Probing Ultrafast Dynamics of Anharmonically Coupled Phonons in Few-Layer Hexagonal Boron Nitride

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Abstract: Nonequilibrium dynamics of transverse optical (TO) phonons in few-layer hexagonal boron nitride is studied in mid-infrared pump-probe experiments. TO phonons display a 1.2 ps lifetime and a transient redshift due to anharmonic coupling with low-frequency interlayer modes.

Few-layer hexagonal boron nitride (hBN) is an emerging quantum material with a broad range of applications in optoelectronics and quantum phononics [1, 2]. A hBN layer consists of six-rings of alternating boron and nitrogen atoms bonded covalently [3]. The much weaker van der Waals interaction between layers results in a highly anisotropic stacked crystal structure. Transverse and longitudinal optical phonons are connected with intralayer atomic motions (inset of Fig. 1(a)) and complemented by interlayer phonons at much lower frequency. The TO phonon of hBN has a frequency of 1366 cm^{-1}, while interlayer shear and breathing modes show ten to hundred times lower frequencies. In contrast to the bulk material, few-layer hBN has the interlayer shear and breathing modes split into a multitude of phonon branches, some of which are Raman active [4]. So far, linear vibrational spectroscopy and theory have mainly addressed phonons in bulk hBN. Insight in nonequilibrium dynamics of phonon excitations and in intermode anharmonic couplings has remained very limited.

Here, we present the first femtosecond pump-probe study of TO phonon excitations in few-layer hBN, revealing the TO phonon lifetime, the time scale of energy redistribution between lattice modes, and the specific anharmonic coupling between TO and interlayer phonons [5]. The mid-infrared pulse excites TO phonons resonantly and concomitantly generates a nonequilibrium population of low-frequency interlayer phonons via impulsive Raman scattering within the pump bandwidth. Such simultaneous excitation enables a direct mapping of nonequilibrium dynamics of the coupled high- and low-frequency phonons. The experiments were complemented by extensive theoretical calculations of phonon dynamics and anharmonic couplings, based on density-functional theory.

The few-layer hBN sample was grown directly on a sapphire substrate and has an average thickness of 2.5 nm, corresponding to 8-9 hBN layers [6]. The linear reflectivity spectrum of the sample (dashed line in Fig. 1(a)) exhibits a TO phonon peak at 1366 cm^{-1} with an amplitude of 0.7 %. The ultrafast nonlinear TO phonon response is studied in temporally and spectrally resolved pump-probe measurements with femtosecond mid-infrared pulses. Independently tunable pump and probe pulses were generated in two home-built optical parametric amplifiers driven by a Ti:sapphire oscillator/amplifier system [7]. The energy of the pump pulses was varied between 70 nJ and 1 μJ, the probe pulse had an energy of 10 nJ. The temporal cross correlation of pump and probe pulses had a width of approximately 150 fs. A gold-coated prism was used for the interaction of the femtosecond beams with the sample in reflection geometry, which enables reflectivity measurements in a transmission setup. Both pump and probe pulses are linearly polarized and interact with the sample in *s* polarization. The spectra of pump and probe pulses cover the full TO phonon reflection peak. The probe pulse reflected from the sample was spectrally dispersed in a monochromator and detected with a 64-element HgCdTe detector array. A reference pulse reflected from an unexcited part of the sample was detected by a second array. The spectral resolution was 2 cm^{-1}.

Pump-probe spectra recorded with a pump energy of 1 μJ are summarized in Fig. 1(a). The reflectivity change $\Delta R/R_0 = (R - R_0)/R_0$ is plotted as a function of probe frequency (R, R_0: reflectivity of the sample with and without excitation). The spectra display a dispersive lineshape with a reflection increase at low and a decrease at high frequencies. The reflectivity changes essentially occur within the spectral range of the TO phonon resonance.

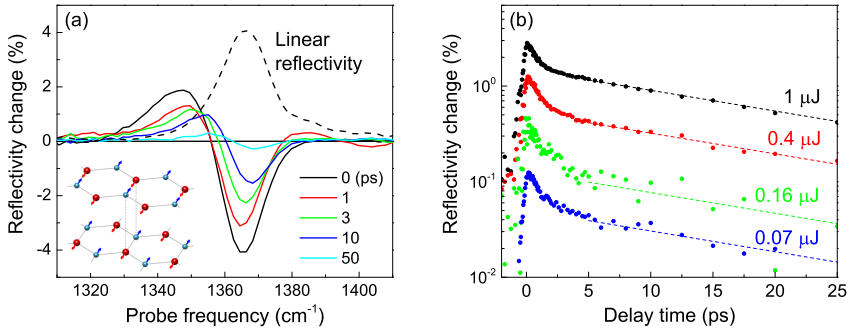

Fig. 1. (a) Measured reflectivity change as a function of probe frequency under mid-infrared pump excitation of 1 μJ, for several pump-probe delay times. The dashed line indicates the linear reflectivity measured with FTIR. The inset shows corresponding atomic motions of TO phonons. (b) Integrated reflectivity change near the TO phonon frequency as a function of delay time, for several pump pulse energies. The dashed lines are to guide the eye, representing an exponential decay of the interplane phonon component.

As a function of pump-probe delay, reflectivity changes at a fixed probe frequency follow a biphasic decay with time constants of 1.2 ps and 22 ps (Fig. 1(b)). The 1.2 ps decay is assigned to TO phonon relaxation through a four-phonon interaction with the zone center A_{2u} phonon at 820 cm^{-1} and out-of-plane optical/acoustic phonons at the M and K points of the Brillouin zone with frequencies around 300 cm^{-1} [8]. The 22 ps component reflects the time evolution of low-frequency phonon populations.

Two different mechanisms underline the dispersive shape of the pump-probe spectra: (i) At early delay times, the transient population of the $v = 1$ phonon state gives rise to a positive reflectivity change on the $v = 1$ to 2 transition, in parallel to a negative reflectivity change on the $v = 0$ to 1 transition. The $v = 1$ to 2 component is redshifted by the small diagonal anharmonicity of 5 cm^{-1} of the TO phonon. Both components decay with the $v = 1$ population lifetime of 1.2 ps. (ii) The population of low-frequency phonons via the impulsive Raman process gives rise to a redshift of the TO phonon resonance, caused by the anharmonic intermode coupling between the TO and the low-frequency phonons. Experiments with different spectral bandwidth of the pump pulses suggest that predominantly the excitation of interlayer shear and breathing modes cause the TO frequency shift. The corresponding change of reflectivity displays a substantially longer decay time of 22 ps, reflecting the depopulation of the Raman-excited low-frequency phonons and formation of a thermalized phonon system. Theoretical calculations of the layer-number-dependent Raman cross-section support this scenario and underline the relevance of interphonon interactions for the nonlinear phonon dynamics. The distinctive interplane mode excitation and coupling with the TO mode are shown to be a genuine property of few-layer hBN.

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