Coherent and squeezed phonons in single wall carbon nanotubes

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Abstract. Coherent states of phonon manifest in macroscopic beatings of reflectance or transmittance following the phonons frequencies when a material is excited with an ultrashort pulse. Such beatings predominantly arise from a single phonon excitation. The two-phonon (overtone or combination modes) excitations, such as the $G'$ (or 2D) band phonons in single wall carbon nanotubes (SWNTs), on the other hand, are not compatible with the coherent phonon states picture. Nevertheless, their macroscopic beatings are observed in the experiment. Here we formulate a more general framework involving the so-called squeezed states of phonon to explain the origin of the two-phonon signals in the pump-probe experiment of SWNTs. For a given SWNT chirality, the $G'$ band phonon intensity in terms of the squeezed states of phonons is compared with that in terms of coherent states of phonons. Our calculation reveals that the $G'$ band intensity from the squeezed states of phonons is some orders of magnitude larger than that from the coherent states of phonons. We also compare the $G'$ band phonon intensity with the intensities of other coherent phonon modes generated in ultrafast spectroscopy such as the G band. Furthermore, the coherent G band and squeezed $G'$ band phonon intensities are found to be sensitive to the laser pulse width used in ultrafast spectroscopy.

1. Introduction

Over the last two decades, single wall carbon nanotubes (SWNTs), which are characterized by the chiral index $(n,m)$ [1, 2], have been an important material that provide us with a one-dimensional system to study the dynamics and interactions between electrons, photons, and phonons [3]. Especially, recent advances in ultrafast pump-probe spectroscopy have allowed us to observe lattice oscillations of SWNTs with the same phase in real time, known as coherent phonon spectroscopy [4–9]. The coherent phonons can be observed as oscillations of macroscopic optical properties, such as the differential transmittance ($\Delta T/T$) or differential reflectivity ($\Delta R/R$), as a function of delay time between pump and probe pulses. The coherent phonon spectra as a function of phonon frequency are obtained by performing a Fourier transform of the oscillations of $\Delta T/T$ or $\Delta R/R$ with respect to time. Several peaks found in the coherent phonon spectra of a SWNT are similar to the Raman active phonon modes, such as the radial breathing modes (RBMs), D bands, G bands, and $G'$ bands [10]. Recently, Lim et al. even showed that, for a purified $(6,5)$ SWNT sample, ultrafast spectroscopy is able
to recognize previously unknown but well-resolved weak peaks in the single SWNT chirality sample, which are currently assigned as multiple-order phonon excitations [11,12].

The $\Delta T/T$ or $\Delta R/R$ oscillations as a function of delay time $t$ between pump and probe pulses in coherent phonon spectroscopy are directly related to the modulations of the absorption coefficient $\alpha$ as a function of the probe energy $E_{\text{probe}}$ and $t$ [13]. To calculate the coherent phonon spectra, we have to firstly calculate the absorption coefficient $\alpha(E_{\text{probe}}, t)$ for a given coherent phonon amplitude, in which this amplitude is expressed as a coherent state of phonons [14]. Some previous works have discussed the physical reasons why several phonon modes can be present in the coherent phonon spectra of a given SWNT [5,7,11]. For example, in the case of RBMs, these phonons can modulate the SWNT energy gap, which are inversely proportional to the nanotube diameter, and thus such energy gap oscillations give rise to differential transmittance beating with the RBM frequency [5,7]. In the case of G bands, which are assigned to degenerate one-phonon process of longitudinal-optical (LO) and in-plane transverse-optical (iTO) phonon modes at the $\Gamma$ point of the Brillouin zone [3], it is known that these modes do not significantly modify the energy gaps because the SWNT diameters are not sensitive to the LO/iTO vibrations [15]. Thus, the coherent G band phonon spectra is known instead to come from the modulation of atomic optical matrix elements which are sensitive to the changes in the C-C bond length optical interaction [11].

However, we recently realize that the coherent phonon spectra of higher-frequency modes such as the $G'$ band could not be calculated using the coherent states of phonons as previously considered in the case of RBMs and G bands. The reason is mainly because the $G'$ band phonons correspond to two-phonon ($q \neq 0$) processes [3] thus incompatible with coherent states picture. Moreover, in ultrafast spectroscopy, Hu and Nori argued that the so-called squeezed states of phonons, a generalized form of coherent states of phonons, are more relevant to the phonon modes generated within the multi-phonon processes [16]. A recent study by Sato et al. for the generation of higher-frequency coherent phonons in SWNTs [17] might serve as a support for the idea of generating squeezed phonons in SWNT. Therefore, in this work, we calculate coherent and squeezed phonon intensities of the $G'$ band for a given SWNT. In this paper, we take the (6,5) SWNT as a model calculation. We then compare the squeezed phonon intensity with the coherent phonon intensity. In particular, we will show that the squeezed phonon spectra of the $G'$ band strongly depend on the laser pulse width used in ultrafast spectroscopy, which might allow a selective excitation of a single phonon mode in the SWNT systems in the near future by simply varying physical parameters such as the laser pulse width and excitation energy.

This paper is organized as follows. In Section II, we explain theoretical methods which include a general theory for the generation and detection of coherent phonons in SWNTs. In Section III, we present the calculation results and especially discuss how the $G'$ band phonon intensity calculated with the squeezed phonon states have a larger value rather than that calculated with the coherent phonon states. We then give a conclusion of this work in Section IV.

2. Theoretical methods
To calculate the phonon spectra generated by ultrafast spectroscopy, basically we can follow the methods described in our earlier works [9,14]. Here, we note that we have to emphasize the difference between the equations of motion for the coherent state of phonons and a more generalized squeezed states of phonons. In the case of the coherent state representation, the equation of motion of a coherent phonon mode with a wavevector $q = 0$ ($\Gamma$ point phonon) and
amplitude $Q_m$ can be written as [14]

$$\frac{\partial^2 Q_m(t)}{\partial t^2} + \omega_m^2 Q_m(t) = S_m(t),$$  \quad (1)

where $m$ and $\omega_m$ denote the phonon mode (e.g. RBM, gTO, LO, iTO) and its frequency, respectively. Equation (1) is solved subject to the initial conditions $Q_m(0) = 0$ and $\dot{Q}_m(0) = 0$. The driving function $S_m(t)$ in the right hand side of Eq. (1) is given by [14]

$$S_m(t) = -\frac{2\omega_m}{\hbar} \sum_{nk} \mathcal{M}^m_n(k) \left( f_n(k,t) - f_n^0(k) \right).$$  \quad (2)

where $f_n(k,t)$ is the time-dependent electron distribution function and $f_n^0(k)$ is the electron distribution function in the initial equilibrium state. The index $n$ labels an electronic state, while $k$ gives the electron wavevector. The electronic states of a SWNT are calculated within the extended tight-binding (ETB) approximation [18,19]. The electron-phonon matrix element $\mathcal{M}^m_n(k)$ in Eq. (2) is in general written as $\mathcal{M}^{m,q}_{nk,nk'}$, where $\mathcal{M}^{m,q}_{nk,nk'}$ is the deformation potential electron-phonon matrix element in the ETB model with phonon wavevector $q = k - k'$ and with a transition from the state $n$ to $n'$ [20]. For the coherent phonon equation of motion, only $q = 0$ is taken into account [21].

On the other hand, in the case of the squeezed state representation, Hu and Nori has noted that the squeezed phonon mode amplitude is nothing but correspond to a two-phonon (second-order) process and thus the amplitude can be expressed as a summation of two coherent phonon amplitudes with $\pm q \neq 0$ [16]. With respect to such an assumption, we obtain the equation of motion for a squeezed phonon mode in SWNTs is the same as that in Eq. (1), except that now we have to consider each one-phonon mode at a certain $q$ value:

$$\frac{\partial^2 Q_{m,q}(t)}{\partial t^2} + \omega_{m,q}^2 Q_{m,q}(t) = S_{m,q}(t),$$  \quad (3)

The squeezed phonon amplitude $Q_{m,q}(t)$ with phonon frequency $\omega_m = \omega_{m_1,q} + \omega_{m_2,-q}$ is then expressed as:

$$Q_{m,q}(t) = \langle Q_{m_1,q}(t) + Q_{m_2,-q}(t) \rangle,$$  \quad (4)

where the outer $\langle \rangle$ in the right hand side means that the we consider the average amplitude for all possible combinations of two modes with phonon index $m_1$ and $m_2$.

The driving function $S_{m}(t)$ in Eq. (2) depends on the photoexcited electron distribution functions, which can be calculated directly from the Fermi’s golden rule. Using the Fermi’s golden rule, we obtain the photogeneration rate for the distribution functions [22],

$$\frac{\partial f_n(k)}{\partial t} = \frac{8\pi^2 e^2 u(t)}{\hbar^2 n^2 g (E_{\text{pump}})^2} \left( \frac{\hbar^2}{m_0} \right)^2 |P_{nn'}(k,t)|^2 \left( f_{n'}(k,t) - f_n(k,t) \right) \delta \left( E_{nn'}(k,t) - E_{\text{pump}} \right),$$  \quad (5)

where $E_{nn'}(k,t) = |E_n(k,t) - E_{n'}(k,t)|$ are the $k$-dependent transition energies at time $t$ of the phonon oscillation, $E_{\text{pump}}$ is the pump laser energy, $u(t)$ is the time-dependent energy density of the pump pulse, $e$ is the electron charge, $m_0$ is the free electron mass, and $n_g$ is the refractive index of the surrounding medium. The time dependence in $E_{nn'}$ comes from the fact that the coherent phonon or squeezed phonon amplitudes $Q_m$ modulate the lattice constants and thus alter the hopping parameters which are necessary in obtaining $E_{nn'}$ from the ETB.
method [18,19]. The pump energy density $u(t)$ is related with the pump fluence $F$ by a relation

$$F = \frac{(c/n_g) \int u(t) dt}{\tau_p},$$

where $A_p = \frac{(2n_g F \sqrt{2/\pi})}{(c\tau_p)}$ and $c$ is the speed of light. In Eq. (6), $\tau_p$ is defined as the laser pulse width. In this paper, we use parameters $F = 10^{-5}$ J cm$^{-2}$ and $n_g = 1$. To also account for spectral broadening of the laser pulses, we replace the delta function in Eq. (5) with a Lorentzian lineshape

$$\delta(E_{nn'} - E_{\text{pump}}) \rightarrow \frac{\Gamma_p/(2\pi)}{(E_{nn'} - E_{\text{pump}})^2 + (\Gamma_p/2)^2},$$

where $\Gamma_p = 0.15$ eV is the spectral linewidth (FWHM) of the pump pulse [14]. The optical matrix element $P_{nn'}(k,t)$ in Eq. (5) is calculated within the dipole approximation by considering light polarized parallel to the tube axis and also taking into account possible modulation of the optical interaction due to the changes in the C-C bond length induced by the coherent phonon or squeezed phonon amplitudes $Q_m$ [11].

In ultrafast pump-probe spectroscopy, a laser probe pulse is used to measure the time-varying absorption coefficient of the SWNT. The time-dependent absorption coefficient $\alpha(E_{\text{probe}}, t)$ is given by the Fermi’s golden rule

$$\alpha(E_{\text{probe}}, t) \propto \sum_{nn'} \int dk \left| P_{nn'}(k,t) \right|^2 \left( f_n(k,t) - f_{n'}(k,t) \right) \delta(E_{nn'}(k,t) - E_{\text{probe}}),$$

We replace the delta function in Eq. (8) with a broadened Lorentzian spectral lineshape with a FWHM of $\gamma = 0.15$ eV [14], similar to that in Eq. (7). Excitation of coherent phonons by the laser pump modulates the optical properties of the SWNTs, which gives rise to a transient differential transmission signal, or the modulations of absorption coefficient. The time-resolved differential gain measured by the probe is then given by

$$\Delta \alpha(E_{\text{probe}}, t) = -[\alpha(h\omega, t) - \alpha(h\omega, t \rightarrow -\infty)].$$

The phonon intensity $I(\omega)$ is then calculated as the power spectrum of such absorption modulations at a given energy $E_{\text{probe}}$,

$$I(\omega) = \int e^{-i\omega t} |\Delta \alpha(E_{\text{probe}}, t)|^2 dt,$$

where $\omega$ represents the phonon frequency that contributes to the coherent phonon spectra.

3. Results and discussion

Firstly, we discuss how different the phonon intensity looks like in the case of considering one-phonon process (coherent states) and two-phonon process (squeezed states). For these two cases, figure 1 displays the phonon intensity for a (6,5) SWNT excited at $E_{\text{pump}} = E_{\text{probe}} = 1.26$ eV with laser pulse width $\tau_p = 10$ fs. Focussing on the process with coherent states (red line), we can see several peaks, in which the most notable peaks are those of the RBM and G band phonons at frequency around 304 cm$^{-1}$ and 1596 cm$^{-1}$, respectively. However, phonon modes with the frequency above the G band’s frequency, such as the $G'$ bands, have much smaller intensity than those below the G band’s. In particular, if we only consider the coherent
states of phonons, the G band and $G'$ band intensity ratio is on the order of $10^4$, while the experiment performed by Lim et al. measured the ratio on the order of about $10^2$ to $10^3$ [12]. The large coherent phonon intensity is only observed up to the G band frequency because the G band originates from the highest phonon branch. Exciting phonons above that frequency requires higher order processes either from overtones or combination modes. If we now take the squeezed states of phonons into account (black line) where the second-order processes have been included, we find that the $G'$ band intensity is enhanced by about 10 times larger so that the calculated G band and $G'$ band intensity ratio can be on the order of $10^3$ similar to the experimental results. This result implies that considering the squeezed states of phonons is necessary to describe the $G'$ band correctly [16]. Below the G band, both coherent and squeezed states produce the same intensity indicating the generality of the squeezed state compared with the coherent state.

Next, we discuss the effects of laser pulse width on the squeezed phonon intensity. In figure 2, we show the phonon intensity calculated by considering the squeezed states of phonons with two different laser pulses: $\tau_p = 5$ fs (black line) and $\tau_p = 10$ fs (red line). The G band intensity is enhanced by about 2 times larger for $\tau_p = 5$ fs compared to that for $\tau_p = 10$ fs, while the $G'$ band intensity is enhanced by about 4 times larger. This result indicates that the $G'$ band has a larger rate of change in the intensity compared to that of the G band by decreasing the laser pulse width. This might be applied generally that the signals arising from the second-order

Figure 1: Phonon intensity for the (6, 5) SWNT as a function of frequency calculated by taking into account coherent states (red line) and squeezed states (black line). Laser pulse width used in the calculation is 10 fs, while its energy is 1.26 eV. The pump and probe energies are considered the same. RBM and G band spectra, which are coherent phonons, can be seen around 304 cm$^{-1}$ and 1596 cm$^{-1}$, respectively. The $G'$ band around 2498 cm$^{-1}$ is enhanced by considering the squeezed states of phonons. Other unassigned peaks in the figure might be related to the multiple-order phonon modes [12].

Figure 2: Squeezed phonon intensity for the (6, 5) SWNT calculated with the use of 5 fs and 10 fs laser pulses. The G and $G'$ band spectra are located around 1596 cm$^{-1}$ and 2498 cm$^{-1}$, respectively. Other unassigned peaks in the figure might be related to the multiple-order phonon modes [12].
processes are twice-amplified compared with that of the first-order processes when the pulse width is halved. Such a fact might be useful for realizing of a single phonon mode excitation in a SWNT sample. We also notice that there are several unassigned peaks in figures 1 and 2. These peaks might correspond to the generation of multiple-order phonon modes [12], which are beyond the scope of the present paper and can be a subject of future studies.

4. Conclusion
We have shown that the coherent oscillations of G' band in SWNTs might be described in terms of squeezed states of phonons. We also found that the high-frequency coherent phonon modes in SWNTs such as the G band and the G' band are very sensitive to the change in the laser pulse width. The coherent phonon intensities are enhanced by decreasing the laser pulse width, in which the higher-frequency modes have larger increase in their intensities compared to the lower-frequency modes.

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