Environmental effects on the carrier dynamics in carbon nanotubes

J. S. Lauret,* C. Voisin,† S. Berger, G. Cassabois, C. Delalande, and Ph. Roussignol
Laboratoire Pierre Aigrain, École Normale Supérieure, 24 rue Lhomond 75231 Paris cedex 05, France

L. Goux-Capes, A. Filoramo
Laboratoire d'Électronique Moléculaire, (SPEC-DRECAM-DSM) CEA Saclay, 91191 Gif-sur-Yvette, France

(Dated: February 2, 2006)

Carrier dynamics is investigated in both luminescent and non luminescent samples of single wall carbon nanotubes -obtained by laser ablation- by means of two-color pump-probe experiments. The recombination dynamics is monitored by probing the transient photobleaching observed on the interband transitions of semi-conducting nanotubes. Interband and inter-subband relaxation times are about one order of magnitude slower in isolated nanotubes than in ropes of nanotubes bringing evidence of the environment influence on the carrier dynamics. The relaxation dynamics is non-exponential and is interpreted as a consequence of the inhomogeneity of the sample. Slow components up to 250 ps are measured which is significantly greater than values previoulsy reported in HiPCo nanotubes. These observations show the great dependence of the electronic properties of carbon nanotubes on the synthesis method and on their environment.

PACS numbers: Valid PACS appear here

The intriguing properties of Single Wall Carbon Nanotubes (SWCNTs) for mechanics [1], transport [2–4] or superconductivity [5] have been highly debated in the last ten years. Since the discovery of the luminescence of SWCNTs under certain conditions [6], their optical properties [6–14], as well as promising applications in nanoelectronic or light emission displays [15], have become a growing field of interest. All these properties are related to the recombination processes affecting the photocreated carriers. In this paper we propose a direct and time-resolved investigation of such processes.

SWCNTs naturally aggregate into ropes of a few tens of nanotubes, with a Van der Waals binding energy of $\sim$ 500 eV per micron of contact [16]. Previous ultrafast spectroscopy experiments have brought evidence of a tunnel coupling between semi-conducting and metallic SWCNTs within a rope, which accounts for the absence of photoluminescence and of any temperature dependence of the relaxation dynamics [17]. On the other hand, the use of an aqueous surfactant combined with ultrasonic agitation leads to the formation of individual nanotubes encased in organic micelles [6]. The main feature of this kind of suspension is the observation of intrinsic photoluminescence at the band gap of the semiconducting nanotubes. This has opened a promising way for new optical methods for sample characterization, and for further applications of SWCNTs in optoelectronics. Ultrafast spectroscopy measurements on such suspensions have been reported for nanotubes made by the HiPCO method [13, 18–20]. They show a complex non-exponential decay dynamics of the photo-created carriers with a slow component of about 10 ps, resonantly enhanced when the photon energy matches an absorption peak (degenerate configuration). This slow component is attributed to interband carrier recombination in resonantly excited HiPCO SWCNTs.

In this paper we report a comparative study of ultrafast carrier dynamics in both suspensions of individual SWCNTs and ropes of SWCNTs grown by laser ablation. The recombination at the band gap as well as the inter-subband relaxation is one order of magnitude faster for the ropes of nanotubes (RNT) than for the isolated nanotubes (INT). This gives evidence of a reduction of some relaxation channels in the latter case. The recombination profile has a non-exponential shape which is interpreted as a consequence of the inhomogeneity of the sample. We propose to ascribe the fast component to residual "dark" nanotubes. Likewise, the slow component corresponds to "bright" nanotubes. Slow components up to 250 ps are measured for the recombination at the band gap of semiconducting nanotubes obtained by laser ablation, which is at least one order of magnitude slower than for the HiPCO nanotubes, even for similar tube diameter.

SWCNTs were obtained by laser ablation of a doped graphite target and purified by chemical treatment [21]. The RNT sample consists in a thin film ($L \sim 100$ nm) of carbon nanotubes obtained by the fast evaporation at 80^oC, of a suspension of nanotubes in ethanol. Atomic force microscopy shows that most of the SWCNTs are aggregated in ropes. Suspensions of INT are obtained from the same laser SWCNTs, and are encased in micelles of SDS (sodium dodecyl sulfate) in D_2O, as described in reference [6]. Heavy water is used for its transparency in the near-infrared. The suspension is sonicated in a low power sonic bath during 3H30, and centrifuged during 16 hours at 30000 g. The sample consists of the upper half of the supernatant that should mainly contains individual SWCNTs encased in a SDS micelle [6].

The absorption spectrum of the suspension of SWCNTs is displayed in Fig. 1 (black squares). The low en-

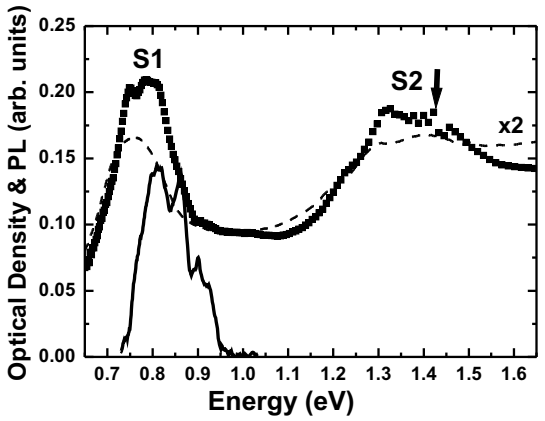

FIG. 1: *Photoluminescence spectrum (black solid line) excited at 1.43 eV (arrow) and absorption spectrum (squares) of a sample of isolated nanotubes (INT). Absorption spectrum (dashed line) of a sample of ropes of nanotubes (RNT) deposed on a glass substrate.*

ergy line (S1), corresponding to the first transition of semi-conducting nanotubes (hereafter called first interband transition), is centered at 0.77 eV, and the inhomogeneous line width is about 140 meV. Therefore, the average diameter can be estimated to 1.1 ± 0.2 nm. The line centered at 1.35 eV (S2) corresponds to transitions between the second pair of van Hove singularities. The shape of the absorption spectrum is very smooth compared to the one obtained for HiPCO nanotubes [6]. This feature is related to the larger mean diameter in the laser nanotubes samples which leads to an overlap of the lines corresponding to each chiral class [9]. The band gap photoluminescence of the same sample is shown in Fig. 1 (black curve). The emission line is centered at 0.84 eV. The apparent blue shift of $\sim$ 70 meV of the photoluminescence line with respect to the absorption line is likely due to the quenching of the PL signal due to the D_2O absorption above 0.7 eV. The luminescence line profile is sharp and structured compared to the absorption. This is due to a partially selective excitation at 1.43 eV in the inhomogeneous line S2. The absorption spectrum of the RNT sample is displayed in Fig. 1 (dashed line). For this sample no photoluminescence can be observed.

We have performed ultrafast carrier dynamics studies in both INT and RNT using two-color pump-probe experiments in the visible and near-infrared domains (0.75 eV to 1.53 eV). Energy injection in the sample is achieved by a strong pump pulse, resulting in a non-equilibrium electronic distribution. A delayed weak probe pulse monitors the temporal evolution of the transient change of transmission (ΔT) induced by the pump pulse. In our case, $\Delta T/T$ is proportional to the opposit of the transient change of absorption [10]. The setup is based on an optical parametric oscillator (OPO) pumped by a cw-mode-locked Ti:sapphire laser. The pulses delivered by the OPO have a temporal width of $\sim$ 180 fs and the photon energy is tunable from 0.65 eV to 0.85 eV. The Ti:sapphire laser delivers pulses of 80 fs duration in the 1.25-1.65 eV range. The pump pulse fluence is typically $15\mu J/cm^2$. The probe beam is approximately 100 times weaker.

We first measured the transient change of transmission in a degenerate configuration for which both pump and probe beams have the same energy corresponding to the first interband transition of semiconducting nanotubes at 0.77 eV (cf. Fig. 2). The overall recombination dynamics

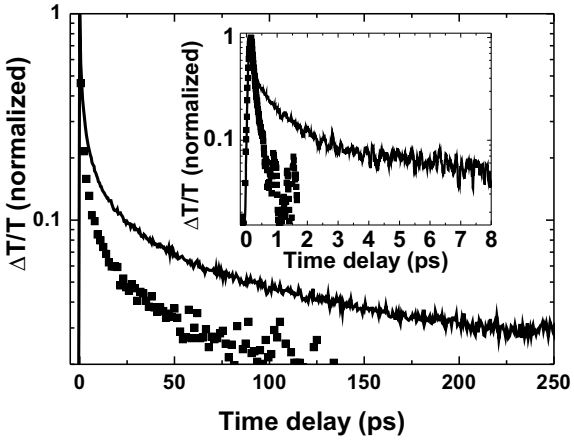

FIG. 2: *Relative change of transmission as a function of the time delay, in a semi-logarithmic scale, in a degenerate configuration in resonance with the first transition of the semiconducting nanotubes (0.77 eV) for INT (black solid curves) and RNT (black squares). Inset : same measurements on the second transition of semi-conducting nanotubes (1.37 eV).*

is slower in INT (solid line) than in RNT (black squares, see figure 2). In both cases the recombination profile is not mono-exponential. However, one can note that 95 % of the signal disappears after 15 ps for RNT whereas the same level is reached after 85 ps for INT. This observation suggests that some recombination channels are quenched when SWCNTs are encased in micelles. In particular the coupling between semiconducting and metallic nanotubes is suppressed for isolated nanotubes [6, 17]. Moreover the micelle encasing of the nanotubes probably leads to a saturation of side-wall defects as already reported for other semiconducting nanostructures [22].

We ascribe the non-exponential shape of the signals to the inhomogeneous nature of the response observed in these experiments. Indeed these measurements give access to the average response of all the nanotubes that do absorb light, and even for isolated nanotubes, only a fraction of them is responsible for the photoluminescence. Most probably, the relaxation dynamics is very different from one nanotube to another which leads to an overall non-exponential decay.

A fast component is observed for both kind of samples. It is partly due to non resonantly excited nanotubes whose photoexcited carriers are expected to recombine within a few hundreds of femtoseconds [13]. However this contribution is supposed to be small since these tubes have a much lower absorption coefficient and are thus weakly perturbed. The main origin of this fast component in the case of RNT is usually ascribed to the inter-tube coupling within a rope [6, 17]. This contribution is expected to vanish for pure isolated nanotubes. Therefore the observation of a fast component in the INT sample is attributed to "dark" nanotubes. These nanotubes can be included in some remaining ropes or can be nanotubes of poor crystallographic quality or nanotubes coupled to remaining particles of catalyst. Likewise, we ascribe the slow component to the response of the "bright" nanotubes. However, even for time delays up to 500 ps the observed relaxation remains non-exponential. This means that the specific behavior of bright nanotubes is inhomogeneous too. We attribute this dispersion in the recombination dynamics of bright nanotubes to differences in their environment. Indeed, microphotoluminescence spectroscopy of single nanotube has been reported [23, 24] showing that the emission energy for a given class of chirality (n, m) varies from one nanotube to another. This supports the hypothesis that the shape, defects or environment fluctuations strongly affect the electronic properties of the nanotubes as observed in our case on the relaxation processes.

By fitting the data at a long time delay which corresponds to the contribution of the nanotubes weakly coupled to their environment, we estimate a lower limit of the radiative recombination time of the order of 250 ps. This value of the recombination time at long time delay is more than one order of magnitude greater than the one obtained on isolated HiPCo nanotubes [13], even for similar tube diameter. This particularity of "laser nanotubes" is probably related to their crystallographic quality or to a lower coupling to remaining small particles of catalyst due to the different growth processes.

However a quantitative comparison of these time-resolved data with stationary PL measurements raises some questions. The signal to noise ratio in PL measurements being greater than 100 for the INT sample, the lack of any PL signal for the RNT sample seems to be hardly compatible with a ratio of recombination times of "only" one order of magnitude, as measured in pump-probe measurements. One explanation would be that the only tubes that emit light are those whose relaxation time is strongly greater than the tens of picoseconds observed for the RNT sample. This would mean that the relative abundance of bright nanotubes in the INT sample is very low, of the order of a few percents only, or even less. Further insight would be given by a quantitative analysis of time-resolved photoluminescence measurements (to be published elsewhere).

We now focus on the inter-subband relaxation processes (within the conduction band (for electrons) or valence band (for holes)) which are investigated for both kind of samples. Pump-probe experiments in resonance with the transition between the second pair of Van-Hove singularities (S2) have been performed in a degenerate configuration (1.37 eV). A photobleaching, due to a band filling effect, is also observed (inset of figure 2). The relaxation is still non-exponential. As observed for the recombination at the band gap, the inter-subband relaxation is slower for isolated nanotubes than for ropes of nanotubes. In fact, 95 % of the signal disappears after 7ps in INT whereas the same level is reached after 500 fs in RNT. Inter-subband relaxation times are thus more than one order of magnitude slower for isolated nanotubes. This means that the inter-subband processes are more affected by the inter-tube coupling than the relaxation processes across the band gap. Indeed the tunnel coupling with neighboring tubes inside a rope is facilited by the excess energy given to carriers photocreated at the S2 energy compared to those created at the S1 energy.

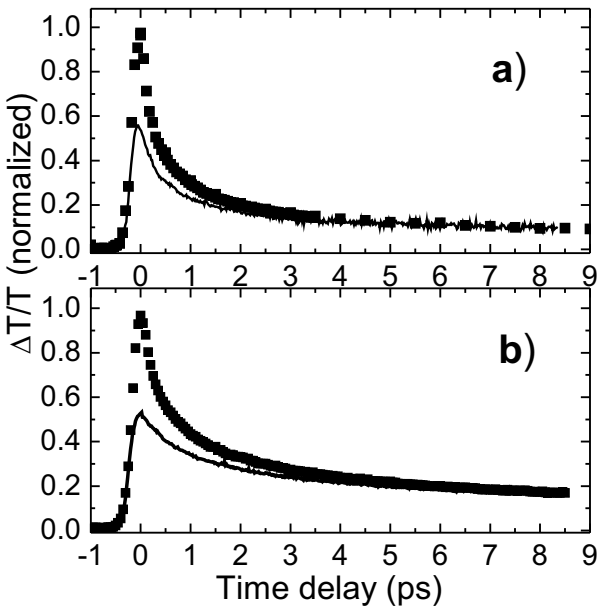

FIG. 3: *Relative change of transmission normalized to the number of photocreated carriers as a function of the time delay in a degenerate configuration (full squares) in resonance with the first transition (S1, 0.77 eV) of semi-conducting nanotubes and in a two-color configuration (black solid lines) where the pump is tuned with the S2 transition (1.53 eV) and the probe with the S1 transition (0.77 eV). a) deposited nanotubes, b) isolated nanotubes in suspension in $D_2O - SDS$. The y axis is normalized.*

Two-color pump-probe experiments give further insight into the relaxation processes between the upper and lower bands. In these experiments, the pump is tuned at

resonance with the S2 transition (1.53 eV) and the probe at the S1 transition (0.77 eV). This way we can follow the population build up at the bottom of the conduction band after an excitation of the carriers at the second conduction band. This configuration probes the electronic processes leading to the photoluminescence signal in the INT sample, when carriers are excited at the S2 transition.

The transient bleaching is (in a low perturbation regime) a quantity proportional to the carrier population at the probe levels. We define a normalized signal which is the relative change of transmission divided by the initial number of photocreated carriers, i.e., we divide the relative change of transmission by the pump fluence (F) and the optical density ($OD \ll 1$) at the pump wavelength and multiplicate by the pump photon energy $\hbar\omega_{pp}$. Therefore this quantity allows us to make a quantitative comparison of carrier relaxation rates for resonant and non resonant pumping as well as for isolated nanotubes or ropes of nanotubes (cf. Fig. 3).

$$\left.\frac{\Delta T}{T}\right|_{norm} = \frac{\hbar\omega_{pp}}{F.OD_{pp}} \cdot \frac{\Delta T}{T}$$

In a degenerate configuration on S1 this quantity ($\Delta T/T|_{norm}(dege)$) would just measure the S1 population recombination. In the ideal case of isolated carbon nanotubes and for a resonant pumping on S2 and probing on S1, if one waits until the carriers relax down to the lowest excited levels (in about 2 ps, much faster than the recombination at the band gap, see Fig. 2), the normalized signal $\Delta T/T|_{norm}(2color)$ is expected to be equal to the latter one ($\Delta T/T|_{norm}(dege)$), reflecting the conservation of the number of carriers.

For large time delays (above 5 ps approximately) the normalized signals for the two-color and degenerate configurations are superimposed and then share the same time evolution. Both signals match within a statistical error of about 20%. This means that after a transient regime, the normalized change of transmission are identical whatever the way the carriers have been injected. And this applies for both INT and RNT samples. The convergence of the signals at long time delays is in agreement with the picture of a population conservation. Therefore, after a transient of about 5 ps, one can reasonably trust that the signal reflects the carrier dynamics in the only nanotubes resonantly coupled to the laser for both probe and pump wavelengths for the S1 and S2 transitions respectively.

In contrast, we observe a strong deviation to this picture at short time delays for both INT and RNT. This deviation is of the order of 50% for both INT and RNT although stastistically slightly higher for the former one. Thus the degenerate and two-color signals are not simply homothetic, which would be the case in the simple picture of some population loss (due for instance to intertube charge transfer within a bundle) during the relaxation from S2 to S1. As stated in the first part of the paper, in a degenerate measurement part of the signal is due to non resonantly excited nanotubes. On the contrary, in the two-color configuration such a contribution does not exist, since non resonantly excited nanotubes are not probed. Moreover in the two-color configuration the population build-up time is of the order of a few picoseconds (cf. Fig. 2) which leads to an apparant reduction of the signal at short time delays compared to the degenerate case where the population build-up is instantaneous. This also explains why the shape mismatch is stronger in the case of the INT sample : the intersubband relaxation time is greater in this case. These reasons explain the lower signal level at short time delays for two-color measurements.

In conclusion, we have performed time resolved pump-probe measurements on both ropes of nanotubes and isolated nanotubes obtained by the laser ablation method. Transient photobleaching of the first interband transition is observed for both of them. The relaxation dynamics are about one order of magnitude slower in nanotube suspensions than in nanotube ropes, showing the suppression of the intertube coupling between metallic and semi-conducting nanotubes inside a rope. A quantitative comparison of the relaxation rate of the photocreated carriers for isolated nanotubes and ropes of nanotubes is achieved by means of two color measurements and it is shown that both degenerate and two-color signals fairly reflect the carrier dynamics in resonantly excited nanotubes after a transient regime of the order of several picoseconds. However a quantitative understanding of the PL quenching for the RNT sample from a comparison of the overall relaxation times is not straightforward and would require further investigation. In any case, these observations emphasize the key role of the environment on the carrier dynamics and more generally on the electronic properties of SWCNTs.

The authors are grateful to L. Sarger at the University of Bordeaux I for the use of the OPO and O. Jost at the TU Dresden for providing the nanotubes. LPA de l'ENS is "Unité Mixte de Recherche associée au CNRS (UMR 8551) et aux universités Paris 6 et 7." This work has been done in the framework of the GDRE n^o 2756 'Science and applications of the nanotubes - NANO-E' and was partially supported by the "Région Ile de France" through the project SESAME E-1751.

* Now at Laboratoire de Photonique Quantique et Moleculaire, Ecole Normale Superieure de Cachan, 61 avenue du President Wilson, 94235 Cachan, France

† Electronic address: christophe.voisin@lpa.ens.fr

[1] M. Treacy, T. Ebbesen, J. Gibson, Nature **381**, 678

(1996).
[2] P. Collins *et al.*, Science **278**, 100 (1997).
[3] T. W. Ebbesen *et al.*, Nature **382**, 54 (1996).
[4] A. Bachtold *et al.*, Science **294**, 1317 (2001).
[5] A. Y. Kasumov *et al.*, Science **284**, 1508 (1999).
[6] M. J. O'Connell *et al.*, Science **297**, 593 (2002).
[7] S. M. Bachilo *et al.*, Science **298**, 2361 (2002).
[8] T. Hertel, G. Moos, Phys. Rev. Lett. **84**, 5002 (2000).
[9] J. S. Lauret *et al.*, Physica E. **21**, 1057 (2004).
[10] J. S. Lauret *et al.*, App. Phys. Lett. **85**, 3572 (2004).
[11] J. Lefebvre, Y. Homma, P. Finnie, Phys. Rev. Lett. **90**, 217401 (2003).
[12] O. Korovyanko *et al.*, Phys. Rev. Lett. **92**, 017403 (2004).
[13] G.N. Ostojic *et al.*, Phys. Rev. Lett. **92**, 117402 (2004).
[14] S. Lebedkin *et al.*, J. Phys. Chem. B **107**, 1949 (2003).
[15] W. B. Choi *et al.*, Appl. Phys. Lett. **75**, 3129 (1999).
[16] R. Saito, G. Dresselhaus, M.S. Dresselhaus, Imperial College Press (1998).
[17] J. S. Lauret *et al.*, Phys. Rev. Lett. **90**, 057404 (2003).
[18] F. Wang *et al.*, Phys. Rev. B **70**, 241403 (2004).
[19] F. Wang *et al.*, Phys. Rev. Lett. **92**, 177401 (2004).
[20] L. Huang, H.N. Pedrosa, T.D. Krauss, Phys. Rev. Lett. **93**, 017403 (2004).
[21] L. Capes *et al.*, Proceedings IEE conference on nanotechnology (2000).
[22] D.J. Norris *et al.*, Phys. Rev. Lett. **72**, 2612 (1994).
[23] H. Htoon *et al.*, Phys. Rev. Lett. **93**, 027401 (2004).
[24] A. Hartschuh *et al.*, Science **301**, 1354 (2003).