Electronic Supplementary Material (ESI) for Nanoscale.


# 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 3*d* and Sn 4*d* electrons in lattice dynamics

Fig. S1 shows the phonon dispersion for germanene (stanene) taking into account only the 4*s* and 4*p* Ge (5*s* and 5*p* Sn) valence states. The calculated phonon dispersion overall agrees with the results from the Ge_*d* (Sn_*d*) pseudopotential, which includes Ge 3*d* (Sn 4*d*) electrons as valence electrons. However, without considering Ge 3*d* and Sn 4*d* 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.[1,2] In fact, for accurately describing the lattice dynamics of InP, treating In 4*d* electrons as valence electrons is required, while neglecting In 4*d* 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.

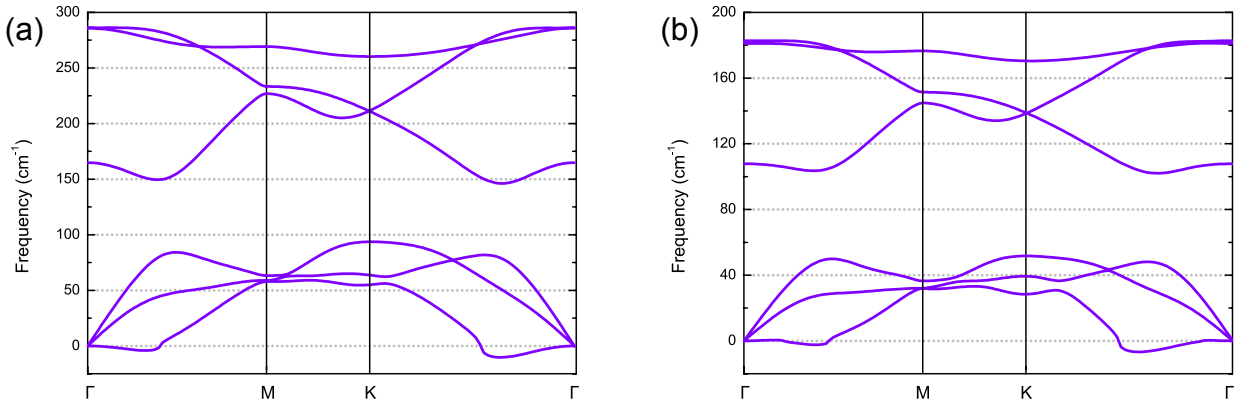


Figure S1: Phonon dispersion for (a) germanene taking into account only the 4*s* and 4*p* Ge valence states and (b) stanene taking into account only the 5*s* and 5*p* Sn valence states along different symmetry lines.

## 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,[4–6] 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.

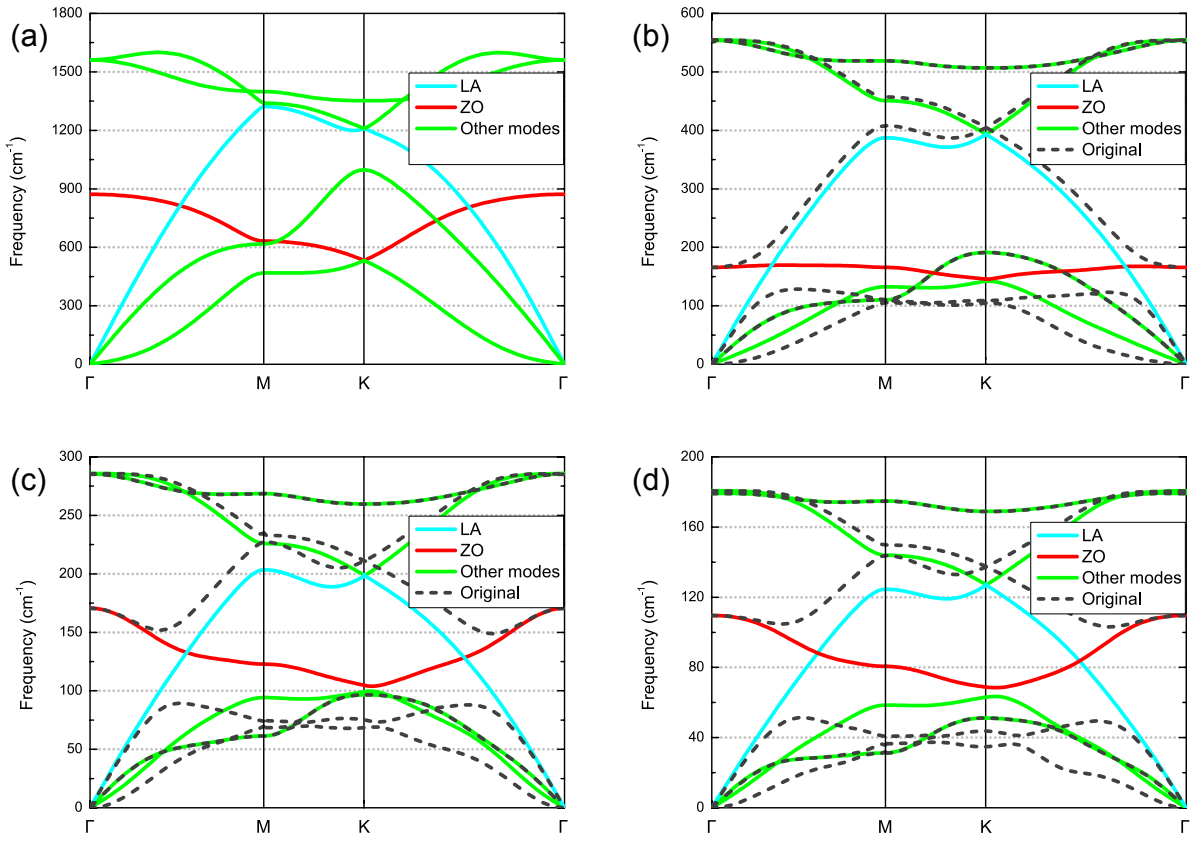


Figure S2: Phonon dispersion for (a) graphene, (b) silicene, (c) germanene and (d) stanene along different symmetry lines with zero off-diagonal components XZ and YZ of the interatomic force constants. The original phonon dispersion (grey dash) for silicene, germanene and stanene are shown for comparison.

# 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.

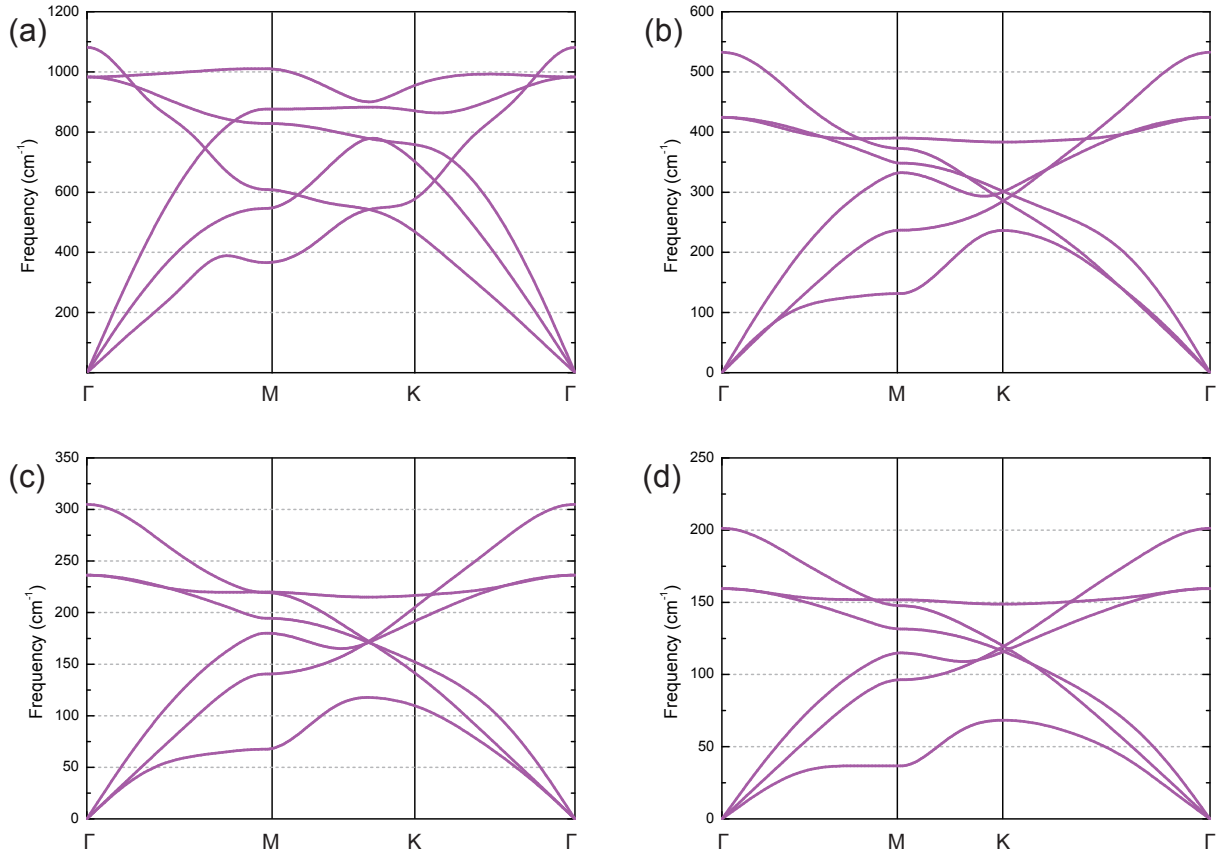


Figure S3: Phonon dispersion for (a) nitrogene, (b) blue phosphorene, (c) arsenene and (d) antimonene along different symmetry lines with zero off-diagonal components XZ and YZ of the interatomic force constants.

## References


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