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Coherent phonons in carbon nanotubes and graphene

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ABSTRACT

We review recent studies of coherent phonons (CPs) corresponding to the radial breathing mode (RBM) and G-mode in single-wall carbon nanotubes (SWCNTs) and graphene. Because of the bandgap-diameter relationship, RBM-CPs cause bandgap oscillations in SWCNTs, modulating interband transitions at terahertz frequencies. Interband resonances enhance CP signals, allowing for chirality determination. Using pulse shaping, one can selectively excite specific-chirality SWCNTs within an ensemble. G-mode CPs exhibit temperature-dependent dephasing via interaction with RBM phonons. Our microscopic theory derives a driven oscillator equation with a density-dependent driving term, which correctly predicts CP trends within and between $(2n + m)$ families. We also find that the diameter can initially increase or decrease. Finally, we theoretically study the radial breathing like mode in graphene nanoribbons. For excitation near the absorption edge, the driving term is much larger for zigzag nanoribbons. We also explain how the armchair nanoribbon width changes in response to laser excitation.

1. Introduction

The physical, chemical, and optical properties of crystalline solids are determined by the atomic-level interplay between light and the electrical and vibrational forces that tightly bind each atom inside the crystal lattice [1]. Thus, a microscopic understanding of the dynamics and interactions of electrons, phonons, and photons is needed to correctly interpret macroscopic material properties and predict new phenomena. Recent progress in the fabrication of nanomaterials has been impressive and holds promise for future optoelectronic device applications [2]. In order to assess their optimum capabilities, it is necessary to probe their microscopic properties under non-equilibrium conditions with ultrashort time resolution. With ultrafast laser spectroscopy, one can probe electronic and vibrational dynamics in real time. Numerous time-resolved detection techniques have been developed over the past few decades, and ultrafast phenomena can now be studied with a time resolution shorter than 1 fs, which is shorter than one optical phonon period in most solids [3].

This article focuses on ultrafast optical phenomena in two carbon-based nanostructures with extraordinary properties: single-wall carbon nanotubes (SWCNTs) [4,5] and graphene [6–8]. With uniquely simple but unusual band structures, SWCNTs and graphene provide low-dimensional prototypes for studying the dynamics and interactions of electrons and phonons in one- and two-dimensions (1D and 2D), respectively. Recent continuous wave (CW) optical studies of SWCNTs and graphene have produced a world of intriguing phenomena, including strong Coulomb interactions enhanced by the low-dimensionality as well as interaction between excited electronic/excitonic states and phonons [9].

We have reported time-dependent observations of the lattice vibrations in these low-dimensional carbon structures [10–15]. Using femtosecond pump–probe spectroscopy, we observed coherent phonons (CPs) corresponding to the low-frequency RBM and the high-frequency G-mode. The observed phonon frequencies exactly correspond to those seen in traditional Raman spectroscopy in the same sample, but with narrower phonon linewidths, no photoluminescence signal or Rayleigh scattering background to obscure features, and high resolution allowing normally blended peaks to appear as distinct features. We found that CP signals are resonantly enhanced when the pump pulse resonantly excites excitons, allowing us to obtain precise information on chiralities present in a given SWCNT sample [13]. Furthermore, because the bandgap and diameter in SWCNTs are inversely proportional to each other, the bandgap coherently oscillates as the lattice undergoes coherent RBM oscillations [10]. This is a novel way of

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modulating interband optical absorption at terahertz (THz) frequencies and opens intriguing possibilities for novel THz devices. In addition, using tailored trains of femtosecond pulses, we selectively excited RBM CPs of specific-chirality SWCNTs within an ensemble sample [11]. For G-mode CPs in SWCNTs, we observed thermally activated dephasing with an activation energy that coincides with the RBM energy [16]. This suggests that the high-energy G-mode (i.e., optical phonons) can dephase via interaction with the RBM similar to the decay of the zone-center optic phonon into two zone edge acoustic phonons in GaAs [98]. The dephasing time of the G-mode in graphene was found to be shorter than in semiconducting SWNCTs but longer than in metallic SWCNTs. In both SWCNTs and graphene, strong polarization dependence was observed in CP generation and detection [12,14].

We have also developed a microscopic theory explaining our observations [17–20]. We find that the CP amplitudes satisfy a driven oscillator equation with a driving term depending on the photoexcited carrier density. We find that the RBM CP amplitude is a strong function of the photon excitation energy and polarization. In particular, we accurately predict the relative strengths of the CP signal for different chirality nanotubes [17,19]. Furthermore, we predict that the nanotube diameter can initially either increase *or* decrease in response to femtosecond laser excitation. Finally, we developed a microscopic theory for CP generation and detection in armchair and zigzag graphene nanoribbons [20]. We examined the CP radial breathing like mode (RBLM) amplitudes as a function of excitation energy and nanoribbon type. For photoexcitation near the optical absorption edge, the CP driving term for the RBLM is much larger for zigzag nanoribbons where strong transitions between localized edge states provide the dominant contribution to the CP driving term. Using an effective mass theory, we explain how the armchair nanoribbon width changes in response to laser excitation.

This paper is organized as follows. In Section 2, we review the fundamental concepts of coherent phonon spectroscopy and give an overview of the basic optical and vibrational properties of carbon nanotubes and graphene. In Section 3, detailed descriptions are given of the experimental techniques used in our investigations. Section 4 presents experimental results, while Section 5 showcases some of the new predictions that have come out of our theoretical studies. Finally, we will summarize our findings and conclusions and provide an outlook for future studies and possible uses of coherent phonons.

2. Basic concepts

In this section, we provide an introduction to the theory of coherent phonon spectroscopy in semiconductor nanostructures including single-wall carbon nanotubes and graphene nanostructures. We also discuss the optical properties and Raman modes in graphitic materials.

2.1. Coherent phonon spectroscopy

Ultrafast femtosecond pump–probe spectroscopy is a useful tool for studying non-equilibrium carrier dynamics in a variety of semiconductor nanostructures since scattering times in these systems are in the 10–100 fs range. The decay of the reflection or transmission of the probe pulse as a function of delay time from the pump pulse provides information concerning details of the non-equilibrium carrier dynamics. Information obtained from these experiments includes: (i) scattering rates, (ii) electronic structure, and (iii) many-body effects.

In addition to carrier dynamic effects, ultrafast pump–probe experiments have been shown to produce oscillating signals superimposed on the background carrier dynamics signal. These oscillations typically match one of the vibrational frequencies of the nanostructure and are known as *coherent phonons (CPs)* and the study of these oscillations is the field of CP spectroscopy [21–23]. Coherent optical phonons can be generated by the absorption of an ultrashort laser pulse whose duration is shorter than the period of the lattice vibration [24]. They are usually observed as periodic oscillations in the time-resolved differential reflectivity [25–30] or differential transmission. The oscillation frequency in transmission or reflection matches one of the phonon modes, which indicates that the phonon mode becomes coherently excited by the pulse.

Time-resolved CP spectroscopy is a powerful tool for investigating vibrational dynamics and allows direct measurement of the excited state phonon dynamics in the time domain, including phase information and dephasing times. To visualize the vibrational motion in a medium, light pulses with duration much shorter than the vibrational period are required.

2.1.1. Coherent phonons

When an ultrafast optical laser pulse rapidly creates electron–hole pairs across the bandgap in a semiconductor, the hot electrons and holes relax and lose energy primarily through the emission of optical and acoustic phonons. The phonons emitted, however, are *incoherent* phonons and not related to the oscillations observed in the differential transmission, and reflectivity spectra, although they can be responsible for the decay of the background signal (see Fig. 1(a)). *Coherent* phonons are not states with a definite number of phonons but are formed from a coherent superposition of phonon harmonic oscillator eigenstates (i.e., the states with definite phonon number). If a large number of phonon harmonic oscillator eigenstates can be excited, then an example of a coherent phonon state is given by the well known superposition

$$\Psi^{coh} = |z\rangle = \sum_n \frac{|z|^n}{\sqrt{n!}} e^{-|z|^2/2} |n\rangle. \tag{2.1}$$

These states in Eq. (2.1) are essentially the same as those used in quantum optics to describe the quasi-classical photon states of the electromagnetic field.

The states in Eq. (2.1) are eigenfunctions of the phonon annihilation operator b_q for phonons with wave vector q,

$$b_q|z\rangle = z|z\rangle, \tag{2.2}$$

and represent minimum-uncertainty Gaussian wavepackets that oscillate back and forth in the parabolic potential without broadening, as shown in Fig. 1(b).

2.1.2. Coherent phonon generation mechanisms

The excitation of the CP displacement amplitude Q can be described phenomenologically as a harmonic oscillator driven by an external force, which depends on the electron and hole densities. When the femtosecond laser pump pulse rapidly creates electrons and holes across the gap, the force changes and triggers the coherent oscillations.

A phenomenological model for the CP amplitude Q, first introduced in Ref. [25], can be written as

$$\mu^* \left(\frac{\partial^2 Q(t)}{\partial t^2} + 2\gamma \frac{\partial Q(t)}{\partial t} + \Omega^2 Q(t) \right) = S^Q(n_e, n_h, t), \tag{2.3}$$

where μ^* is a reduced lattice mass, γ is a damping constant, Ω is the vibrational frequency, and $S^Q(n_e,n_h,t)$ is a driving force that depends on time through the electron and hole densities n_e and n_h that change rapidly with the laser pump pulse. The second term in Eq. (2.3) is a damping term, and the damping constant γ is related to the dephasing time T_2 of the coherent mode via $\gamma = 1/T_2$. The notion of a dephasing time has been established for coherent excitations;