# Linear and non-linear optical transmission from multi-walled carbon nanotubes

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The multi walled carbon nanotubes grown by the CVD technique were suspended in methanol and their linear and non-linear transmission properties have been studied. It is observed that the linear transmission spectrum, measured in the range 450–1100 nm, depicts features similar to those of single walled nanotubes. The observed features may be well characterized as the van-Hove singularities of the one-dimensional electronic density of states. Further, excellent non-linear optical properties have been observed in these suspensions. Experiments are conducted to study the optical limiting behavior in the visible (532 nm) as well as in the near infra-red (1064 nm) region by using a dual beam pulsed pump-CW probe, technique. The grown multi walled carbon nanotubes show a strong limiting behavior at both of these wavelengths. The recovery time as observed from the probe beam transmission is measured at different values of the incident pulse energy. The results are discussed in the light of the existing results.


## 1. Introduction

The one-dimensional (1D) structure of carbon nanotubes has given rise to their extraordinary electronic, mechanical and optical properties [1]. Many of these properties are believed to be governed by the presence of the van-Hove singularities (vHs) in the electronic density of states (DOS), a characteristic of 1D electronic system. These singularities have experimentally been observed in the single wall nanotubes (SWNTs), which essentially possess small diameter, through the scanning tunneling spectroscopy [2–4], the resonant Raman spectroscopy [5, 6] and more recently in the optical absorption spectra [7, 8].

On the other hand, the multi walled nanotubes (MWNTs) are the ensemble of many concentric graphene cylinders and their diameter ranges typically between 10–100 nm. Therefore, it is generally believed that the interactions between the shells as well as the large diameter to length ratio may alter the electronic structure of these MWNTs, which may be significantly different from that of SWNTs. In particular, many of the 1D characteristic features may be masked during the experimental observations. It is important to note that the optical transmission/absorption spectra of MWNTs have been shown to be featureless suggesting that the van-Hove singularities are absent in the electronic DOS. However, Brennan *et al.* [9] have recently identified the presence of van-Hove singularities in the optical absorption spectra of MWNTs measured in the visible region (400–900 nm). They have also explained the observed non-linear photoluminescence on the basis of these singularities in the electronic structure of MWNTs. The other efforts initiated to exploit the third harmonic generation [10] and the ultra fast optical switching [11] in SWNTs also indicate a close relationship between the 1D electronic structure and the non-linear optical properties of carbon nanotubes.

In addition to the above mentioned studies, the most extensively studied non-linear phenomena is the intensity dependent transmission through the suspension of carbon nanotubes. A decrease in the transmittance on increasing the incident flux intensity, a typical optical limiting property, has been shown to be ubiquitously present in both the SWNTs and the MWNTs suspended in a variety of solvents [12–16] as well as to some extent in the samples embedded in the polymer films [17]. Due to their enhanced capability as an optical limiter over a wide range of wavelength, the carbon nanotubes are now much preferred candidates even over the materials of the same class like carbon black and $C_{60}$ suspensions. The experimental observations indicate that the physical mechanism giving rise to the optical limiting in carbon nanotubes shares a common origin with that of carbon black suspension. Recently, Vivien *et al.* [15, 16] have extensively studied the limiting behavior of SWNTs suspended in water and chloroform. Their detailed investigation shows that the limiting is essentially due to the scattering of light by the cavitations bubbles. In fact, the carbon nanotubes act as a black-body and the incident pulse produces heat which is immediately transferred to the surrounding liquid and this rapid thermal transfer leads to the formation of vapor bubbles.

In the present work, we report the linear transmission spectrum and the optical limiting behavior of our CVD grown MWNT samples. The growth technique and various parameters are described in detail in Section 2. The linear transmission spectrum is measured from the visible (450 nm) to the near infra-red (1100 nm) region. The measurements show that the transmission spectrum of these as prepared samples, suspended in methanol, is remarkably different from the previously observed spectra. In fact, many of the features are common to those observed in the optical spectra of SWNTs. The details of the linear transmission spectrum are provided in Section 3. In Section 4, the results for the non-linear transmission of the sample in the visible (532 nm) as well as in the near infra-red (1064 nm) region are given. A pulsed pump-CW probe technique is employed to investigate the non-linear behavior and results are compared with the existing results. A summary of the work is presented in Section 5.

## 2. Growth of multi walled carbon nanotubes

Growth of multi walled carbon nanotubes is carried out using in-house developed chemical vapour deposition reactor having 40 mm diameter quartz reactor tube with three independent process gas lines for sequential or simultaneous flow of gases. Mass flow controllers are used to read and control the flow of gases. Before the actual experiments, the constant temperature zone was identified inside the reactor. The growth of carbon nanotubes is carried out, over n-type Si (100) substrate having resistivity ($\rho$) 4–6 Ωcm. The substrates are cleaned and iron films of 100 nm are deposited over silicon. The substrates are kept over the quartz sample holder inside the CVD reactor and the temperature is ramped up to 850°C in 70 min with $NH_3$ flow of ~60 sccm. Next, $C_2H_2$ is introduced in to the reactor at the rate of 15 sccm and growth is carried out for 20 min. The well aligned bundles of the carbon nanotubes are thus obtained. Large number of samples were thus prepared and the reproducibility was excellent. The SEM image of one of these aligned multiwalled carbon nanotube samples is shown in Fig. 1. A rough estimate of the dimensions indicates that the nanotubes grown under these conditions range in between 20–50 nm in diameter.

## 3. Linear transmission

The as grown MWNTs through the procedure described in Section 2, are dispersed in methanol and mixed rigorously ultrasonically to disintegrate the bundles. A quartz cell of 1 cm path length is used for further optical investigations. The linear transmission spectrum of the suspended MWNTs is measured with a double beam spectrophotometer and is normalized with that of pure methanol placed simultaneously in an identical cell. The observed normalized transmittance in the visible-near infra-red region is shown in Fig. 2 for one of the typical samples. Clearly, the spectrum shows several sharp features, which have not been observed in the previous studies. The sharp drops at various energies in the transmission spectrum correspond to the enhanced absorption, essentially due to the regions of large electronic density of states. The theoretical calculations [18, 19] have shown that in SWNTs, the regions of large density of states correspond to the van-Hove singularities, which is proportional to $(E–E_o)^{-1/2}$, at energies $\pm E_o$ of the dispersion relation. However, the presence of such features in MWNTs has been a subject of on going investigations and is not well established so far.

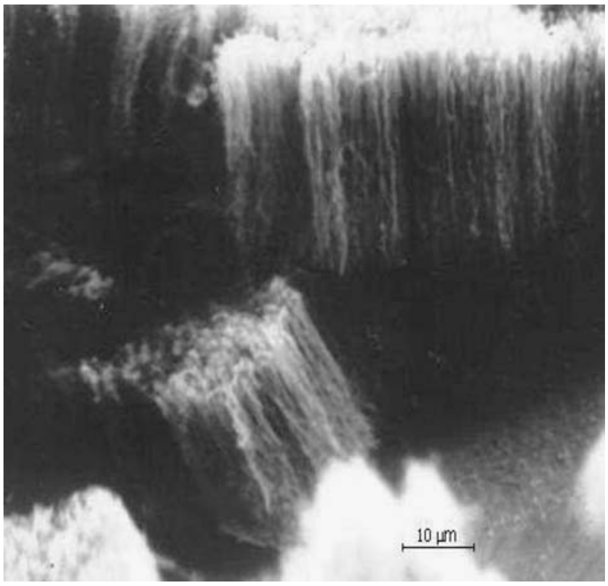


*Figure 1* STM image of aligned bundles of carbon nanotubes.

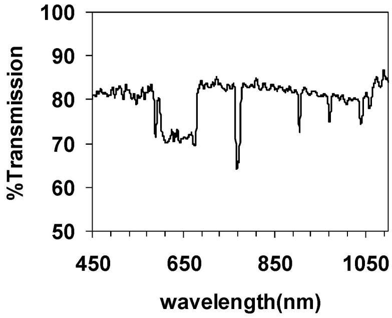


*Figure 2* Linear transmission spectra of carbon nanotubes, suspended in methanol.

We mention that the possible impurities in the suspension are iron and the residual carbon particles. It is worth mentioning that the metals generally do not show absorption. Moreover, the linear transmission of suspensions containing only carbon particles is featureless [13]. Thus it seems that the sharp absorption features observed in case of these nanotubes are likely because of the growth conditions used in the present studies. It is important to note that microscopically the electronic mean free path ($l_e$) plays an important role in determining the dimensionality of a system. Thus, the MWNTs having $l_e$ much larger than the nanotube diameter ($d_t$) may be well characterized as 1D systems and may share many of the features common to that of SWNTs. In view of this, the sharp absorption observed

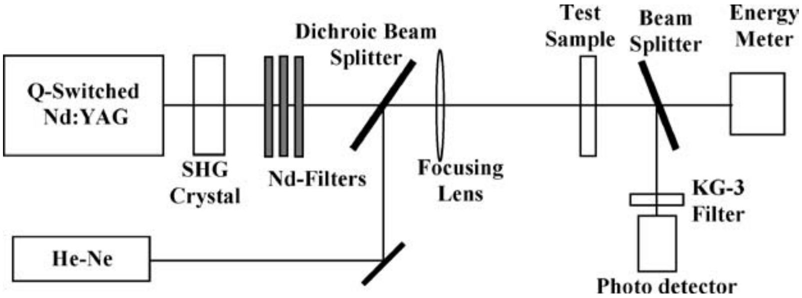


*Figure 3* Schematics of experimental setup for the measurements of the non-linear transmission from the carbon nanotube suspesion. Nd-YAG is the pump laser, He-Ne is the probe laser (633 nm) and SHG is the second harmonic generator used for 532 nm pulse.

in our MWNT samples may be associated with the van-Hove singularities in the electronic density of states.

The position ($E_o$) of these singularities may be identified directly. Fig. 2 shows that the first three singularities appear in the near infra-red region at 1.16, 1.19 and 1.26 eV. The presence of more singularities below 1.16 eV are not ruled out, however, they are beyond the range of our measuring instruments. These singularities fall well within the first sub-band ($E_{11}$) of the direct band gap semiconducting tubes, which extends and overlap with the second sub-band ($E_{22}$) lying between 580–910 nm. The van-Hove singularities in this region are obtained at energies 1.36, 1.6 and 2.10 eV. The contribution from the metallic tubes falls in the range 450–580 nm. Recently Brennan *et al.* [9] have also observed three peaks in the absorption spectra of MWNTs in the visible region at energies 1.38, 1.56 and 1.80 eV. Our observations carried over the wider region (450–1100 nm), thus provide a better understanding of the electronic structure of MWNTs and agree well with the results of Brennan *et al.* in the visible region. Further, the position of the singularities depends on the chirality and the diameter of the tubes. A slight difference in the energy position of the singularities in our results with that of ref. [9] is thus understandable.

From Fig. 2, one can observe the presence of an absorption band between 600–700 nm in addition to the well defined van-Hove singularities in the spectrum. Such absorption band has not been observed previously in the optical spectra of both the SWNTs as well as the MWNTs. The origin of this feature is not clear at present; however, further efforts are being made to investigate this point.

## 4. Non-linear transmission

A Q-switched 20 ns pulsed Nd:YAG laser ($\lambda = 1064$ nm) producing maximum energy $E = 80$ mJ and a CW He-Ne laser ($\lambda = 633$ nm) were used as near infra-red pump source and the probe beam respectively. The beam is focused using a lens having focal length 175 mm and the spot size is calculated to be 0.42 mm. The sample cell is placed in the focal plane and the incident pulse energy is varied using combinations of ND filters. The incident as well as the transmitted energy is measured through the pyroelectric sensor based energy meter (OPHIR) and the probe beam transmission is measured using a Si-detector. The second harmonic ($\lambda = 532$ nm) is used to study the transmission in the visible region. Fig. 3 shows the basic set-up for these studies. The laser is operated in the single shot mode unless otherwise stated. The transmitted energy is normalized with the 80% transmission in the linear region as obtained in Fig. 2.

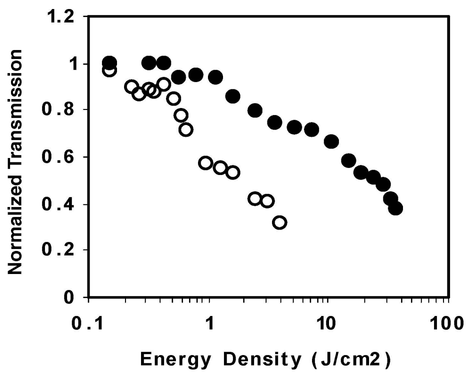


*Figure 4* Normalized non-linear transmission measured at various incident energies (J/cm$^2$) for 1064 nm (filled circles) and 532 nm (open circles).

The normalized transmission versus the incident pulse energy ($E$) is plotted in Fig. 4 for the near infra-red (1064 nm, upper curve) and the visible (532 nm, lower curve) regions respectively. These results clearly demonstrate the typical optical limiting property of MWNT suspension. The transmittance decreases as $E^\alpha$ on increasing the incident energy. It may be easily noted that the limiting is much pronounced at $\lambda =$ 532 nm as compared to that in the near infra-red region ($\lambda = 1064$ nm). The observed trends for the limiting behavior of MWNTs suspended in methanol are in fair agreement with the previously reported results for the MWNT/SWNT suspensions in ethanol and water [12, 14, 17]. The limiting threshold, where the transmittance drops to 50%, is measured to be $E_{th} \approx 20$ J/cm$^2$ for near infra-red and $E_{th} \approx 2$ J/cm$^2$ for the visible region. However, because of the different concentration of MWNTs in the suspension, the measured limiting threshold is almost two times higher than that measured previously in ethanol [12]. We have also measured the recovery time of the probe beam transmittance, which ranges between 5–15 msec, depending upon the incident flux.

Here, we mention that due to the presence of the van-Hove singularities in the linear transmission spectrum of these MWNTs, the electronic excitations may play an important role in the non-linear dynamics of these systems. It seems plausible that the excited states

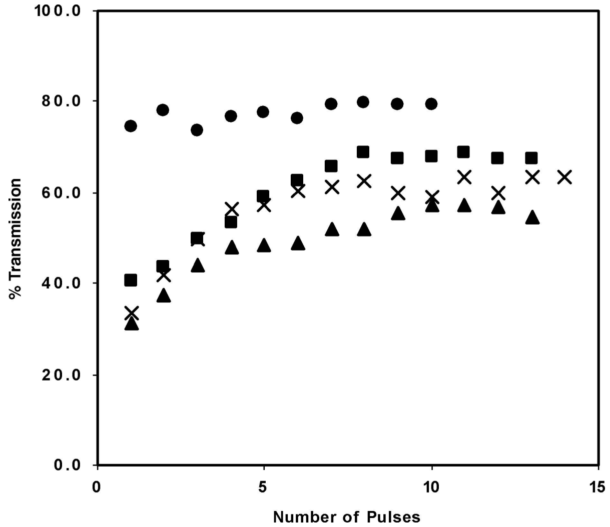


*Figure 5* Pulse to pulse variation of non-linear transmission at various pulse energies for 532 nm @1 Hz. 0.864J/cm$^2$ (circles), 4.81 J/cm$^2$ (squares), 6.81 J/cm$^2$ (crosses) and 9.46 J/cm$^2$ (triangles).

achieved by the absorption of incident photons of energies 1.16 eV ($\lambda = 1064$ nm) and 2.32 eV ($\lambda = 532$ nm) decay through the fast non-radiative transitions. The liberated heat is immediately transferred to the surrounding liquid and then the non-linear scattering due the formation of cavitations bubbles, self-focusing and thermal lensing etc. in the suspension, give rise to the observed optical limiting behavior. Further, it is well known that the van-Hove singularities are the regions of higher density of states and hence possess higher lifetime. Therefore, when the sample is irradiated with an energy resonant with the energy position of these singularities (e.g. $E = 1.16$ eV or $\lambda = 1064$ nm), the fast non-radiative transitions are expected to be suppressed significantly. A larger limiting threshold ($\sim$20 J/cm$^2$) at $\lambda = 1064$ nm as compared to that at $\lambda = 532$ nm ($\sim$2 J/cm$^2$) is consistent with this mechanism. This view is further strengthened by the investigations where the pump beam transmittance itself is found to increase considerably by operating the laser in multi-shot mode. Using $\lambda = 532$ nm, @ 1 Hz, the transmission increases, essentially due to the thermal lensing, for the successive pulses as shown in Fig. 5. After few pulses, saturation in the transmittance may be noted where the thermal equilibrium sets in and the thermal energy transfer between the carbon nanotubes and the liquid is minimum. On the other hand, this effect is less pronounced at $\lambda = 1064$ nm being operated even at much higher frequency (@20 Hz), suggesting that the non-radiative transitions are much suppressed and hence the thermal effects are much weaker.

## 5. Summary

In summary, we have grown the multiwall carbon nanotubes using the CVD technique. The parameters are optimized for obtaining the aligned bundles of MWNTs. The linear and the non-linear optical transmissions are studied in the suspension of these nanotubes. We have observed the sharp absorption features in the linear transmission spectrum measured from the visible to the near infra-red region. These features are associated with the van-Hove singularities, which are well known to be present in the electronic density of states of 1D systems. The non-linear transmission is closely related to the observed electronic structure of MWNTs. In fact, the relaxation of the excited states through the non-radiative transition is discussed to be the microscopic origin of the optical limiting behavior. The observed limiting behavior is in fair agreement with the existing results.

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