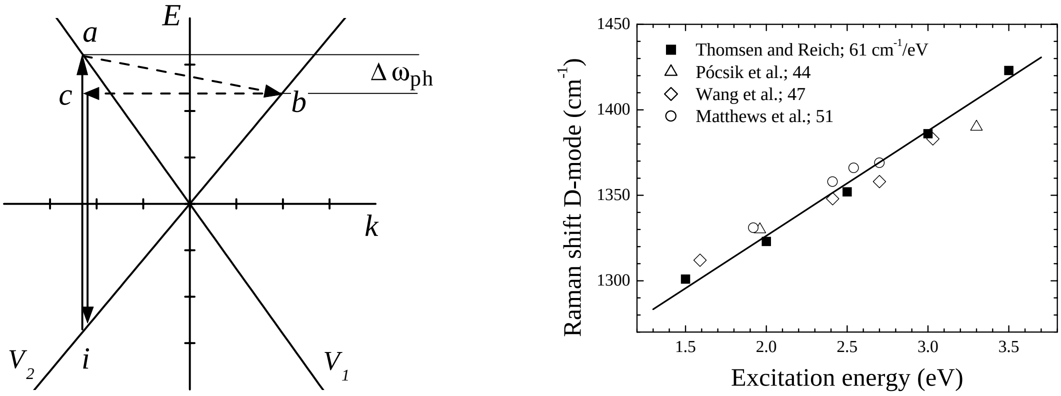

FIGURE 1. Schematic of the double resonance Raman process in graphite. The slopes of the bands, v_1 and v_2 are the Fermi velocities. Shown is the incoming resonance of the first order Stokes process (left). The phonon momentum needed for double resonance apparently depends on the incident laser energy. Through the phonon dispersion this dependence translates into a shift of the D-mode as is compared to various experiments (right) After Ref. [10].

emission of a phonon with the wave vector of the absorbed photon ($\Delta k = \Delta q$). A change in incoming light energy would result in a nearly linear increase of phonon momentum and hence phonon energy in graphite. Unfortunately, this process, which was picked up and later extended by Matthews *et al.* [9], does not conserve momentum for the scattered photon which is no longer a $\Delta k \approx 0$ transition as it must. If a defect is invoked to conserve momentum it remains unclear why $\Delta k = \Delta q$ should be preferred over any other momentum with which a phonon is emitted. Lastly, this idea does not account for the observed differences in the Stokes and anti-Stokes frequencies.

The second attempt, a resonance in parabolic bands as possible in semiconductors, was suggested by Sood. The band structure of graphite however, in the vicinity of the Fermi level, does not show a gap (the electronic bands of graphite cross the Fermi level linearly at the K point), and it is difficult to see how quantitative agreement between experiment and theory could be obtained.

Instead, we put forward the idea of a double resonance between the approximately linear bands of graphite at the K-point. Figure 1 shows the basic idea in one dimension as it actually occurs for one particular slice through the Brillouin zone of graphite (Γ-K-M). For carbon nanotubes the schematic picture is similar except that more (non-crossing) bands and tube-specific selection rules must be taken into account. In fact, in armchair tubes the specific transition shown is forbidden by symmetry and, as we shall show, higher bands contribute to the D-mode signal.

It is obvious that the process is the same for graphite and carbon nanotubes, modified by a chirality-specific change in selection rules and slightly differing material parameters such as γ_0, the overlap integral, or curvature-induced changes in the force contstants of the nanotubes [11]. No fundamentally different mechanism, as recently proposed [12, 13], appears necessary to explain the D-mode shift in carbon nanotubes. The process is that an incoming photon is absorbed resonantly, the excited electron emits a phonon and is scattered, again resonantly, across the mininum (at K, in graphite), then scattered back elastically (not resonantly) to a virtual state where it can recombine with the hole in

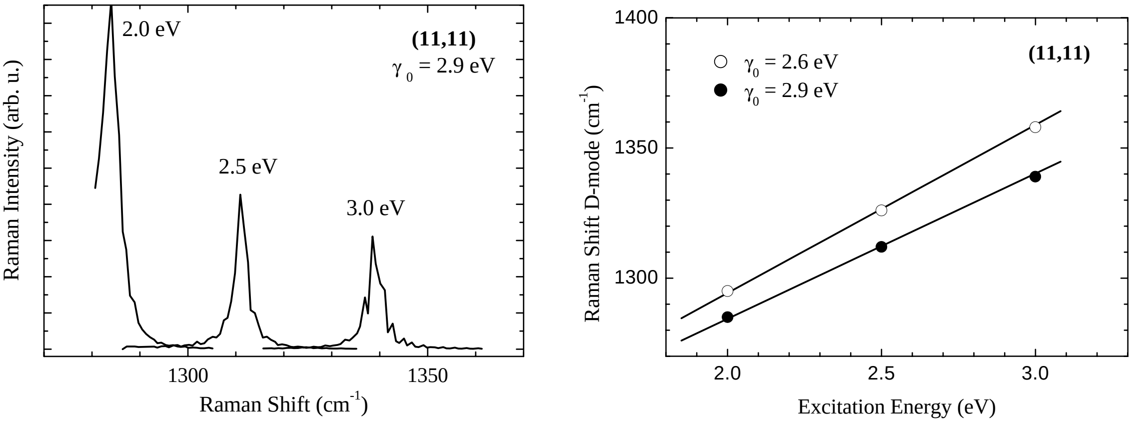

FIGURE 2. Calculated D-mode spectrum of a (11,11) SWNT for three different incident laser energies (left). Dependence on incident laser energy for two different values of γ_0 (right).

a $\Delta k \approx 0$ transition. This process conserves momentum and explains the defect-induced nature of the process. It also explains why a particular phonon q is dominant over all other ones: the resonant scattering of the electron makes a much stronger contribution to the Raman cross section than any other intermediate electron state and hence emitted phonon. The corresponding outgoing resonance is an equivalent process.

In the approximation of linear bands the double resonance condition may be found analytically for

$$q = \frac{E_1 - \hbar\omega_{ph}(q)}{v_2} \quad \text{incoming, and} \quad q = \frac{E_1 - \hbar\omega_{ph}(q)}{-v_1} \quad \text{outgoing} \qquad (1)$$

resonance [10]. Equation (1) has to be solved self consistently because the phonon energy, in general, depends on q. Since the phonon dispersion is small compared to the dispersion of the electronic bands in graphite Eq. (1) converges rapidly to yield the resonant phonon momentum and energy.

A straightforward extension to two dimensions using the tight-binding electron band structure of graphite [14] and a model phonon dispersion yielded a D-mode excitation-energy dependence of 60 cm^{-1}/eV which compared well with the observed values of $\approx$ 50 cm^{-1}/eV of various authors in the literature (Fig. 1) [7, 9, 15]. The difference in Stokes and anti-Stokes frequency is also given by Eq. (1) by exchanging the sign of $\hbar\omega_{ph}$.

As an example of the D-mode's excitation-energy dependence in an (11,11) armchair carbon nanotube we show in Fig. 2 the incoming resonance of the D-mode for three different excitation energies. The calculated spectra were obtained by cutting slices through the electronic and phononic bandstructure suitable for an (11,11) tube (i.e., parallel to the Γ-K-M direction) and integrating the Raman cross section numerically as in Ref. [10] for graphite. Different values of the overlap integral γ_0 affect the slope as well as the absolute value of the D-mode frequency at a particular laser energy (Fig. 2). The so determined energy shift is 65 cm^{-1}/eV for γ_0 = 2.6 eV and 56 cm^{-1}/eV for γ_0 = 2.9 eV For the same broadening parameter (30 meV) as used for graphite the calculated D-mode is much sharper (FWHM = 3 cm^{-1} at 3 eV) than in graphite (20 cm^{-1}). This behavior, which has been seen experimentally [16], comes naturally out of our model because in graphite the D-peak is smeared out when averaging in two dimensions due to the trigonal distortion of the (phonon and electronic) band structure. In nanotubes, the linewidth of the D-mode is more directly related to lifetime effects than in graphite.

In conclusion we have shown that the excitation-energy dependence of the D-mode in graphite and in carbon nanotubes can be explained consistently with a double resonance process in the band structure. We explicitely show the D-mode energy shift in an (11,11) single walled carbon nanotube. The D-mode is much sharper (by a factor of 7) in SWNTs because the trigonal distortion is not averaged over in the 1-D systems. Stokes and anti-Stokes peaks of the same nanotube have different frequencies. The curvature of the nanotube affects the actual D-mode position and slope of a particular chirality tube through its electronic and phononic band structure.

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