Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ESI: Computational investigations of Dienes defect- and vacancy-induced changes to electronic and vibrational properties of carbon fiber structural units

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Parameter	Value
Processor grid	1×1×1
Energy convergence criterion	1×10^{-9} Ha = 2.72 $\times10^{-8}$ eV
RMS convergence criterion	1×10^{-8} Ha = 2.72 $\times10^{-7}$ eV
Wavefunction grid (7×7 cell)	100 ×100×80
Wavefunction grid (8×8 cell)	112×112×80
Wavefunction grid (10×10 cell)	144×144×80

Table 1: RMG-specific and additional computational parameters.

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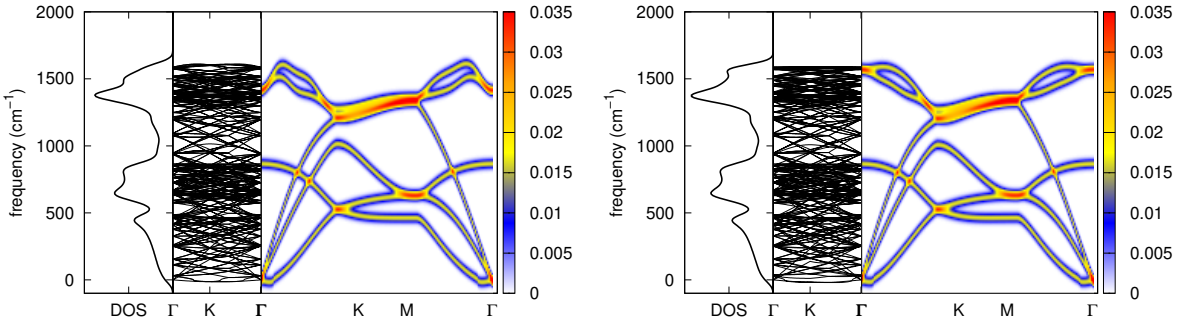

Figure 1: Phonon DOS, folded, and unfolded phonon band structure of 8×8 pristine graphene calculated with a symmetry tolerance of 0.1 Å (left) and 0.00001 Å (right).

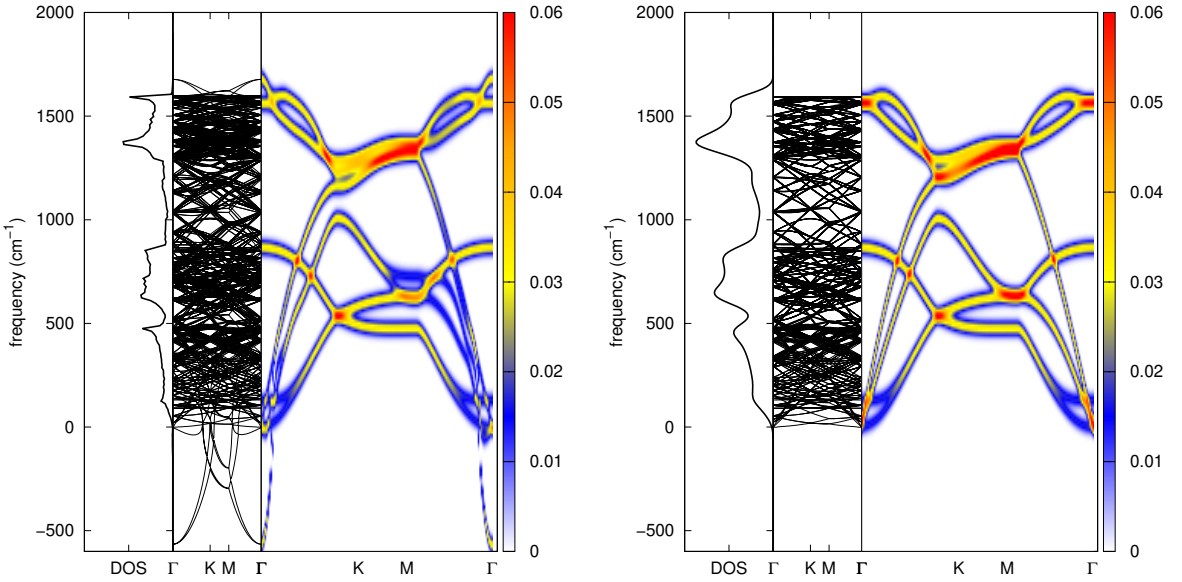

Figure 2: Phonon DOS, folded, and unfolded phonon band structure of 7×7 pristine graphite calculated with a symmetry tolerance of 0.1 Å (left) and 0.01 Å (right).

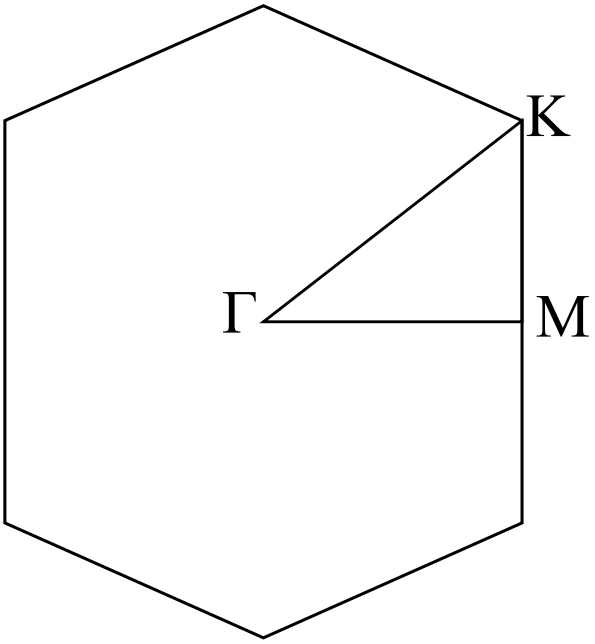

Figure 3: Γ, K, and M high-symmetry points in the Brillouin Zone of a P6/mmm hexagonal cell.

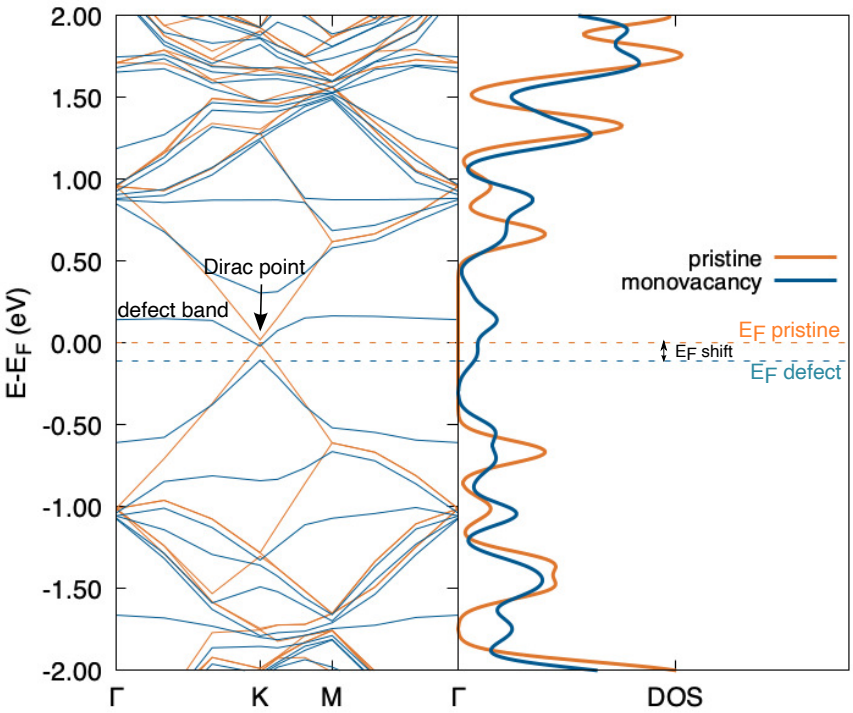

Figure 4: Annotated version of the left panel of Figure 3 which points out the Fermi energies, Dirac point at K, and defect band at Γ which will aid in the interpretation of Figures 3 and 9 in the main text.

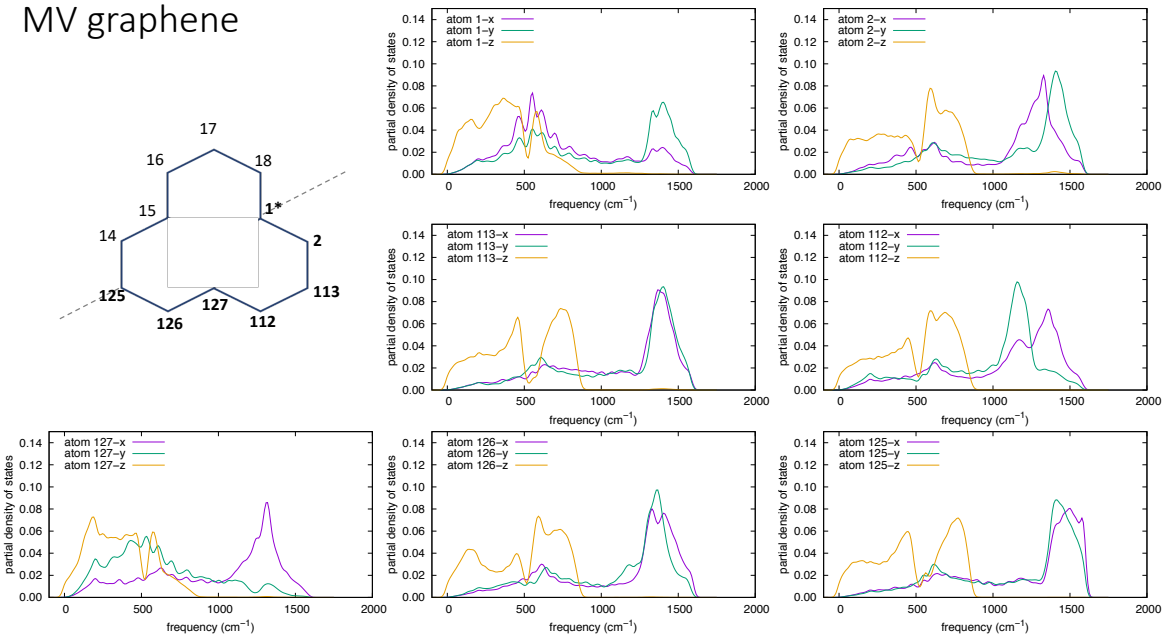

Figure 5: Projected phonon DOS of select atoms around the monovacancy defect in graphene. The relation between atom numbers and the defect structure are also given.

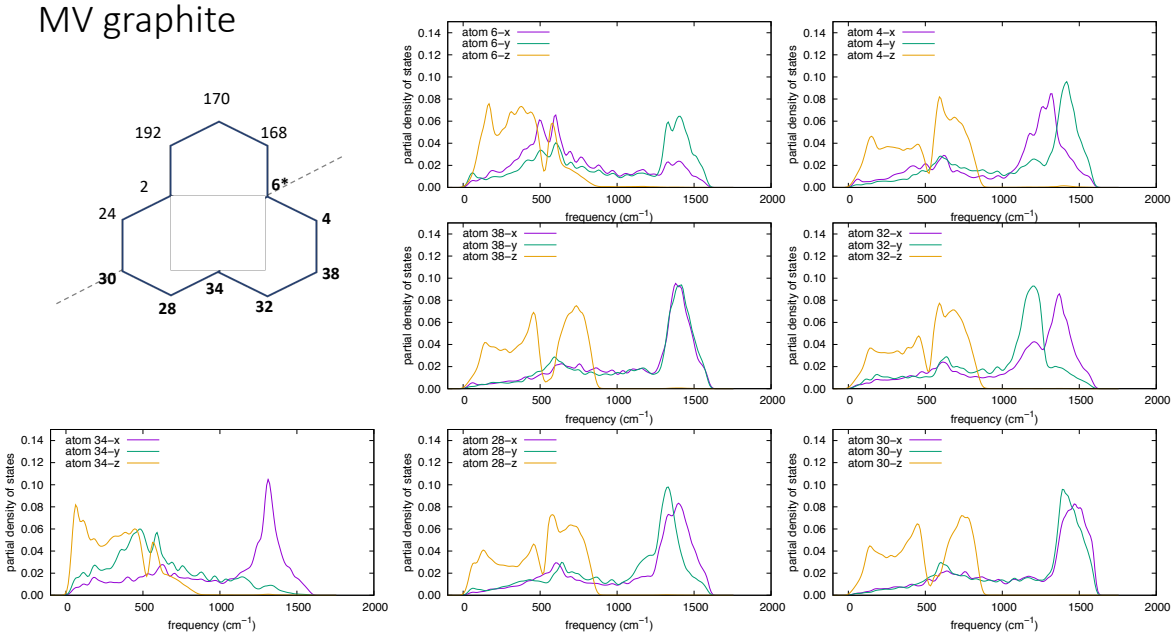

Figure 6: Projected phonon DOS of select atoms around the monovacancy defect in graphite. The relation between atom numbers and the defect structure are also given.

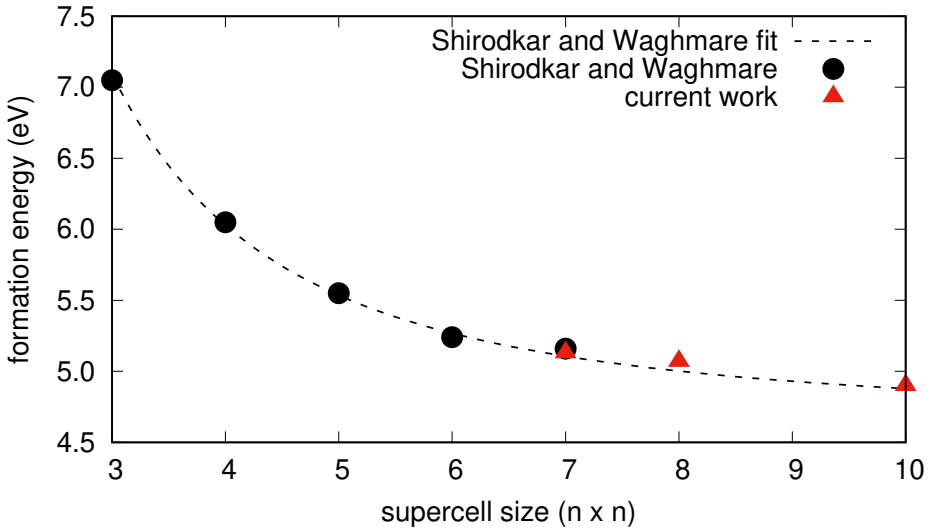

Figure 7: Formation energy of Dienes defect as a function of computational cell size from the Shirodkar and Waghmare[1] and this work.

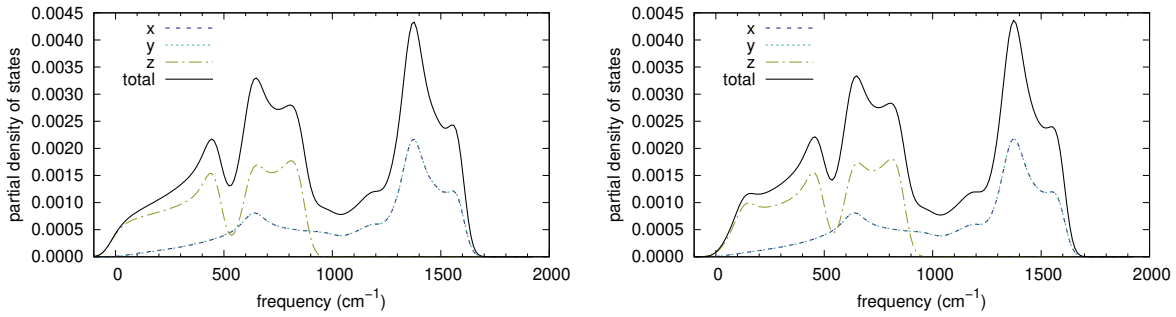

Figure 8: Phonon DOS of graphene (left) and graphite (right) projected along the in-plane (x- and y-) and out-of-plane (z-) directions. The dashed black line shows the sum along all three directions. A mesh of 10×10×8 was used to generate the projected density of states.

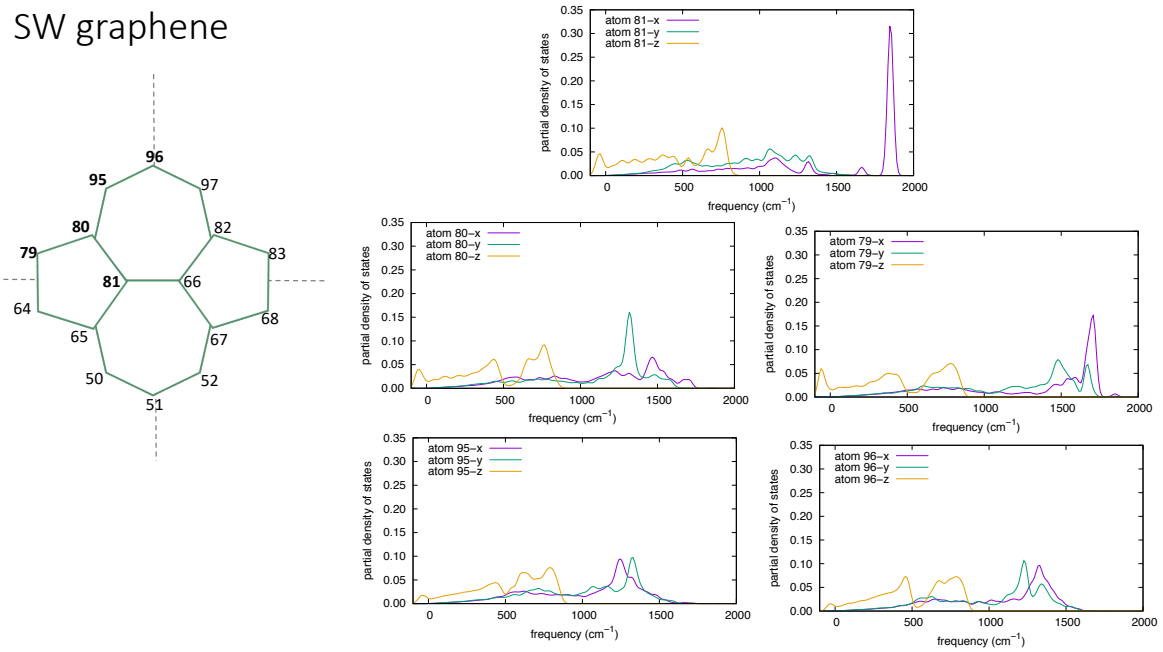

Figure 9: Projected phonon DOS of select atoms around the Dienes defect in graphene. The relation between atom numbers and the defect structure are also given.

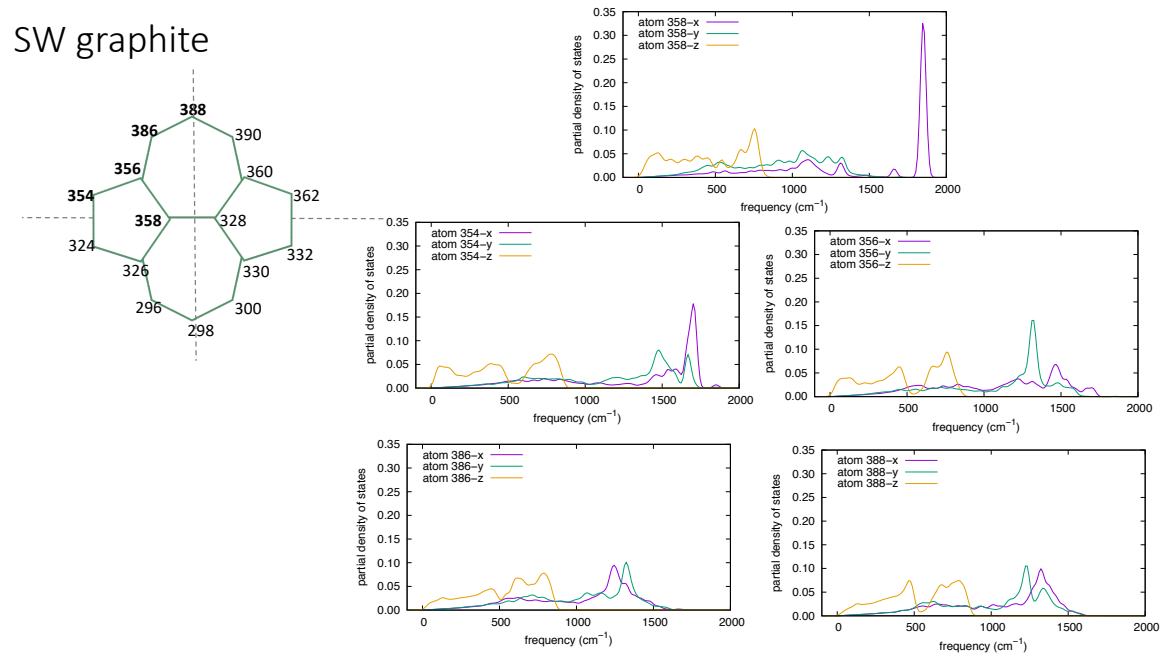

Figure 10: Projected phonon DOS of select atoms around the Dienes defect in graphite. The relation between atom numbers and the defect structure are also given.

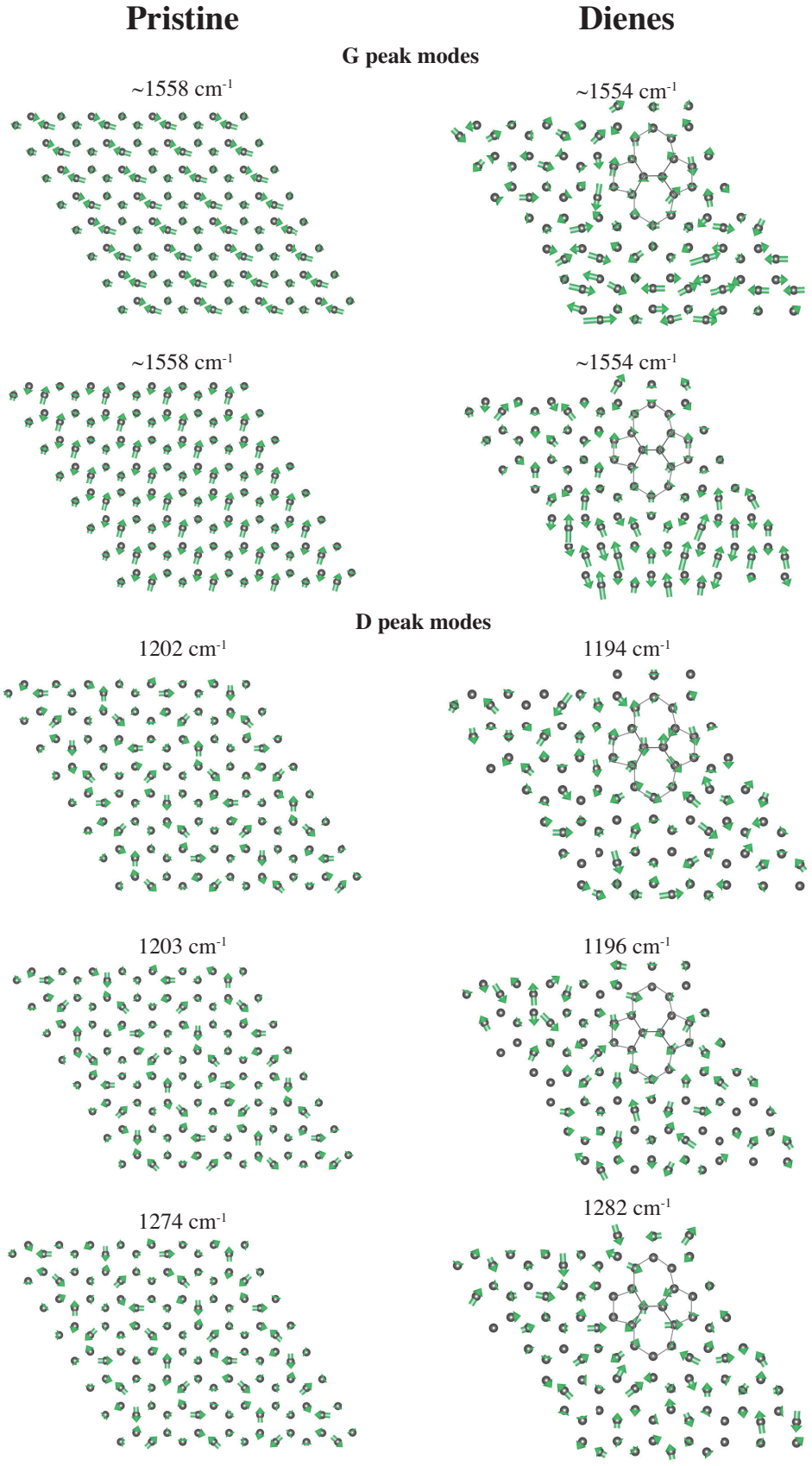

Figure 11: Eigenvectors of select modes in Dienes defective graphene which may contribute to the experimental Raman peaks. The left column are the calculated eigenmodes in pristine graphene and the right column are the corresponding modes in Dienes defective graphene.The top two panels are the degenerate G peak modes and the bottom three panels are possible D peak modes.

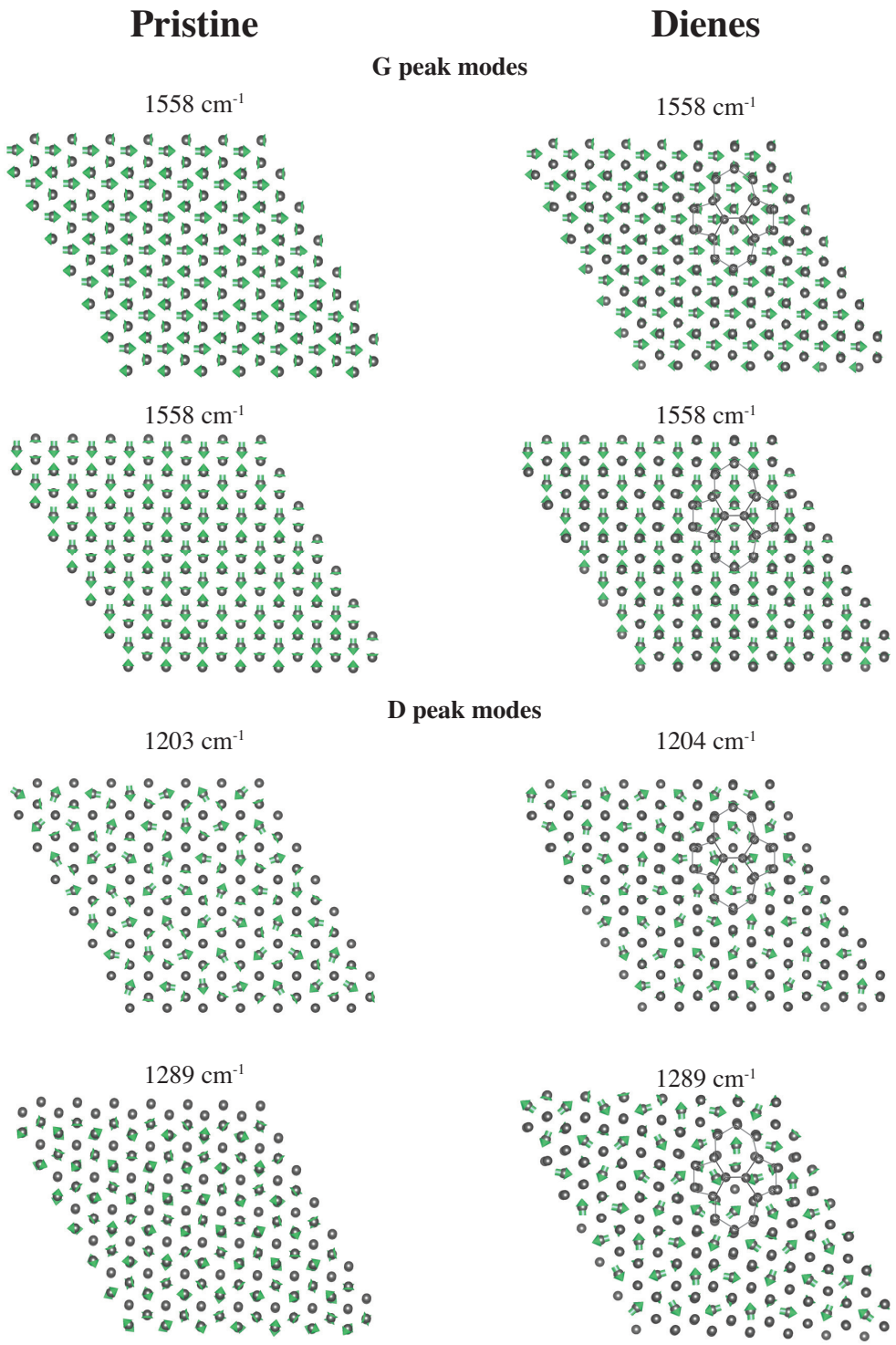

Figure 12: Eigenvectors of select modes in Dienes defective graphite which may contribute to the experimental Raman peaks. The left column are the calculated eigenmodes in pristine graphite and the right column are the corresponding modes in Dienes defective graphite.The top two panels are the degenerate G peak modes and the bottom two panels are possible D peak modes.

References

[1] Shirodkar, S. N.; Waghmare, U. V. *Physical Review B* **2012**, *86*, 165401.