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Raman characterization of carbon materials under non-hydrostatic conditions

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ABSTRACT

Raman spectroscopy experiments on double-wall carbon nanotube and highly oriented pyrolytic graphite (HOPG) samples subjected to non-hydrostatic conditions have been conducted in anvil cells to study the effect of the pressure on the bands assigned to defects. Typical diamond anvils used in high pressure experiments have been substituted by moissanite (6H-SiC) and sapphire (Al_2O_3) anvils to allow the observation of the D band (around 1350 cm^{-1}) and the second-order Raman scattering without interference. We demonstrate that Raman experiments at high pressure provide unique information to probe the mechanical behaviour of carbon materials (CMs). We also show that this can be also a powerful technique to assign controversial spectral features such as those appearing in the second order region of the spectra of CMs. In HOPG samples we find that the D´/D band intensity ratio is independent of pressure. The results indicate that an increase of non-hydrostatic stresses on HOPG generates graphitic domains with sizes around 20-30 nm when the sample is recovered to room conditions.

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1. Introduction and background

A new interdisciplinary research in material science has arisen around of carbon nanotubes and other carbon materials (CMs) due to their remarkable mechanical, electrical and optical properties. However, the external aspect of most CMs is very similar, making essential a complete and unambiguous characterization of a given sample. One of the most extensively used characterization technique for CMs is Raman spectroscopy. Apart from its non-destructive nature, it is very sensitive to structural disorder that breaks the lattice symmetry in graphite. The Raman spectrum of HOPG at room conditions is well known,[1] and this will be our reference to compare the spectra of other CMs. However, the physical origin of some Raman features is still the subject of recent and significative works. Such is the case of the so-called D and D´ bands, related to disordered carbons, that appear in all CMs,[2] except in single crystal graphites and graphene.[3] That is the reason why the D band has been used to determine the sizes of graphitic crystallites in natural graphite,[4] carbon fibers and other graphite-derived materials like carbon nanotubes.

High pressure research has provided essential information in CMs. Lattice parameters,[5] deformation potentials,[6] Grüneisen parameters[7] and phase transition,[8] among others, have been studied for some of these materials using high pressure techniques. So high pressure experiments can provide new information about the origin of the D band, since pressure changes the selection rules, so modifying the observed Raman spectrum. The ultimate advance in high pressure experiments begins with the introduction of the diamond anvil cell. The basic principle of the cell is that a force (1 tonne) applied over a small area (1 square milimeter) results in a large stress (around ten thousand atmospheres). The force is applied by the approximation of the two anvils between which the sample is located. Detailed reviews have appeared concerning the design and operation with the diamond anvil cell.[9-12] In Figure 1 we present a schematic picture of the anvil cell designed and used in our laboratory. One of the anvils is centered on a support which allows the in-plane alignment and the other anvil is placed on a sliding piston.

The most common anvil in high pressure experiments is diamond due to its hardness and optical transparency to radiation (allowing measurements of Raman and luminescence spectroscopy or X-ray diffraction, among others). However, for Raman experiments on CMs the intense band of diamond at 1333 cm^{-1} completely overlaps the D band of the sample, as we render in Figure 2a. That is the reason why, until very recently,[13] there was no information about the behaviour of the D band with increasing pressure. In ref. 13 we used moissanite (hexagonal polytype of SiC) anvils, so the only interference concerns the second order Raman spectrum of moissanite, which appears in the same spectral range than the intense G band of CMs (see Figure 2b); then, a proper subtraction of the contribution of moissanite will allow access to the whole spectral range of interest. Sapphire anvils have already been used to perform Raman spectroscopy of diamond under high pressure.[14] When using synthetic sapphire anvils a slight luminescence background from the anvils may appear due to the presence of Cr^{3+} impurities from the synthesis process (see Figure 2c), but this effect can be conveniently minimized by using an appropriate excitation wavelength.

Available experiments on CMs under pressure have been usually developed under hydrostatic conditions. In hydrostatic experiments the sample must be immersed in a pressure transmitting medium (alcohols or noble gases), together with a pressure marker, usually a ruby microcrystal, whose luminescence shift provides the pressure. Pressure medium, sample and pressure marker are contained inside a hole practiced on a thin metallic gasket.

We are interested in the less known behaviour of CMs under non-hydrostatic conditions. This presents some advantages and drawbacks. The advantages are that no additional signals (pressure medium and pressure marker) interfere with that of the sample and that we prevent interaction between the pressure medium and the sample. The latter issue is quite important, since previous studies reveal differences in the pressure behaviour of the DWCNTs depending on the pressure transmitting medium used (alcohols, argon, oxygen). These differences have been explained by different local ordering and adsorption of the molecules of such substances around of the wall of the carbon nanotube, meaning a different pressure transmission to the tubes.[15]

In non-hydrostatic experiments the sample is placed directly onto the anvils, as shown in Figure 3a. In this configuration no pressure marker can be used, so the pressure must be estimated by indirect methods. As the anvils become closer an effective stress gradient is generated inside the cell. The stress profile can be compared with the uniform pressure generated under hydrostatic conditions, as shown in Figure 3b. In our case, the stress gradient is enhanced by the fact that the culet of the anvils was slightly rounded off in order to avoid the breakage of the anvils as they get in contact when we compress the CM samples. This allows us to perform measurements in several locations on the sample at different stress without changing the force applied to the cell.

As we mentioned above, we are interested in studying the behaviour of CMs under non-hydrostatic extreme conditions of pressure. We propose the use of moissanite and sapphire anvils and we shall demonstrate that both anvils are suitable for this purpose and provide information about some Raman features of CMs not observed until now. Of course, the use of softer anvils will limit the maximum pressure reachable on the anvil cell. Here we shall analyze results on DWCNTs and HOPG up to 13 GPa.[13]

2. Experimental

Our experimental set up is based on a gem (moissanite or sapphire) anvil cell coupled to a micro-Raman spectrometer.[14] For the excitation of the Raman spectra of sample we used either an air-cooled ILT argon ion laser operating at 488.0 nm or a solid state laser operating at 532.0 nm. The laser light is focused on to the sample by using a tiny focussing lens providing a laser spot at the sample of about 20 µm. The Raman signal is collected in near backscattering geometry using a 10x Mitutoyo long working distance objective coupled to a 10x Navitar zoom system and focused on to the slit of an ISA HR460 monochromator (with a grating of 600 grooves mm^{-1}). A liquid nitrogen-cooled CCD detector (ISA CCD3000, 1024 x 256 pixels) is used to record the spectra, using a small slit width (30 µm). The optical system is always calibrated with a standard neon discharge lamp. The spectral resolution of the reported spectra is close to 4 cm^{-1}.

3. Results

3.1 Spectra analysis

The Raman spectra recorded for samples placed in anvil cells usually present two contributions: one from the sample and the other one from the anvil. That is the reason why, in our experiments, before the analysis of the spectra, a subtraction of the anvil background is required. In Figure 4a we show the Raman spectrum of a graphite sample inside the moissanite anvil cell as it is measured. As it can be observed, for this anvil the interfering spectral features between 1200 and 2000 cm^{-1} must be subtracted as follows. Firstly the sample and moissanite spectra must be properly scaled by making coincident the intensity of the two spectra in the 1750 to 2000 cm^{-1} spectral region, where there is no overlapping between the features of the sample and those of the moissanite anvil. This process can be performed numerically, but it can be also programmed in most spectral analysis software packages. The resulting spectrum for a HOPG sample is exemplified in Figure 4b. Both D and D´ bands, as well as the second order bands, are clearly observed in the spectrum. With sapphire anvils the background subtraction is quite straightforward, since only weak sloping backgrounds are involved (see Figure 4c). As we can observe the sapphire luminescence background appears above 2500 cm^{-1} at 488 nm excitation. The baseline can be corrected either using a Lorentzian-like tail fit or by direct subtraction of a reference spectrum of sapphire. In Figure 4d we present the Raman spectrum of the graphite sample once the background has been removed. From the comparison between the two background-corrected spectra, Figures 4b and 4d, we demonstrate that the subtraction of moissanite contribution can be effectively carried out yielding consistent results.

For the analysis of the background-corrected spectra we first calculate the second derivative of such spectra, and we locate the center of the most intense bands of the spectra as the minima in the second derivative spectrum. This procedure is more convenient because the minima are much sharper than the shoulders or weak features of the original spectra. In Figure 5 selected examples for samples of DWCNT and graphite are shown. Each spectrum is split into several Lorentzian contributions centered at the frequencies obtained from the second derivative analysis. The profile analysis optimizes the fit to the corresponding Lorentzian functions at fixed frequencies, so obtaining the area and linewidth of the contributions. In Figure 5a and 5c the different Lorentzian functions (see figures for the followed assignment) which compose the regions between 1200 and 1700 cm^{-1} and 2300 and 3300 cm^{-1} for the DWCNT and graphite samples are shown.

3.2 High Pressure behaviour

As we mentioned above, the profile analysis of the spectra provide information of frequencies, linewidths and intensities of the Raman features. We shall first discuss the frequency analysis of the high pressure Raman spectra of DWCNTs. In Figure 6 we present data obtained by using the sapphire anvil cell. We plotted the frequency of the G_2 band as a function of the frequency of the D band, these results show the following behaviour: $\omega_{G2}(cm^{-1}) = 239.6 + \omega_D\ (cm^{-1})$, in excellent agreement with our previous results conducted in a moissanite anvil cell,[13] where the difference between D and G_2 frequencies remains constant in about (237 ± 4) cm^{-1}. The present result confirm what we already observed: compression has a negligible effect on the frequency difference between D and G_2 bands over the whole pressure range, indicating that very likely both modes belong to the same phonon branch.

High pressure Raman spectroscopy can be also a powerful technique to assign controversial spectral features as those appearing in the second order region of the spectra of CMs. As an example, in Figure 7 we plot the frequencies of a DWCNT sample measured using moissanite anvils. We analyze the bands appearing at 2690 cm^{-1} (2D band), 2930 cm^{-1} (D + G band) and 3165 cm^{-1} (2G band). Thus, if we plot the frequency of the so-called 2D band as a function of twice the frequency of the D band we observe that, except for a small and constant anharmonicity, the results confirm that this band corresponds to the double resonance of the D band. We have performed a similar analysis for the D+G band by plotting its frequency as a function of the sum of frequencies of the D and G_2 bands. Finally, we plot the frequency of the $2G_2$ band as a function of twice the frequency of the G_2 band, providing an unambiguous assignment of this Raman feature.

For HOPG samples we have conducted similar experiments. In this case, we briefly show the analysis of the band intensities of the first order Raman spectra. In Figure 8a we present some Raman spectra at selected high pressures measured at different locations inside the sapphire anvil cell. As we can observe, depending on the location of the sample (meaning different pressure as was explained in Figure 3), the intensities of the D and D´ bands relative to the G band intensity show notable changes. Their intensity ratio correlates very well, as confirmed in Figure 8b, which is in good agreement with the observations of Cançado el al.,[16] although our results present a smaller ratio coefficient. It is interesting to point out that, according to our results, the D´/D intensity ratio is independent of pressure. A result not previously reported to date.

Finally, an interesting observation that merits discussion concerns the size of the graphitic domains resulting after a strong non-hydrostatic compression of HOPG. The correlation between crystallite sizes of graphitic samples and the intensity ratio between D/G and D´/G bands is well established among the scientific community dedicated to the study of CMs (for instance, see ref. 16 for details). Thus, according to our present results, an increase of non-hydrostatic stresses on a HOPG sample generate graphitic domains with crystal sizes down to about 20-30 nm when the sample is recovered to room conditions. To the best of our knowledge, if confirmed, this represents the first report for generation of carbon nanodomains using non-hydrostatic compression of a CM. Further experiments are currently conducted to analyze this effect and to verify whether there exists a relation between compression and size.

4. Conclusions

The purpose of this work was to validate the suitability of moissanite or sapphire to characterize CMs by Raman spectroscopy in experiments under high pressure conditions. We presented examples on different CM samples subjected to non-hydrostatic conditions. The interest of such measurements is that they provide key information about the mechanical properties of CMs, as well as they response to extreme external compression. In addition, here we have verified that these experiments can be used to resolve unambiguous spectral assignments on the basis of the pressure coefficients of the bands. We have demonstrated that we can obtain information about the pressure behaviour of some key Raman features of CMs that cannot be observed in typical diamond anvil cells. Despite the lower hardness of these gem substitutes, we provide experimental evidence that pressures/stresses exceeding 10 GPa can be routinely reached using standard anvil cell designs.

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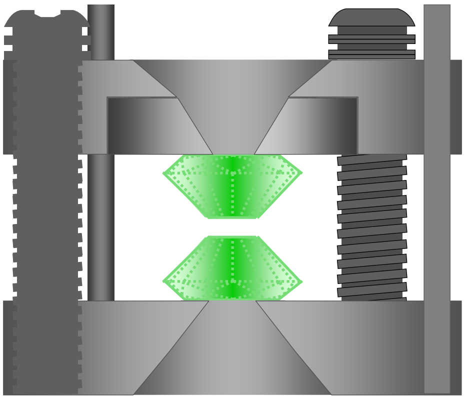

Figure 1. Cut-across view of the anvil cell used in this work. Both moissanite and sapphire anvils were used. The samples were directly compressed between the anvils in order to perform our non-hydrostatic experiments. The pressure was generated by acting on the screws shown in the figure.

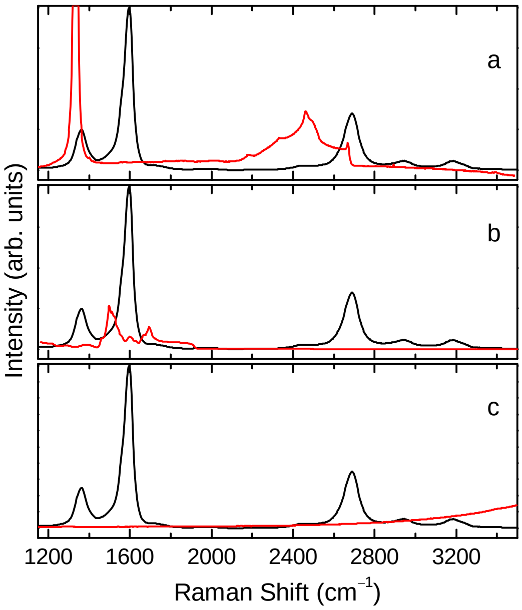

Figure 2. Comparison of the Raman spectrum of a compressed DWCNT sample (black lines) for the region between 1150 and 3500 cm^{-1} with: (a) the Raman spectrum of diamond; (b) the second order Raman spectrum of moissanite (6H-SiC); and (c) the luminescence tail of synthetic sapphire. All spectra were recorded at 488 nm excitation wavelength.

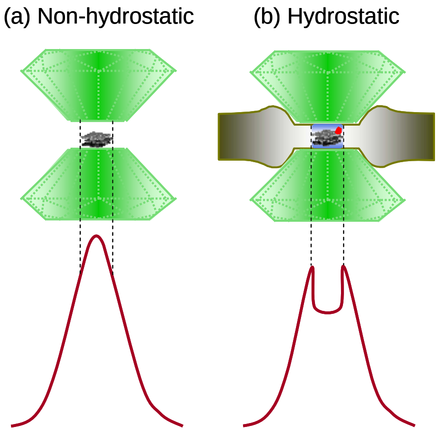

Figure 3. Pressure gradient across the anvil cell in experiments under (a) non-hydrostatic and (b) hydrostatic conditions. Notice that the pressure remains constant across the sample in the hydrostatic case. In (b) the hydrostatic medium and the ruby chip used as pressure marker (see text) are also depicted.

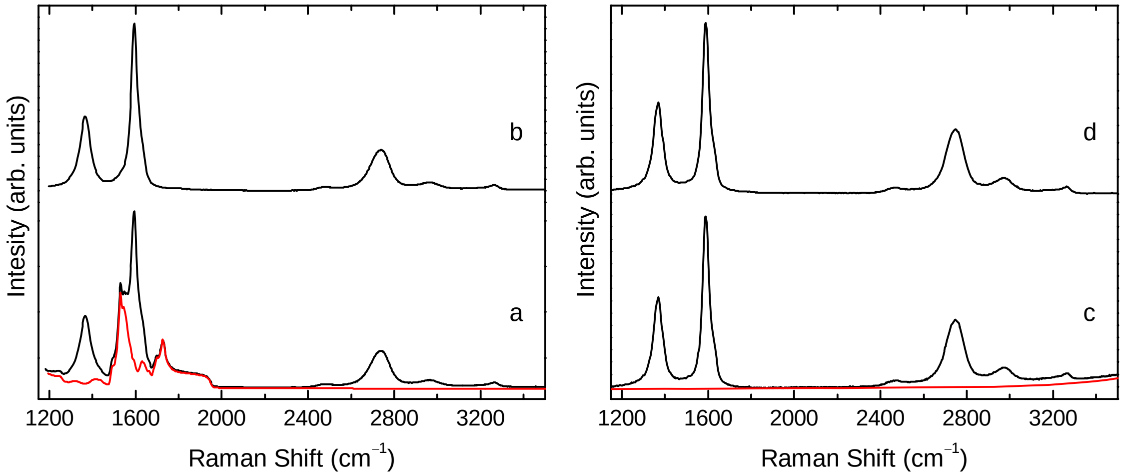

Figure 4. (a, c) Measured Raman spectra of two graphite samples (black lines) by using moissanite (left) and sapphire (right) anvils. Both samples were first compressed between the anvils and then spectra measured after removing the load. In both figures the background contribution from the anvils is shown as a red line. (b, d) Background-corrected Raman spectra of the two HOPG samples.

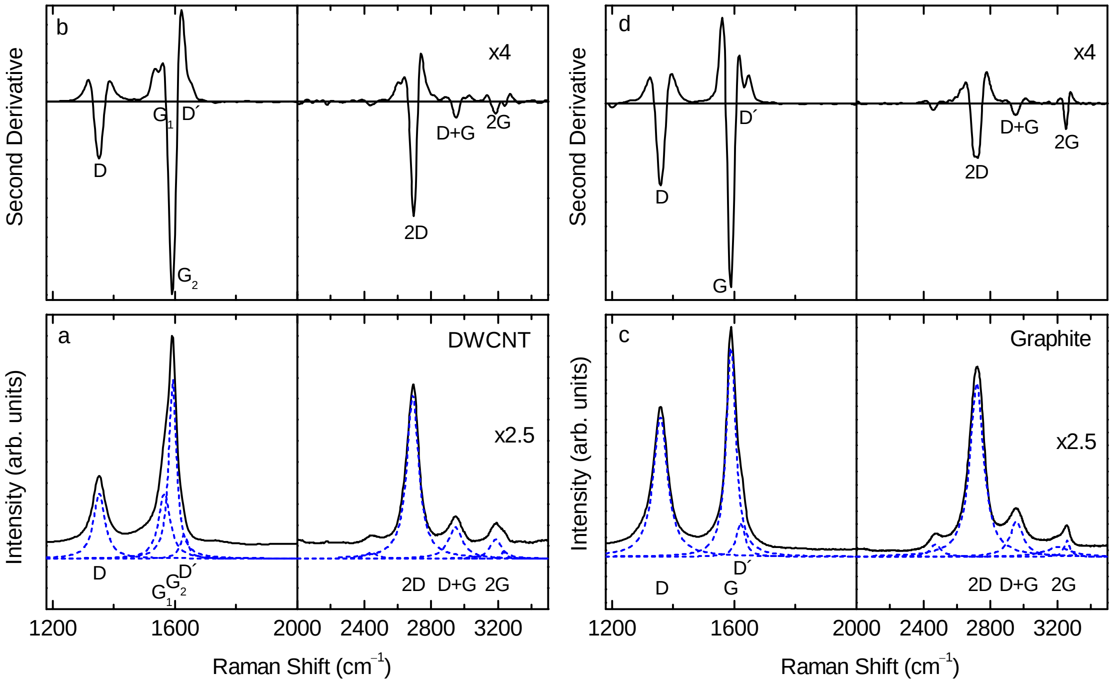

Figure 5. (a, c) Background-corrected Raman spectra of DWCNTs (left) and graphite (right). For each spectrum is also shown the Lorentzian functions in which we split the bands appearing in the spectral regions between 1200-1700 cm^{-1} and 2300-3300 cm^{-1}. We follow the band notation introduced by Puech et al.[17]for the first order spectrum and the assignment of Thomsen and Reich[18] for the second order spectrum. (b, d) Second derivative of the Raman spectra.

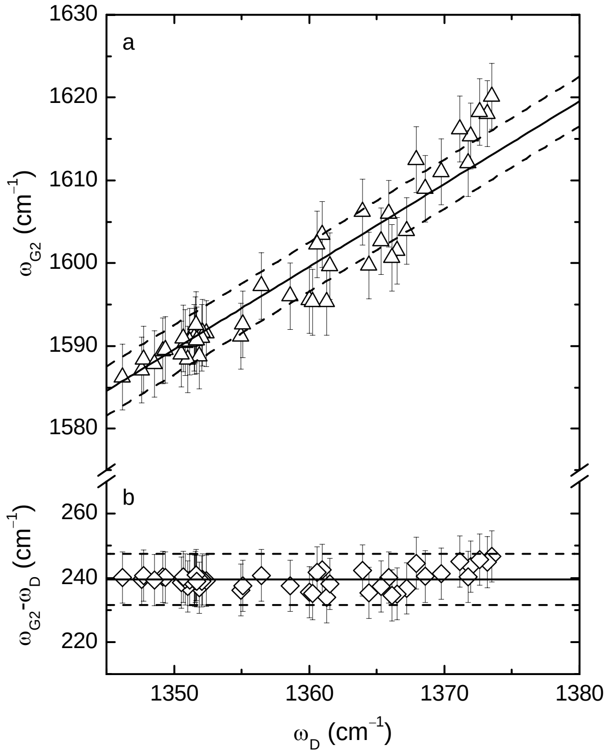

Figure 6. (a) Raman frequency of the G_2 band as a function of the frequency of D band for DWCNTs under non-hydrostatic conditions in a sapphire anvil cell. Solid straight line corresponds to $\omega_{G2}(\mathrm{cm}^{-1}) = 239.6 + \omega_D\ (\mathrm{cm}^{-1})$, in excellent agreement with recent measurements[13] on DWCNTs by using moissanite anvils. Dashed lines represent the estimated uncertainty. (b) Frequency difference between the G_2 and D bands at different compressions. Dashed lines represent the estimated uncertainty.

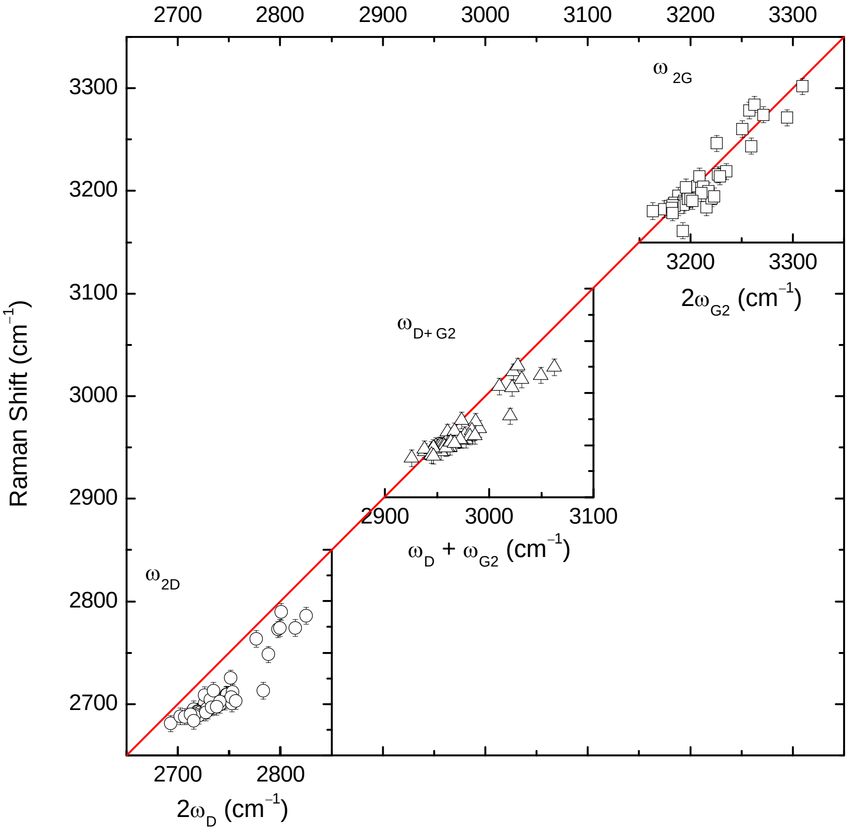

Figure 7. Frequencies of the second order Raman bands of DWCNTs, the frequencies of 2D (open circles), D+G_2 (open triangles), and 2G bands (open squares) are shown as a function of the appropriate frequency combinations of the first-order bands: for the 2D band, twice the frequency of the D band, for the D+G_2 band, the sum of the frequencies of the D and G_2 bands, and for the 2G band, twice the frequency of the G_2 band. Solid line represents the $y = x$ function for the sake of comparison.

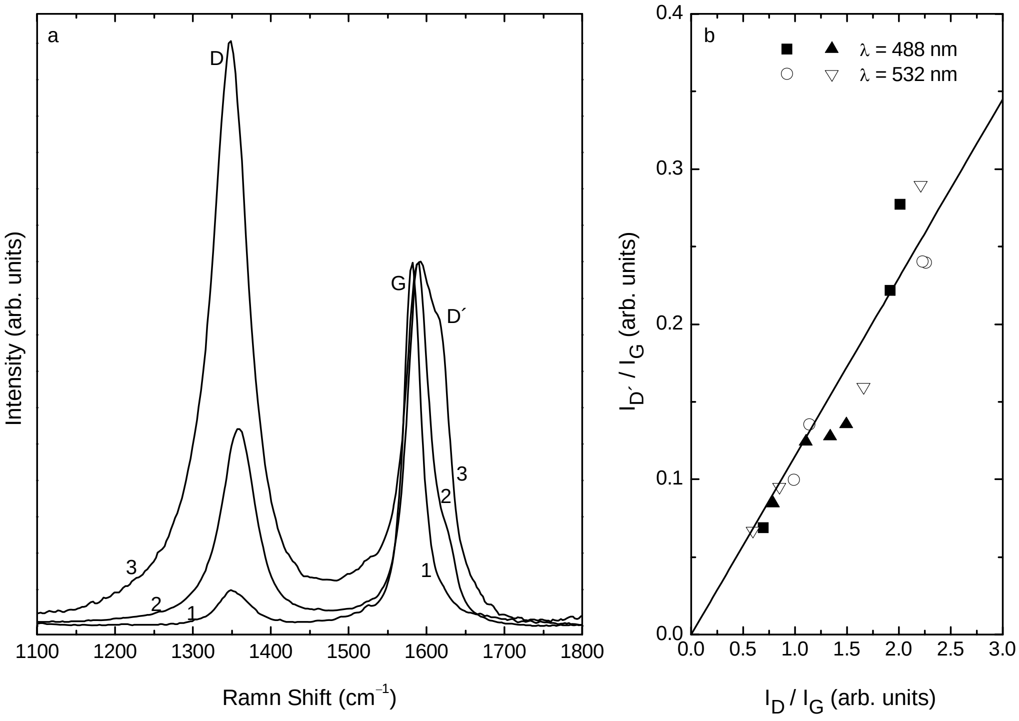

Figure 8. (a) Raman spectra of a HOPG sample at three selected pressures (1, 2, 3 denote increasing pressures). Note the growth of the intensity of the D and D´ bands with the increasing pressure. (b) Ratio of the (D´/G) band intensities as a function of the ratio of the (D/G) band intensities. Different symbols refer to different pressure history and excitation conditions (488 nm, 532 nm). The slope of the solid line is 0.115.

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