Supplemental material

The conflicting role of buckled structure in phonon transport of 2D group-IV and group-V materials

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Role of Ge 3d and Sn 4d electrons in lattice dynamics

Fig. S1 shows the phonon dispersion for germanene (stanene) taking into account only the 4s and 4p Ge (5s and 5p Sn) valence states. The calculated phonon dispersion overall agrees with the results from the Ge_d (Sn_d) pseudopotential, which includes Ge 3d (Sn 4d) electrons as valence electrons. However, without considering Ge 3d and Sn 4d electrons, these calculations do predict an instability for both germanene and stanene with a small region of negative frequencies near the Γ point, as reported before.¹² In fact, for accurately describing the lattice dynamics of InP, treating In 4d electrons as valence electrons is required, while neglecting In 4d electrons leads to negative frequencies near the Γ point, which is probably due to reduced screening and an overestimate of the bonding strength.³ This might be the case in germanene and stanene.

![Fig S1: Phonon dispersion for (a) germanene taking into account only the 4s and 4p Ge valence states and (b) stanene taking into account only the 5s and 5p Sn valence states along different symmetry lines.](image)

The formation of the acoustic-optical gap

In a buckled system the covalent bonds become nonorthogonal to both the XY plane and Z direction, which results in the hybridization between the vibrations in the XY plane and Z direction,⁴⁶ corresponding to nonzero XZ and YZ components of the harmonic interatomic force constants. Figure S2 shows the phonon dispersion of all-studied 2D group-IV materials with zero off-diagonal
components XZ and YZ of the interatomic force constants. When the off-diagonal components XZ and YZ of the interatomic force constants are set to be zero, the XY modes are completely decoupled with the Z modes, which is exactly the case in graphene. For silicene, germanene and stanene, if there were no hybridization between the vibrations in the XY plane and Z direction, a similar dispersion could be observed in the LA and ZO branch. However, in the real case the LA-ZO coupling leads to flattened LA branch and stiffened ZO branch, while the TA and TO branches remain the same. Thus the acoustic-optical gap is formed.

Figure S2: Phonon dispersion for (a) graphene, (b) silicene, (c) germanene and (d) stanene along different symmetry lines with zero off-diagonal components XZ and YZ of the interatomic force constants. The original phonon dispersion (grey dash) for silicene, germanene and stanene are shown for comparison.
Phonon dispersion for 2D group-V materials with zero off-diagonal components XZ and YZ of the interatomic force constants

As shown in Figure S3, if we set the off-diagonal components XZ and YZ of the interatomic force constants to be zero, the acoustic-optical gap will disappear as well in 2D group-V materials.

Figure S3: Phonon dispersion for (a) nitrogene, (b) blue phosphorene, (c) arsenene and (d) antimonene along different symmetry lines with zero off-diagonal components XZ and YZ of the interatomic force constants.

References


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