Comment on "Large Optical Nonlinearity of Semiconducting Single-Walled Carbon Nanotubes under Resonant Excitations"

In a recent Letter Maeda *et al.* studied the optical nonlinearities of single-walled carbon nanotubes (SWNT) films using both "Z-scan" and "pump and probe" (PP) techniques with ~100 fs time resolution [1]. They found that SWNTs have a large resonant third-order nonlinear optical susceptibility ($\chi^{(3)}$), which was interpreted in terms of "coherent process rather than by saturation of absorption," possibly due to "optical Stark effect and stimulated emission." This interpretation was based on degenerate PP measurements, in which an ultrafast response was found for $t < t_p$ (pulse duration), superimposed on a slower response with ~1 ps time constant. Importantly, the ultrafast response was not found in nondegenerate PP measurements [1,2].

In this Comment we show that the ultrafast response found in SWNTs [1] is in fact a well-known phenomenon dubbed "coherent artifact" [3,4] that is formed in degenerate PP and four-wave mixing measurements for $t < t_p$ *regardless of the material studied*. This was ignored in the Maeda *et al.* analysis [1]. The coherent artifact response can be quantitatively obtained using *polarized* PP measurements, and thus carefully eliminated from the transient response; and it does not form in nondegenerate PP experiments [4]. This shows that the resonant $\chi^{(3)}$ response in SWNTs is not governed by "exotic" coherent effects as claimed in [1], but rather is the result of saturation of the absorption, placing SWNT on equal footing with other quasi-1D organic semiconductors with large $\chi^{(3)}$ [5].

Detailed understanding of the ultrafast response in degenerate PP measurements is essential for analyzing data in the time interval $t < t_p$ [3,4]. It was shown that the transient photoinduced absorption (or transmission) is in fact composed of two superimposed contributions: $\gamma(t)$ and $\beta(t)$. $\gamma(t)$ is the principal response, where the pulse autocorrelation function, $G^{(2)}(t)$, is convoluted with the material response function, $A_{ijkl}(t)$, that is proportional to $\mathrm{Im}\chi^{(3)}_{ijkl}(t, \omega, -\omega)$. On the contrary, $\beta(t)$ is the coherent artifact term given by the convolution of $A(t)$ with the electric field autocorrelation function resulting in a similar transient as that of $G^{(2)}(t)$. The coherent artifact contribution may be rationalized as pump beam scattering off the transient grating formed on the sample for $t < t_p$ by the PP beams, into the direction of the probe beam [3]. For PP beams with parallel polarizations, both γ and β are related to A_{xxxx}. However, when the PP polarizations are perpendicular to each other, then $\gamma \sim A_{xxyy}$ whereas $\beta \sim A_{xyxy}$. The different terms of γ and β in the perpendicular PP polarization leads to an elegant method for obtaining $\beta(t)$ directly from the data [4], and may help eliminating its contribution from the transient response altogether. If $\rho(t)$ is the polarization memory, $\rho = A_{xxyy}/A_{xxxx}$, then:

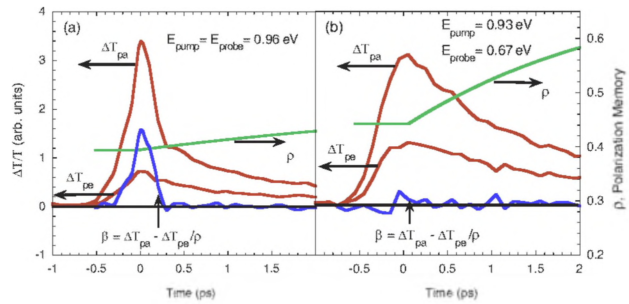

FIG. 1 (color online). $\Delta T(t)$ response of an HiPco SWNT film measured with degenerate (a) and nondegenerate PP beams, having parallel (ΔT_{pa}) and perpendicular (ΔT_{pe}) polarizations, respectively. The polarization memory, $\rho(t)$, and the coherent artifact term, $\beta(t)$, extracted from the parallel and perpendicular responses using Eq. (1) are also shown.

$$\beta(t) = (\Delta T(t)_{pa} - \Delta T(t)_{pe}/\rho), \tag{1}$$

where ΔT_{pa} and ΔT_{pe} are the photoinduced absorption (or transmission) measured with parallel and perpendicular PP beam polarization, respectively [4].

In Fig. 1 we show the polarized transient $\Delta T(t)$ of a HiPco SWNT film for degenerate [Fig. 1(a)] and nondegenerate [Fig. 1(b)] PP beams, measured with our ultrafast laser system in the mid-infrared range [2]. We plot both parallel and perpendicular $\Delta T(t)$, as well as the transient polarization memory $\rho(t)$. It is clear that in the degenerate PP case there is an extra response for $t < t_p$ that is stronger for parallel PP polarizations [4]. However, this ultrafast response is absent in the nondegenerate case, in agreement with the theory [4]. We also plot in Fig. 1 the coherent artifact response $\beta(t)$ extracted from the data using Eq. (1). It is obvious that the ultrafast response formed in the degenerate PP case is in fact the coherence artifact term. It does not result from any exotic coherent mechanism in SWNT [1]. On the contrary, this ultrafast response is related with the basic SWNT nonlinearity, which at resonant condition was identified as absorption saturation or photo bleaching [1,2].

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