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# Ultrafast Carrier Dynamics in Single Wall Carbon Nanotubes

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Time-resolved carrier dynamics in single wall carbon nanotubes is investigated by means of two-color pump-probe experiments. The recombination dynamics is monitored by probing the transient photo-bleaching observed on the first interband transition of the semi-conducting tubes. The carrier dynamics takes place on a one picosecond time scale which is one order of magnitude slower than in graphite. Transient photo-induced absorption is observed with exactly the same dynamics for non-resonant probe conditions and is interpreted as a global red shift of the  $\pi$ -plasmon resonance. We show that the opening of the band gap in semi-conducting carbon nanotubes determines the non-linear response dynamics over the whole visible and near-infrared spectrum.

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Carbon nanotubes and especially Single Wall Carbon Nanotubes (SWCNT) have attracted much attention in the last ten years. The novel properties of these one-dimensional nanostructures make SWCNTs very promising for applications in various domains such as mechanics [1], thermal conductivity [2], electronics [3, 4], conductivity [5], magnetism [6] or optics [7]. A SWCNT is usually described as an enrolled graphene sheet and depending on its chirality, the boundary conditions lead to either semi-conducting or metallic tubes [8, 9]. So far, extensive experiments provide evidence that bulk proportions of SWCNT are always mixtures of metallic ( $\sim 1/3$ ) and semiconducting ( $\sim 2/3$ ) tubes [10]. The progress in the growing and purification steps have improved the samples quality and allowed the development of optical studies. Optical Absorption (OA) spectroscopy or Raman scattering spectroscopy offer powerful tools for characterizing SWCNT samples, in particular for the determination of the average tube size [11].

However very little is known about the non-linear properties and the carrier dynamics in these nanostructures whereas it is a key issue for understanding and developing their optoelectronic properties [12]. Femtosecond studies of carrier dynamics have been performed in bulk-like films of graphite by Seibert *et al.* [13]. In this semi-metallic material, intraband relaxation of the photo-created carriers occurs in a few hundreds of femtoseconds. Recently, femtosecond time-resolved photo-emission spectroscopy in SWCNTs has been performed for a non-resonant excitation. The response of the metallic tubes was selectively monitored by tuning the energy of an ultraviolet pulse generating hot photo-electrons, therefore giving insight into the dynamics of the free electron gas near the Fermi level [14]. The photo-excited electronic distribution returns to a Fermi-Dirac distribution in about 100 fs and then relaxes to the initial temperature through electron-phonon interactions on a 1 ps time scale.

In this Letter we report the first time-resolved study of carrier dynamics in single wall carbon nanotubes by means of two-color pump-probe experiments with a selective injection of energy in the semi-conducting nanotubes. Transient photo-bleaching is observed on the first interband transition of the semi-conducting tubes, with a typical recovery time of 1 ps. This dynamics is one order of magnitude slower than in graphite. Transient photo-induced absorption is observed for non-resonant probe conditions and is interpreted as a global red shift of the  $\pi$ -plasmon resonance. We show that the non-linear optical properties dynamics of the semi-conducting SWCNTs is determined, even in non-resonant conditions, by the recombination dynamics of the carriers at the lowest band edges of the semi-conducting tubes.

SWCNTs are obtained by laser ablation of a doped graphite target and purified by ultrasonic and chemical treatment [15]. The solution containing the nanotubes is evaporated on a glass substrate. The average diameter is estimated to 1.2 nm by OA measurements. The thickness  $L$  of the deposited layer is about 50 nm; in the visible range, its linear transmittivity is about 70% and its reflectivity about 10%. We study the ultrafast dynamics of carriers by pump-probe experiments in the visible and near-infrared domains (0.4 to 1.9  $\mu\text{m}$ ). Energy injection in the sample is achieved by a strong pump pulse, resulting in a non-equilibrium electronic distribution. A delayed weak probe pulse allows us to measure the temporal evolution of the transient change of transmission ( $\Delta T$ ) or reflection ( $\Delta R$ ) induced by the pump pulse. The two beams have an angular separation of about  $30^\circ$ . Standard synchronous detection methods, involving mechanical chopping of the pump beam, lock-in amplification and slow scan of the optical delay serve to enhance the signal to noise ratio and we achieve detection of relative changes of transmission ( $\Delta T/T$ ) as low as  $10^{-5}$ . 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 approximately a temporal width of 180 fs and their energies are tunable from 0.65 to 0.85 eV. The Ti:Sapphire laser generates pulses of 60 fs duration in the 1.25-1.65 eV range. Pulses around 3 eV are generated by frequency doubling the Ti:Sapphire pulses in a BBO crystal. The pump pulse fluence is typically  $20 \mu\text{J}/\text{cm}^2$ . The probe beam is approximately 100 times weaker. Depending on the configuration, the pump and probe beams are issued either from the Ti:Sapphire laser or from the OPO, as explained below.

Typical OA spectra on an assembly of SWCNTs exhibit a set of lines ranging from 0.6 to 2.2 eV (Inset of Fig. 1). They correspond to the inhomogeneously broadened transitions between the Van Hove singularities, hereafter called interband transitions, of these one-dimensional objects. In our sample the two low energy lines (peaks A and B at 0.75 and 1.3 eV, respectively) are attributed to the interband transitions in the semi-conducting tubes and the third peak (peak C at 1.9 eV) to the first interband transition of the metallic tubes [16]. The position of the lines as well as their shape are well reproduced by means of tight binding models taking into account bundling effects [17]. These peaks are superimposed on a significant background representing usually more than 70% of the optical density at the energy of the peak C. Residual carbonaceous impurities or metallic catalysts may contribute to this background which is sometimes treated as an extrinsic feature [11]. However this background is always present whatever the purification protocol. In fact the optical absorption spectrum in the near ultraviolet range clearly exhibits a broad line around 5 eV (peak D) which is attributed to the  $\pi$ -plasmon resonance of the SWCNTs [16, 18]. We will see in the following that our time-resolved measurements allow us to clarify the role of the  $\pi$ -plasmon tail in the non-linear response of the SWCNTs.

We first measured the transient change of transmission in a degenerate configuration (Fig. 1, black curve) for which both pump and probe beams have the same energy (0.8 eV) centered on the first interband transition of the semi-conducting tubes (peak A). One observes an increase of the transmission corresponding to a transient photo-bleaching of the peak A. The signal decay is quasi exponential with a time constant of about 1 ps. Similar data have been obtained for a degenerate configuration in resonance with the peak B (Fig. 1, grey curve) with a much shorter time decay ( $\sim 130$  fs). Note that in the latter case, the temporal resolution is about 80 fs (pulses from the Ti:Sapphire laser) in contrast to the former case where it is about 200 fs (pulses from the OPO). This explains well the apparent difference in the rise times of the curves of Fig. 1.

In these experiments the change of reflection is about 10 times weaker than the change of transmission in absolute values. This allows us to identify the relative change of transmission with the opposite of the absorption change  $\Delta\alpha$  ( $\Delta T/T \simeq -L\Delta\alpha$ ,  $L$  being the thick-

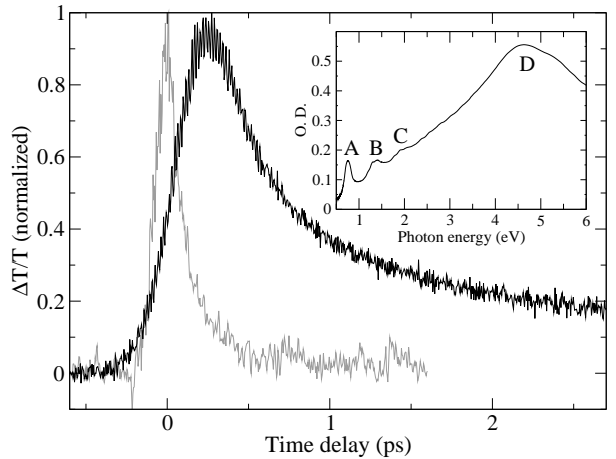


FIG. 1: Normalized change of transmission for a mixture of semi-conducting and metallic SWCNTs in a degenerate pump/probe experiment at 0.8 eV (black line) and 1.47 eV (grey line). Inset : Linear optical absorption spectrum. A and B denote the peaks related to the semi-conducting tubes, C the one related to the metallic tubes and D the  $\pi$ -plasmon resonance.

ness of the sample). In this approximation, the transient photo-bleaching of the first interband transition of the semi-conducting tubes can be explained within a simple model. Absorption of the pump pulse creates a population of electrons in the conduction band and holes in the valence band and until these carriers relax, one observes transient saturation of the line due to filling effects on the final states. In the simplified picture of a two-level system, this saturation should result in a transient broadening of the line. We checked for symmetric energies on the low- and high- energy sides of the peak A that one still observes the same positive change of transmission. Moreover the signal amplitude reaches its maximum at the central energy of the line. We can thus exclude any shift of the line which would on the contrary result in a negative change of transmission on one side of the line. Finally, note that the amplitude of the signal is proportional to the pump power as expected for the photo-created population and that the decay time is independent of the pump fluence as expected in the low perturbation regime. We therefore end up with a first interband transition of the semi-conducting nanotubes modeled by a simple two-level system weakly saturated by the pump beam. The phenomenology is similar for the peak B with a shorter decay time (130 fs) which may be attributed to more efficient relaxation channels within the conduction band. This intraband relaxation time of 130 fs is in agreement with the relaxation times measured in bulk graphite by Seibert *et al.* [13].

In order to observe the intraband relaxation of these carriers at the edges of the conduction and valence bands, we performed two-color pump-probe measurements. In this non-degenerate configuration, the probe is tuned on peak A keeping the pump at high energy, in resonance

with peak B. The signal is roughly similar to the one observed in a degenerate configuration on peak A, in particular we observe the same decay dynamics of 1 ps. The expected rise time corresponding to the population build-up at the lowest band edges is beyond our time resolution ( $\sim 200$  fs). Still it is consistent with the decay time of 130 fs measured for the photo-created population in a degenerate configuration on peak B.

This set of experiments clearly brings evidence that the photo-created carriers first decay in about 130 fs down to the edges of the conduction and valence bands and that the overall carrier relaxation in SWCNTs is limited by carrier recombination processes at the lowest band edges of the semi-conducting tubes on a 1 ps time scale. This is a crucial difference with the dynamics observed in bulk graphite where the relaxation of carriers occurs through intraband mechanisms down to the Fermi level on a 100 fs time scale. Here the boundary conditions imposed by the nanotube structure lead to the opening of a band gap at 0.8 eV which drastically changes the nature of relaxation processes and increases the recombination time by one order of magnitude with respect to a graphite film.

Several mechanisms such as direct recombination, electron-phonon interactions, electron-impurity interactions, or inter-tube charge transfer may cause this interband relaxation. Since no photoluminescence has been observed, even at 10K, direct radiative recombination can be excluded. We also performed low temperature pump-probe measurements (down to 10K) and we did not observe any change in the relaxation time constant. Therefore, phonon assisted decay channels via carrier trapping in localized states may also be excluded [19]. Charge transfer to the neighboring metallic tubes via coherent tunneling processes would account for this temperature independence. Indeed such a temperature independent interband relaxation time is currently observed in  $C_{60}$  fullerene films and is usually interpreted as a consequence of tunneling charge transfer between the neighboring macromolecules [20, 21]. However further measurements far beyond the scope of this work are required to unambiguously identify the nature of the relaxation processes in SWCNTs.

In order to get insight into the physical origin of the background observed on OA spectra (Inset of Fig. 1), we also performed two-color pump-probe experiments where the probe pulse is at *higher* energy than the pump one and *out of resonance* with any of the peaks. The energy is selectively injected in the nanotubes thanks to a pump in resonance with the first peak of the semi-conducting nanotubes (peak A). A clear transient photo-induced *absorption* (negative change of transmission) is observed (Fig. 2). The decay of the signal is mono-exponential with a time constant of 1 ps. Moreover as we tuned the pump energy in the vicinity of the peak A, the signal amplitude follows linearly the absorption of the sample (Inset of Fig. 2) which means that it is proportional to the amount of injected energy. The signals obtained for a probe energy of 1.53 eV (between the peaks B and C) and

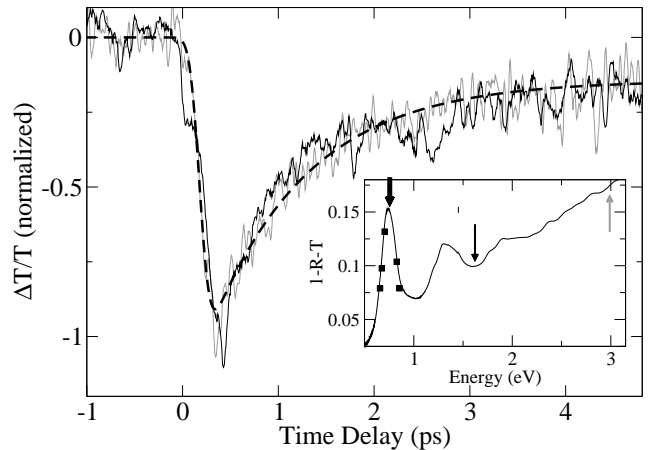


FIG. 2: Normalized change of transmission for a SWCNT's mixture in two-color pump/probe experiments with a pump energy at 0.8 eV and a probe energy at 1.53 eV (black line) or 3.1 eV (grey line). The dashed line is a mono exponential fit with a time constant of 1 ps. Inset : Thin (thick) arrows on the OA spectrum indicate the probe (pump) energies; the black squares correspond to the normalized amplitude of the signal when the pump is tuned near the top of the peak.

3.06 eV (between the peaks C and D) are fully identical after normalization, as shown on Fig. 2. We now interpret the non-resonant response of the SWCNTs in both cases as the photo-induced dynamics of the  $\pi$ -plasmon resonance.

The  $\pi$ -plasmon is a collective excitation of the  $\pi$ -electrons, and its position, which corresponds to the singularities of the loss function  $-Im(1/\epsilon)$ , is given by [22]:

$$\epsilon_1(\Omega_p) = 0 \quad (1)$$

where  $\epsilon_1$  denotes the real part of the dielectric constant of the nanotubes, and  $\Omega_p$  the frequency of the plasmon. In a bulk medium this resonance is not coupled to light. But in the case of a finite medium, like SWCNTs, it can be seen as a surface plasmon resonance and it corresponds in a classical picture to a collective oscillation of the  $\pi$ -electrons along the axis of the nanotubes. As we noticed before, injection of carriers in the nanotubes leads to a transient saturation of the excited transition (peak A) and corresponds to a transient modification of the imaginary part of the dielectric constant  $\epsilon_2$  at this energy.

In the framework of Kramers-Kronig analysis one can calculate the corresponding change of the real part of the dielectric constant  $\Delta\epsilon_1$  for wavelengths in the vicinity of the plasmon resonance. As previously mentioned, let us model the first interband transition of the semi-conducting tubes as a two-level system with central frequency  $\omega_0$  and width  $\Gamma$ . The saturation effect of the transition leads to a relative change of absorption given by [23]:

$$\frac{\alpha + \Delta\alpha}{\alpha} = \frac{\Gamma^2 + (\omega - \omega_0)^2}{\Gamma^2 + g + (\omega - \omega_0)^2} \quad (2)$$

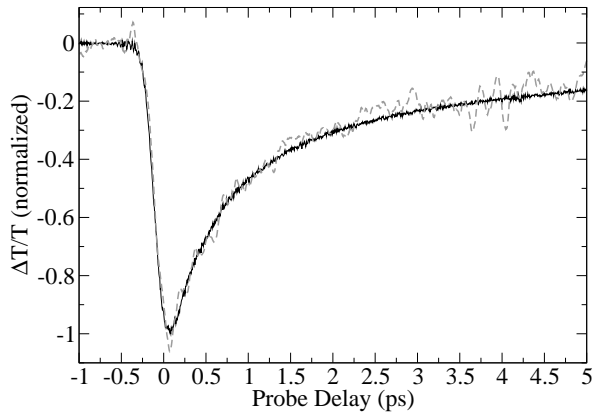


FIG. 3: Normalized change of transmission for a pump (probe) energy of 0.8 eV (1.53 eV) calculated from the data obtained with a probe at 0.8 eV (black line), experimental signal (grey line).

where  $g$  denotes the saturation parameter, proportional to the population of the final state. We take for  $\Gamma$  the value used by Lin *et al.* in their calculation in order to reproduce the optical spectrum of an assembly of carbon nanotubes [22]. We evaluate the maximum of the saturation parameter  $g$  (at a time delay of 300 fs in Fig. 1) from an analysis of our data in the degenerate configuration with a resonant excitation on the peak A. For a pump fluence of  $20 \mu\text{J}/\text{cm}^2$ ,  $g$  turns out to be of the order of  $10^{-4} \text{eV}^2$ . From this value and the knowledge of the linear absorption on peak A, we compute  $\Delta\epsilon_2$  and then  $\Delta\epsilon_1$  from Kramers-Kronig relations.

From Eq. (1) we deduce that the corresponding spectral shift of the  $\pi$ -plasmon resonance is about -0.03 meV. Assuming a global shift of the line, the corresponding change of absorption at a given frequency  $\omega$  is at first order :  $\Delta\alpha(\omega) \simeq \frac{d\alpha(\omega)}{d\omega} \cdot \Delta\omega_p$ . We finally evaluate an amplitude of the induced relative change of transmission at 1.53 eV of the order of  $3 \cdot 10^{-6}$ , in good agreement with the measured one ( $10^{-5}$ ).

Extending the procedure for all time delays, we calculate the signal dynamics for a non-resonant probe at 1.53 eV from the measurements with a probe at 0.8 eV.

The agreement with the experimental signal is excellent (Fig. 3). Such a similarity comes from the low perturbation regime approximation where all the relevant physical parameters are linearly related. Thus the signals with a probe in or out of resonance with peak A are almost homothetic. This point also explains the striking similarity between the signals obtained for a probe at 1.53 eV and 3.06 eV (Fig. 2) and more generally at any energy corresponding to non-resonant probing conditions. Indeed, Kramers-Kronig analysis shows that the change of the real part of the dielectric constant (that drives our signal here), for frequencies far from any states whose occupation number is modified by the pump, is directly proportional to the dynamics of the overall excess of energy stored in the system. Thus, the dynamics of the signal is driven by the electron relaxation at the lowest band edges of the semi-conducting tubes (peak A).

In conclusion we have performed the first time-resolved pump-probe measurements under resonant excitation in an assembly of metallic and semi-conducting tubes. Transient photo-bleaching is observed for degenerate measurements on the first interband transition of the semi-conducting tubes, with a typical recovery time of 1 ps. This dynamics is one order of magnitude slower than in graphite and this effect comes from the opening of a band gap in semi-conducting SWCNTs, whereas intraband relaxation is as fast as in bulk graphite. Transient photo-induced absorption is observed for two-color measurements with non-resonant probe conditions and is interpreted as a global red shift of the  $\pi$ -plasmon resonance. We show that the non-linear optical properties dynamics of SWCNTs is determined, even in non-resonant conditions, by the recombination dynamics of the carriers at the lowest band edges of the semi-conducting tubes. We thus conclude that the opening of the band gap in semi-conducting carbon nanotubes determines the non-linear response dynamics over the whole visible and near infrared spectrum.

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