Double resonance features in the Raman spectrum of carbon nanotubes

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A weak feature is observed in the Raman spectra of single-wall carbon nanotube bundles at a frequency between 1410 and 1430 cm^{-1} . The band shifts slightly toward lower frequencies as the excitation energy increases from 2.17 to 2.71 eV. An inverse correlation is found between the frequency of the band and that of the average radial-breathing mode, indicating a dependence on the nanotube diameter. The frequency can be extrapolated quadratically to 1487 cm^{-1} for infinite diameter. Two different hypotheses are considered, ascribing the band to modes around either K or M points of the graphite dispersion relations. The appearance of a band close to 1480 cm^{-1} in defective graphite and its dependence with the laser energy, as well as the strong sensitivity of high-frequency K -point modes to structural or impurity defects, support the interpretation of the mode as arising from the upper phonon branch of graphite around the K point activated by the double-resonance mechanism.

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In spite of intense theoretical and experimental efforts, lattice dispersion of graphite and other sp^2 carbons are still controversial, especially as concerns the high-energy branches in the vicinity of the K points. According to different calculations,^{1–7} the LO and the TO branches cross or do not cross along the Γ – K , K – M , and Γ – M directions and thus the energy of the TO phonon at the K point varies from less than 1300 cm^{-1} (Refs. 2 and 3) to 1400–1480 cm^{-1} .^{1,8} Similarly, the LO branch goes along the Γ – K direction down to a frequency of 1250 cm^{-1} (Ref. 1), 1200 cm^{-1} (Ref. 2), or nearly 1500 cm^{-1} , if the LO band does not cross the TO band.³

According to a recent review on lattice dynamics calculations of graphite,⁵ the question of crossing or noncrossing seems to be mainly an issue of the method of calculation. In general, *ab initio* methods predict a crossing of the upper bands both along the Γ – M and Γ – K branches, while in force-constant approaches branches along Γ – M (and also along Γ – K , in Ref. 3) do not cross.⁵ As regards experimental results, they are not very coincident: In the recent work of Maultzsch *et al.*² in single crystalline graphite the high-frequency K mode was found at about 1265 cm^{-1} , a frequency much lower than the 1450–1480 cm^{-1} range found in Raman spectra of certain forms of graphite⁹ and attributed to i -TO modes (i for in plane).^{1,10} Other techniques, such as high-resolution electron energy loss (HREELS) of surface phonons in graphite yield an intermediate value close to 1400 cm^{-1} .¹¹ More reliable data in this frequency region are clearly needed.

In this work we present what we propose is an observation in single-wall nanotubes (SWNT) of the higher-lying band around the K point, activated through the double-resonance (DR) mechanism, with a frequency between 1410 and 1430 cm^{-1} . Another possible interpretation of the band as arising from the high density of vibrational states around the M point is discussed.

In short, DR Raman scattering is a fourth-order process in which two of the processes involved are resonant with real

electronic states.^{1,3,12–14} For first-order phonons, one of the processes is mediated by impurities or defects. Through this mechanism, out-of- Γ vibrations may become visible with intensity higher than usual for just disorder-activated modes. In SWNT, *forbidden* features are expected, besides the allowed and well-known tangential modes at $\nu \approx 1500$ –1600 cm^{-1} (G band), and radial-breathing modes (RBM), at $\nu \approx 100$ –400 cm^{-1} . DR, for instance, is at the origin of the D band at $\nu \approx 1350$ cm^{-1} ,^{12–16} and enhances the intensity of second-order bands, such as those labeled as M^- and M^+ that appear in the range 1700–1800 cm^{-1} (Ref. 17) and those close to 2700 or 3200 cm^{-1} , or even higher energies.^{15,18}

One of the most characteristic manifestations of DR is the variation of the vibrational frequency with the laser energy, E_L , and in fact all the features mentioned above show such a dependence. The activation through DR mechanism of $\mathbf{q} \neq 0$ modes provides a good means of studying the dispersion relations of sp^2 carbons. In general, a good correspondence is found between the frequency of extra features in carbon nanotubes (CNT) and those of phonon branches in the graphite, the differences being attributed to curvature effects.^{6,19} Conversely, Raman frequencies of modes activated through the DR mechanism have been used to fit graphite dispersion relations in force-constant calculations.³

SWNTs were prepared by the arc-discharge method using Ni/Y (4/1 or 2/0.5 at.%) as catalysts in the graphite precursor.²⁰ They form as bundles associated with other carbon phases and metal nanoparticles. Besides the raw SWNT material, SWNTs oxidized in air at temperatures between 300 and 400°C for 1 h have also been used in this work. No structural differences were found between raw and modified materials. The NT diameter range in our samples is 1.30–1.65 nm. Raman experiments were performed with a Dilor XY spectrometer. A microscope with a $\times 50$ objective lens was used; the area explored by the incoming beam being of about 4 μ^2 . Lines of an Ar⁺ laser between 2.41 and 2.71 eV, and a dye laser at 2.11–2.17 eV, were used as ex-

FIG. 1. Raman spectra of SWNT bundles. The long spectrum corresponds to the raw soot material prior to purification and is measured at $E_L=2.41$ eV. The inset shows the evolution of the G -band region with E_L from 2.17 to 2.71 eV, as indicated on the right-hand side. The spectra have been normalized to the same G -band intensity. The sample used for the spectra of the inset had been heated at 300°C for 1 h.

citation light. Power at the sample was always less than 2 mW.

Figure 1 shows a Raman spectrum at 2.41 eV of SWNT bundles. Besides other well-known bands, a weak feature (we shall call it F) is observed at a frequency ν_F between 1410 and 1430 cm^{-1} . By comparing many different spectra, a correlation was found between the appearance of the F feature and the D/G relative intensity: the F band is seen when the D/G ratio is very low, denoting a high degree of NT crystallinity. In other cases, this feature is obscured by the usually more intense D band. On the other hand, the band is not observed in high quality, highly oriented pyrolytic graphite (HOPG), suggesting that, as for the D band, some defectiveness is necessary to activate it.

The band can be observed, at frequencies close to those reported here and always with very weak intensity, in spectra reported in the literature taken on SWNT samples grown in a wide variety of conditions: by laser ablation with Ni/Y catalysts;²¹ by chemical vapor deposition (CVD) with an Fe catalyst;^{17,22} by arc-discharge using as a catalyst Co,²³ Ni-Co,²⁴ Ni-Fe-Co,²⁴ or Ni/Y;²⁵ in purified samples with Ni/Y catalysts,²⁶ etc. It is also found in multiwall nanotubes (MWNT) grown by arc discharge.²⁷

As regards other carbonaceous materials, low intensity features have been detected between 1450 and 1500 cm^{-1} in the Raman spectra of some defective graphites and HOPG.^{9,18,28,29} In Ref. 9 the authors were unable to interpret this feature as any combination of modes. The remarkable dependence of the frequency with elaser E_L ($\Delta\nu = -83 \text{ cm}^{-1}/\text{eV}$) remained also unexplained. The band was attributed in Refs. 1 and 10 to high-frequency i -TO modes activated by DR.

In fullerene C_{60} the pentagonal “pinch” mode is seen between 1458 and 1470 cm^{-1} .^{30,31} This frequency is quite higher than ν_F and, moreover, fullerenes would not explain the unambiguous dependence of ν_F on NT diameter shown below. The possibility that F is a Raman allowed, weakly active mode is also excluded, since the intensity predicted for such modes by a bond polarizability model is

FIG. 2. (a) The frequency of feature F , ν_F , is plotted against the average frequency of the radial-breathing mode, ν_{RBM} , indicating that a correlation exists between ν_F and the NT diameter. The dashed line is the fitting of the data to a quadratic expression of the form $\nu_0 + C' \nu_{\text{RBM}}^x$ with $\nu_0 = 1487.4 \text{ cm}^{-1}$, $C' = -0.029331 \text{ cm}^{0.96}$, and $x = 1.96$. (b) Correlation between ν_F and the frequency of the lowest component of the G band, G^- . The dashed line is only a guide for the eye. Data were taken at 2.41 eV.

negligible.³² All these observations support the intrinsic origin of the F band as arising from NT.

The inset in Fig. 1 shows the 1200–1800 cm^{-1} region as a function of laser energy from 2.17 to 2.71 eV. The spectra have been normalized to the same G -band intensity. The shift of D and M^- , M^+ bands upon changing the excitation energy is explained by the DR mechanism.^{12,15,17} The F band, on the contrary, shifts down very slightly with increasing excitation energy ($\Delta\nu \approx -10 \text{ cm}^{-1}$ from 2.17 to 2.71 eV).

As shown in Fig. 2(a), an inverse correlation exists between ν_F and the average RBM frequency, ν_{RBM} : the higher ν_{RBM} (the narrower the tube), the lower ν_F . This trend is similar to that of some high-frequency bands, such as the D band (Ref. 33) or the circumferential component of the G band, G^- .^{22,34} Figure 2(b) shows the correlation between ν_F and ν_{G^-} .

The frequency of diameter-dependent excitations is usually fitted to a law of type $\nu = \nu_0 + C/d^x$, where, for high-frequency bands, ν_0 is interpreted as the graphite value since it would be obtained for infinite diameter.³³ The dashed line in Fig. 2(a) gives the fit to such a dependence or, more precisely, to $\nu_0 + C' \nu_{\text{RBM}}^x$, where we have introduced the relation $\nu_{\text{RBM}} \propto 1/d$. Fitting parameters are $\nu_0 = 1487.4 \text{ cm}^{-1}$, $C' = -0.029331 \text{ cm}^{0.96}$, and $x = 1.96$.

Two aspects can be pointed up from the latter results. First, the exponent obtained from the fitting (1.96) is very close to that of G^- , for which a value of 2 has been given in

Ref. 22 (although 1.4 in a subsequent work, Ref. 34) suggesting that both features involve closely related vibrations. We note that, according to the calculations of Ref. 6, circumferential vibrations, among the tangential bands, are expected to be the most sensitive to NT diameter. The other remarkable fact is the close similarity between ν_0 (1487 cm^{-1}) and the value found in some Raman experiments on graphite ($\approx 1480\text{ cm}^{-1}$ for $E_L=2.41\text{ eV}$).

Two approaches are usually followed to attribute vibrational features of CNT. One is the *ab initio* calculation of the phonon frequencies and density of states. The other approach, the folding method, assumes that, to a first approximation, NT vibrations will not be very different from those of a graphene sheet or from graphite. Then, the graphite dispersion relations are folded along appropriate directions to account for the one-dimensional (1D) character of CNT. This procedure has been widely used to explain the frequencies and symmetries of allowed modes, mainly in the high-frequency region. In the case of forbidden features a first step is to look at the graphite dispersion relations for modes having similar frequencies, and then propose a mechanism for the activation of such mode. Up to now, all forbidden features (and some allowed ones) of the Raman spectra of CNT are seen to involve the DR mechanism.

Following this procedure, we look for graphite modes close to 1420 cm^{-1} , either in lattice-dynamics calculations or within experimental data. According to different calculations, modes close to 1420 cm^{-1} can be found either around the K - or M points (see Ref. 5 and references therein). As mentioned above, experimental data on high-frequency K -point modes show great dispersion, due to the use of different techniques or, more likely, to the high sensitivity of those modes to structural defects, impurities, or even the carbon-carbon distance, as suggested in Ref. 5. The observation of a Raman band around 1480 cm^{-1} in some defective graphites, attributed to i -TO modes close to the K point,^{1,10} and its dependence with E_L , clearly indicative of DR being involved, lead in a natural way to consider these modes to be the origin of the F band in CNT, and DR as the mechanism activating it. Moreover, the diameter dependence of ν_F (Fig. 2) is such that it tends, for infinite diameter, toward a value very close to 1480 cm^{-1} . We then consider first this possibility and, later on, an alternative one based on modes around the M point.

Two strong indications of DR being involved in the activation of a given phonon are the frequency shift of the band upon changing the laser energy ($\Delta\nu/\Delta E_L$) and a difference between the Stokes and anti-Stokes (AS) positions. Unfortunately, in spite of long accumulation times, the F band could not be detected in the AS spectrum, but there is experimental evidence of such a behavior in the Raman spectrum of MWNT reported in Ref. 27: While the F band is found at 1430 cm^{-1} in the Stokes spectrum at $E_L=1.58\text{ eV}$, its AS frequency is 1412 cm^{-1} at the same excitation energy, implying a negative dispersion, as in graphite.⁹

The dispersion of the F band is small and negative, $\Delta\nu/\Delta E_L=-18.5\text{ cm}^{-1}/\text{eV}$. This value is much smaller than that of the 1480-cm^{-1} band in PG ($-83\text{ cm}^{-1}/\text{eV}$),⁹ but close to the value predicted for the i -TO band in Ref. 1 ($-11\text{ cm}^{-1}/\text{eV}$). However, the dispersion of any diameter-

dependent band in NT bundles must be taken with precaution, since it involves two different contributions: One is due to the selective resonant excitation of different NT as E_L runs along the Kataura plot;³⁵ the other is due to the DR mechanism, according to which the phonons matching the resonance condition vary as E_L is varied. The first contribution is absent in graphite or isolated NT, but can be important in NT bundles if the diameter distribution is wide. As far as one remains within a given E_{nn} band of van Hove singularities, lower diameters are resonantly excited when E_L is increased. Since ν_F decreases for decreasing diameter (see Fig. 2), lower ν_F , on the average, would be expected for increasing E_L , as observed. However, the situation is not so clear when the NT content is such that several E_{nn} transitions can be excited. From the diameter range present in our samples ($1.30\text{--}1.65\text{ nm}$), and for E_L between 2.1 and 2.7 eV , it derives that E_{33}^s and E_{44}^s transitions may be excited,³⁵ but the average diameter being excited, d_m , does not show a monotonic behavior: From 2 to 2.2 eV only E_{33}^s transitions are excited, and d_m decreases. As E_L approaches 2.4 eV , the E_{44}^s transitions of wider NTs are progressively excited and d_m shifts upwards. This holds up to about 2.6 eV ; beyond this energy narrower tubes are excited in both E_{33}^s and E_{44}^s bands, which yields again a down shift of d_m . This nonmonotonic behavior of d_m is observed in the RBM spectrum, but not for the F band, suggesting that these effects are averaged out due to the peculiarities of the DR mechanism: two resonant processes instead of only one, chirality dependence of the excited vibrational frequency. Another important detail is that the outgoing resonance condition is different for RBM and for F modes, as their frequencies differ by 0.16 eV , so that, in fact, different NT are resonantly excited when measuring each of these regions. From our data we can only say that, as regards the dispersion effect, our results are compatible with the prediction of DR, though they do not constitute, by its own, a proof of that mechanism. Only measurements in isolated SWNT will be able to separate the spring and DR contributions to the F -band dispersion.

We now consider another possible interpretation of feature F as coming from the TO branches around the M point, whose flatness results in a very high density of states at frequencies about 1400 cm^{-1} . The F band might come from this high density of states, without DR being involved at all. However, noncenter modes are not Raman active unless there exists a mechanism that brings them to zone center, either through zone folding or through periodicity breaking. Moreover, even if at Γ point, a high density of states does not guarantee a high Raman activity. In the case of CNT, the M point is not systematically folded to Γ and, even when it is, it does not provide Raman-active modes, so that another mechanism must be proposed to activate those modes. M -point phonons cannot participate in DR processes for laser energies between 2 and 3 eV , since electronic gaps at the M point exceed 5 eV , so that DR is excluded. One possible mechanism would be the presence of defects in the NTs, but without the concurrence of DR, and due to the low laser power used in the experiments, its activity would be probably very low. We note again that the F band is not observed in nondefective HOPG, thus confirming that some defectivity is required. If the band came from modes around the M

point, no dispersion with E_L would be expected, neither for graphite nor for NTs.

In summary, considering the ensemble of experimental results presented here for SWNT bundles and those reported in other works for graphite and MWNT, we attribute feature F as coming from high-frequency bands of the graphite dispersion relations around the K point, activated by the DR mechanism. If this attribution is correct, it provides one more confirmation of the idea that all forbidden bands observed in Raman spectra of CNT are activated through DR. Resonance

experiments in isolated NTs are clearly needed to verify the dispersion behavior of the band. As regards phonon energies we conclude that fitting graphite dispersion relations to experimental data must be done with great care, since the dispersion of values found for different materials and techniques may yield somewhat erroneous conclusions.

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