Extending IR-Spectroscopy to Non-IR-Active Modes

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Coherently excited phonons are a unique tool to control material properties, drive phase transitions or even access hidden phases on ultrafast time scales [1]. The increasing availability of high-field THz and mid-IR (MIR) sources facilitates targeting of specific resonantly driven phonons, while leaving the material in its electronic ground state. Nevertheless, this direct excitation is restricted to IR-active modes, whereas purely Raman-active modes are symmetry protected against even intense resonant THz fields. Thus, for Raman-active modes, nonlinear excitation mechanisms must be employed, which are either mediated by photons through the electronic polarizability or via nonlinearly coupled anharmonic phonons. Respectively, these difference-frequency processes are conventionally impulsive stimulated Raman scattering (ISRS) and, more recently, ionic Raman scattering (IRS), which both lack the precise selectivity of resonant excitation.

Here, we present the THz/MIR sum-frequency counterparts of these two mechanisms, which are more selective, non-impulsive, and provide direct control of the phonon phase. We demonstrate MIR sum-frequency excitation of the archetypal Raman-active phonon in diamond [2]. This two-photon absorption process, the up-conversion counter part of ISRS, directly imprints the carrier envelope phase of the light field onto the coherent phonons phase. Additionally, our theory framework, based on a coupled oscillator model and DFT calculation, also predicted a strong sum-frequency counterpart for IRS [3], which was subsequently confirmed by experimental works of other groups [4]. With this, we complete the map of photonic and ionic Raman excitation mechanisms with their sum-frequency counterparts, providing comprehensive handles for selective and non-impulsive coherent control of phonons and non-IR-active modes by strong THz or MIR fields.

As an outlook, we will show a preview of our current work employing these methods to study the ultrafast response of the highly polarizable lattice of hybrid organic-inorganic lead halide perovskites semiconductors. Based on previous optical Four Wave Mixing studies [5] and modelling [6], we distinguish THz-induced Kerr Effect signatures from electronic and lattice polarizability.

References

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