Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information: Theoretical Study on Synergistic Tuning of Graphene Phonons via Heteroatom Modifications

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Table S1. Calculated highest optical phonon mode at the Γ point for pristine and functionalized graphene systems.

System	Highest Optical Mode (Γ) (THz)	Energy (meV)	Raman Shift (cm^{-1})	Shift vs. G 1580 cm^{-1} (cm^{-1})
Pristine Graphene	41.65	172.23	1388.8	-191.2
N-doped Graphene	44.47	183.84	1483.2	-96.8
Au-loaded Graphene	47.43	196.2	1582.2	+2.2
N-doped-Au-loaded Graphene	45.33	187.41	1511.7	-68.3

The corresponding energy (in meV) and Raman shift (in cm^{-1}) are provided, along with the relative shift compared to the typical G band position at 1580 cm^{-1}, which originates from the in-plane E_{2g} mode of sp^2-carbon[2]. The Raman shift values were obtained by converting the phonon frequency at the Γ point into wavenumber using the relation 1 THz $\approx$ 33.356 cm^{-1}, and the deviation from 1580 cm^{-1} serves as a reference to assess the redshift or blueshift of the G band under different functionalizations[3]. Here, a "redshift" indicates that the Raman shift is lower than 1580 cm^{-1} (i.e., a shift toward lower frequencies), while a "blueshift" denotes a shift toward higher frequencies.

Table S2. Calculated highest optical phonon mode at the K point for pristine and functionalized graphene systems

System	Highest Optical Mode (K) (THz)	Energy (meV)	Raman Shift (cm^{-1})
Pristine Graphene	45.47	187.9	1516.4
N-doped Graphene	47.06	194.61	1570.1
Au-loaded Graphene	47.35	195.94	1579.2
N-doped-Au-loaded Graphene	46.86	193.75	1563.1

Table S2 presents the calculated highest optical phonon mode at the K point for pristine and functionalized graphene systems. The values presented herein were derived by extracting the highest optical phonon mode at the K point from the phonon dispersion curves (refer to Figure 2). The corresponding Raman shift (cm^{-1}) was computed using a conversion factor of 1 THz ≈ 33.356 cm^{-1}. [3]

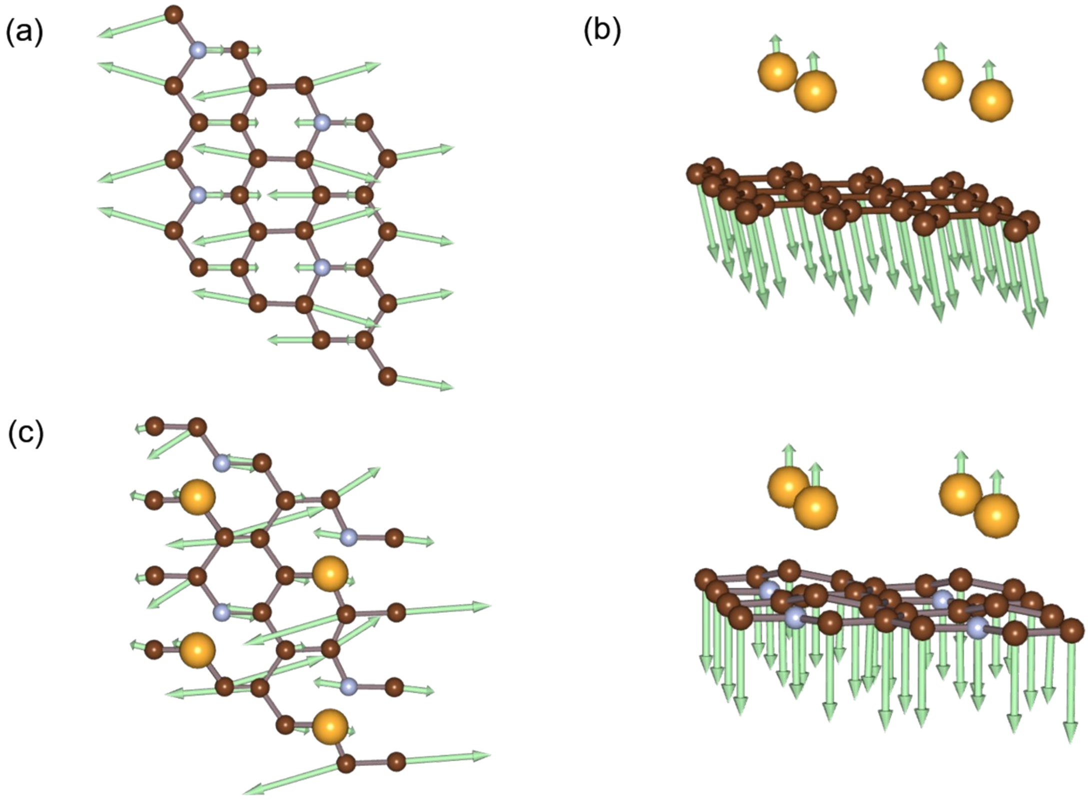

Figure S1. Representative vibrations in modified graphene**.** (a) N-doped graphene, (b) Au-loaded graphene, (c) N-doped-Au-loaded graphene.

Figure S1 shows representative phonon modes in various modified graphene systems. (a) shows a high-frequency vibration (~46.79 THz) at the M point in N-doped graphene, corresponding to in-plane stretching between N and C atoms. (b) shows a low-frequency vibration (~0.95 THz) at the Γ point in Au-loaded graphene, characterized by an out-of-plane "breathing" vibration. (c) shows two distinct vibrations in N-doped–Au-loaded graphene: the left shows a high-frequency vibration (~46.79 THz) at the M point, while the right displays a low-frequency vibration (~5.13 THz) at the Γ point. This comparison indicates that dual heteroatom modification induces diverse phonon characteristics. Arrows indicate the direction and relative amplitude of atomic displacements.

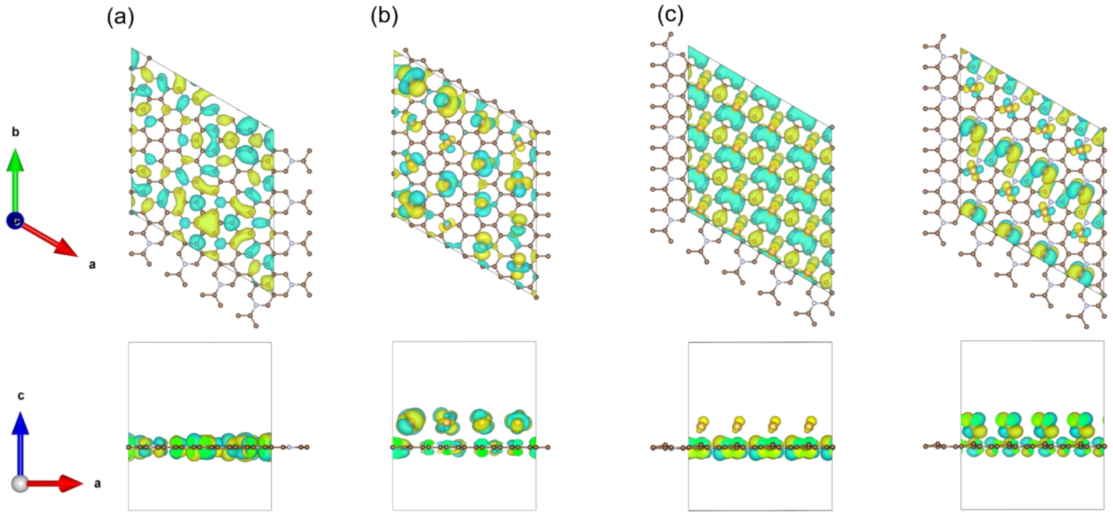

Figure S2. Real-space isosurface plots of representative electronic states for modified graphene. (a) N-doped graphene, (b) Au-loaded graphene, (c) N doped-Au loaded graphene.

Figure S2 illustrates real-space isosurface plots of representative electronic states obtained from DFT calculations for modified Graphene. Figure S2a shows N-doped graphene at the Fermi level, which exhibits a strongly localized electronic density on the substitutional N atom and its nearest-neighbor C atoms, confirming that the new PDOS feature in Figure 3b originates from N 2p-C 2p hybridization. Figure S2b shows Au-loaded graphene, where the state at -1.5 eV displays a wavefunction confined to the Au adatom, indicating that the sharp PDOS peak in Figure 3c is dominated by Au 5d orbitals; this localization on a heavy element is consistent with the emergence and reinforcement of low-frequency out-of-plane vibrations. Figure S2c shows dual-modified (N-doped-Au-loaded) graphene in two views: the left side displays the Fermi level state with the same N-centered localization as in Figure S2a, whereas the right side at -2.5 eV highlights Au 5d; the coexistence of N- and Au-centered states on the same lattice suggests a synergistic effect on the surrounding C atoms, thereby rationalizing the coupling character and the frequency shift of the calculated phonon modes. For better visualization of the spatial distribution, the upper panels are presented in a top view, while the lower panels are presented in a side view.

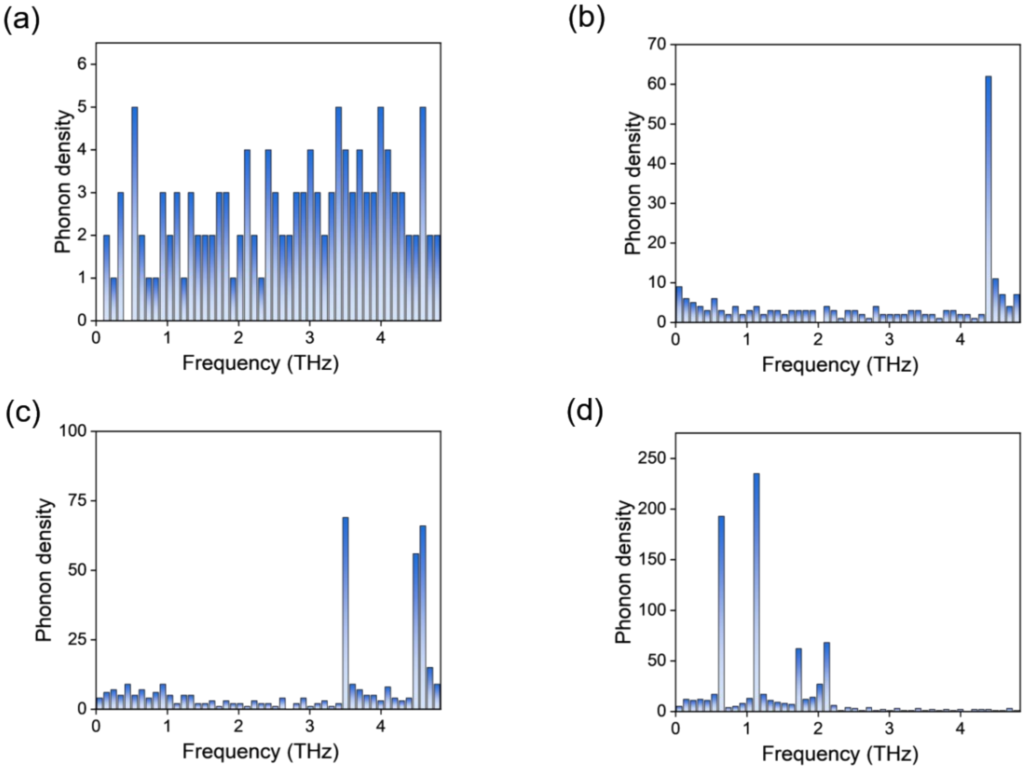

Figure S3. (a) Phonon density in the frequency range of 0-4.837 THz (0-20 meV) of pristine graphene, (b) N-doped graphene, (c) Au-loaded graphene, (d) and N-doped-Au-loaded graphene.

Figure S3 illustrates the phonon density within the frequency range of 0-4.837 THz (0-20 meV). The X-axis denotes the frequency (in THz), while the Y-axis represents the phonon density, defined as the number of modes within each frequency interval. As depicted in Figure S1, the number of phonon modes in the 0-20 meV range increases for N-doped graphene and Au-loaded graphene. The N-doped-Au-loaded graphene exhibits a notable increase in the number of modes within this range.

References

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