# Supplementary materials

# Phonon dynamics in $MoSi_2N_4$. Insights from DFT calculations.

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Table S1. Structural data for α1 structure.

| Cell length, Å | *a* | *b* | *c* |
|---|---|---|---|
| | 2.910606 | 2.910606 | 24.989594 |
| Angle, ° | alpha | betta | gamma |
| | 90 | 90 | 120 |
| Atomic coordinates | x | y | z |
| Mo1 | 0.333333 | 0.666666 | 0.2 |
| Si1 | 0 | 0 | 0.319903 |
| Si2 | 0 | 0 | 0.080097 |
| N1 | 0 | 0 | 0.149914 |
| N2 | 0 | 0 | 0.250086 |
| N3 | 0.666667 | 0.333333 | 0.059944 |
| N4 | 0.666666 | 0.333333 | 0.340056 |

Table S2. Structural data for α2 structure.

| Cell length, Å | *a* | *b* | *c* |
|---|---|---|---|
| | 2.897820 | 2.897820 | 25.210600 |
| Angle, ° | alpha | betta | gamma |
| | 90 | 90 | 120 |
| Atomic coordinates | x | y | z |
| Mo1 | 0.333333 | 0.666666 | 0.2 |
| Si1 | 0 | 0 | 0.319621 |
| Si2 | 0 | 0 | 0.080379 |
| N1 | 0 | 0 | 0.149994 |
| N2 | 0 | 0 | 0.250006 |
| N3 | 0.333334 | 0.666667 | 0.059738 |
| N4 | 0.333333 | 0.666666 | 0.340262 |

Table S3. Structural data for α3 structure.

| Cell length, Å | *a* | *b* | *c* |
|---|---|---|---|
| | 2.912063 | 2.912063 | 24.964600 |
| Angle, ° | alpha | betta | gamma |
| | 90 | 90 | 120 |
| Atomic coordinates | x | y | z |
| Mo1 | 0.333333 | 0.666666 | 0.199597 |
| Si1 | 0 | 0 | 0.320844 |
| Si2 | 0 | 0 | 0.079292 |
| N1 | 0 | 0 | 0.149197 |
| N2 | 0 | 0 | 0.250526 |
| N3 | 0.666667 | 0.333333 | 0.059060 |
| N4 | 0.333333 | 0.666666 | 0.341484 |

Table S4. Energy difference of calculated stacking of bulk $MoSi_2N_4$

| Stacking | AB | AC | AA | AB* | AC* |
|---|---|---|---|---|---|
| Configuration | α1 structure | | | | |
| Energy difference relative to AB (eV) | 0.0000 | -0.0004 | 0.0877 | 0.0849 | -0.0471 |
| Configuration | α2 structure | | | | |
| Energy difference relative to AB (eV) | 0.0000 | 0.0004 | 0.0840 | -0.0383 | 0.0821 |
| Configuration | α3 structure | | | | |
| Energy difference relative to AB (eV) | 0.0000 | 0.0001 | 0.0171 | -0.0235 | -0.0185 |

Table S5. Structural data for two layered α1 structure.

| Cell length, Å | *a* | *b* | *c* |
|---|---|---|---|
| | 2.910606 | 2.910606 | 40.000000 |
| Angle, ° | alpha | betta | gamma |
| | 90 | 90 | 120 |
| Atomic coordinates | x | y | z |
| Mo1 | 0.33333 | 0.66667 | 0.124950 |
| Mo2 | 0.33333 | 0.66667 | 0.374950 |
| Si1 | 0 | 0 | 0.199855 |
| Si2 | 0 | 0 | 0.050040 |
| Si3 | 0.66667 | 0.33333 | 0.449855 |
| Si4 | 0.66667 | 0.33333 | 0.300040 |
| N1 | 0 | 0 | 0.093655 |
| N2 | 0 | 0 | 0.156240 |
| N3 | 0.66667 | 0.33333 | 0.037450 |
| N4 | 0.66667 | 0.33333 | 0.212445 |
| N5 | 0.66667 | 0.33333 | 0.343655 |
| N6 | 0.66667 | 0.33333 | 0.406240 |
| N7 | 0 | 0 | 0.287450 |
| N8 | 0 | 0 | 0.462445 |

Table S6. Structural data for two layered α2 structure.

| Cell length, Å | *a* | *b* | *c* |
|---|---|---|---|
| | 2.89780 | 2.89780 | 40.000000 |
| Angle, ° | alpha | betta | gamma |
| | 90 | 90 | 120 |
| Atomic coordinates | x | y | z |
| Mo1 | 0.33333 | 0.66667 | 0.126055 |
| Mo2 | 0 | 0 | 0.376055 |
| Si1 | 0 | 0 | 0.201445 |
| Si2 | 0 | 0 | 0.050660 |
| Si3 | 0.33333 | 0.66667 | 0.451445 |
| Si4 | 0.33333 | 0.66667 | 0.300660 |
| N1 | 0 | 0 | 0.094535 |
| N2 | 0 | 0 | 0.157570 |
| N3 | 0.33333 | 0.66667 | 0.037650 |
| N4 | 0.33333 | 0.66667 | 0.214455 |
| N5 | 0.33333 | 0.66667 | 0.344535 |
| N6 | 0.33333 | 0.66667 | 0.407570 |
| N7 | 0 | 0 | 0.287650 |
| N8 | 0 | 0 | 0.464455 |

Table S7. Structural data for two layered α3 structure.

| Cell length, Å | *a* | *b* | *c* |
|---|---|---|---|
| | 2.91210 | 2.91210 | 40.000000 |
| Angle, ° | alpha | betta | gamma |
| | 90 | 90 | 120 |
| Atomic coordinates | x | y | z |
| Mo1 | 0.33333 | 0.66667 | 0.124570 |
| Mo2 | 0 | 0 | 0.374570 |
| Si1 | 0 | 0 | 0.200245 |
| Si2 | 0 | 0 | 0.049485 |
| Si3 | 0.33333 | 0.66667 | 0.450245 |
| Si4 | 0.33333 | 0.66667 | 0.299490 |
| N1 | 0 | 0 | 0.093115 |
| N2 | 0 | 0 | 0.156355 |
| N3 | 0.66667 | 0.33333 | 0.036860 |
| N4 | 0.33333 | 0.66667 | 0.213125 |
| N5 | 0.33333 | 0.66667 | 0.343115 |
| N6 | 0.33333 | 0.66667 | 0.406355 |
| N7 | 0.66667 | 0.33333 | 0.286860 |
| N8 | 0 | 0 | 0.463125 |

Table S8. Structural data for bulk α1 structure.

| Cell length, Å | *a* | *b* | *c* |
|---|---|---|---|
| | 2.910606 | 2.910606 | 10.000000 |
| Angle, ° | alpha | betta | gamma |
| | 90 | 90 | 120 |
| Atomic coordinates | x | y | z |
| Mo1 | 0.3333 | 0.66667 | 0.2499 |
| Mo2 | 0.3333 | 0.66667 | 0.7499 |
| Si1 | 0 | 0 | 0.39971 |
| Si2 | 0 | 0 | 0.10008 |
| Si3 | 0.66667 | 0.33333 | 0.89971 |
| Si4 | 0.66667 | 0.33333 | 0.60008 |
| N1 | 0 | 0 | 0.18731 |
| N2 | 0 | 0 | 0.31248 |
| N3 | 0.66667 | 0.33333 | 0.07490 |
| N4 | 0.66667 | 0.33333 | 0.42489 |
| N5 | 0.66667 | 0.33333 | 0.68731 |
| N6 | 0.66667 | 0.33333 | 0.81248 |
| N7 | 0 | 0 | 0.57490 |
| N8 | 0 | 0 | 0.92489 |

Table S9. Structural data for bulk α2 structure.

| Cell length, Å | *a* | *b* | *c* |
|---|---|---|---|
| | 2.897820 | 2.897820 | 10.000000 |
| Angle, ° | alpha | betta | gamma |
| | 90 | 90 | 120 |
| Atomic coordinates | x | y | z |
| Mo1 | 0.33333 | 0.66667 | 0.25211 |
| Mo2 | 0 | 0 | 0.75211 |
| Si1 | 0 | 0 | 0.40289 |
| Si2 | 0 | 0 | 0.10132 |
| Si3 | 0.33333 | 0.66667 | 0.90289 |
| Si4 | 0.33333 | 0.66667 | 0.60132 |
| N1 | 0 | 0 | 0.18907 |
| N2 | 0 | 0 | 0.31514 |
| N3 | 0.33333 | 0.66667 | 0.07530 |
| N4 | 0.33333 | 0.66667 | 0.42891 |
| N5 | 0.33333 | 0.66667 | 0.68907 |
| N6 | 0.33333 | 0.66667 | 0.81514 |
| N7 | 0 | 0 | 0.57530 |
| N8 | 0 | 0 | 0.92891 |

Table S10. Structural data for bulk α3 structure.

| Cell length, Å | *a* | *b* | *c* |
|---|---|---|---|
| | 2.912063 | 2.912063 | 10.000000 |
| Angle, ° | alpha | betta | gamma |
| | 90 | 90 | 120 |
| Atomic coordinates | x | y | z |
| Mo1 | 0.33333 | 0.66667 | 0.24914 |
| Mo2 | 0 | 0 | 0.74914 |
| Si1 | 0 | 0 | 0.40049 |
| Si2 | 0 | 0 | 0.09897 |
| Si3 | 0.33333 | 0.66667 | 0.90049 |
| Si4 | 0.33333 | 0.66667 | 0.59898 |
| N1 | 0 | 0 | 0.18623 |
| N2 | 0 | 0 | 0.31271 |
| N3 | 0.66667 | 0.33333 | 0.07372 |
| N4 | 0.33333 | 0.66667 | 0.42625 |
| N5 | 0.33333 | 0.66667 | 0.68623 |
| N6 | 0.33333 | 0.66667 | 0.81271 |
| N7 | 0.66667 | 0.33333 | 0.57372 |
| N8 | 0 | 0 | 0.92625 |

Table S11. Comparison of wavenumbers (in $cm^{-1}$) of vibrations in the $\alpha$1 structure calculated using various DFT approaches.

| Expt. | *Irreps.* | LDA | GGA PBE [S1] | GGA PBE TS [S2] | GGA PBESol [S3] | GGA BLYP [S4] | meta-GGA [S5] |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| - | $E$" | 126.4 | 128.9 | 126.7 | 126.03 | 121.5 | 146.6 |
| - | $E$' | 169.2 | 167.0 | 163.3 | 163.4 | 168.5 | 157.7 |
| 289 | $A_1$' | 285.1 | 289.9 | 291.0 | 285.3 | 297.51 | 324.7 |
| 348 | $A_2$" | 386.3 | 379.5 | 383.3 | 381.6 | 378.5 | 406.3 |
| 589 | $E$" | 568.2 | 531.9 | 538.5 | 547.9 | 529.3 | 493.6 |
| 634 | $E$' | 647.1 | 612.3 | 621.2 | 627.7 | 600.5 | 588.3 |
| 692 | $A_1$' | 703.3 | 686.1 | 691.0 | 679.4 | 700.2 | 742.5 |
| | $A_2$" | 704.9 | 686.5 | 691.4 | 681.8 | 703.0 | 872.9 |
| - | $E$" | 823.1 | 801.0 | 814.4 | 811.8 | 780.3 | 873.1 |
| - | $E$' | 823.4 | 801.3 | 814.7 | 812.1 | 780.6 | 873.1 |
| | $A_2$" | 1054.9 | 1021.5 | 1033.3 | 1023.8 | 1007.5 | 1046.6 |
| 1051 | $A_1$' | 1060.4 | 1029.4 | 1040.1 | 1030.5 | 1018.6 | 1057.6 |


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[S4] Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. Phys. Rev. A 1988, 38 (6), 3098–3100. https://doi.org/10.1103/PhysRevA.38.3098.

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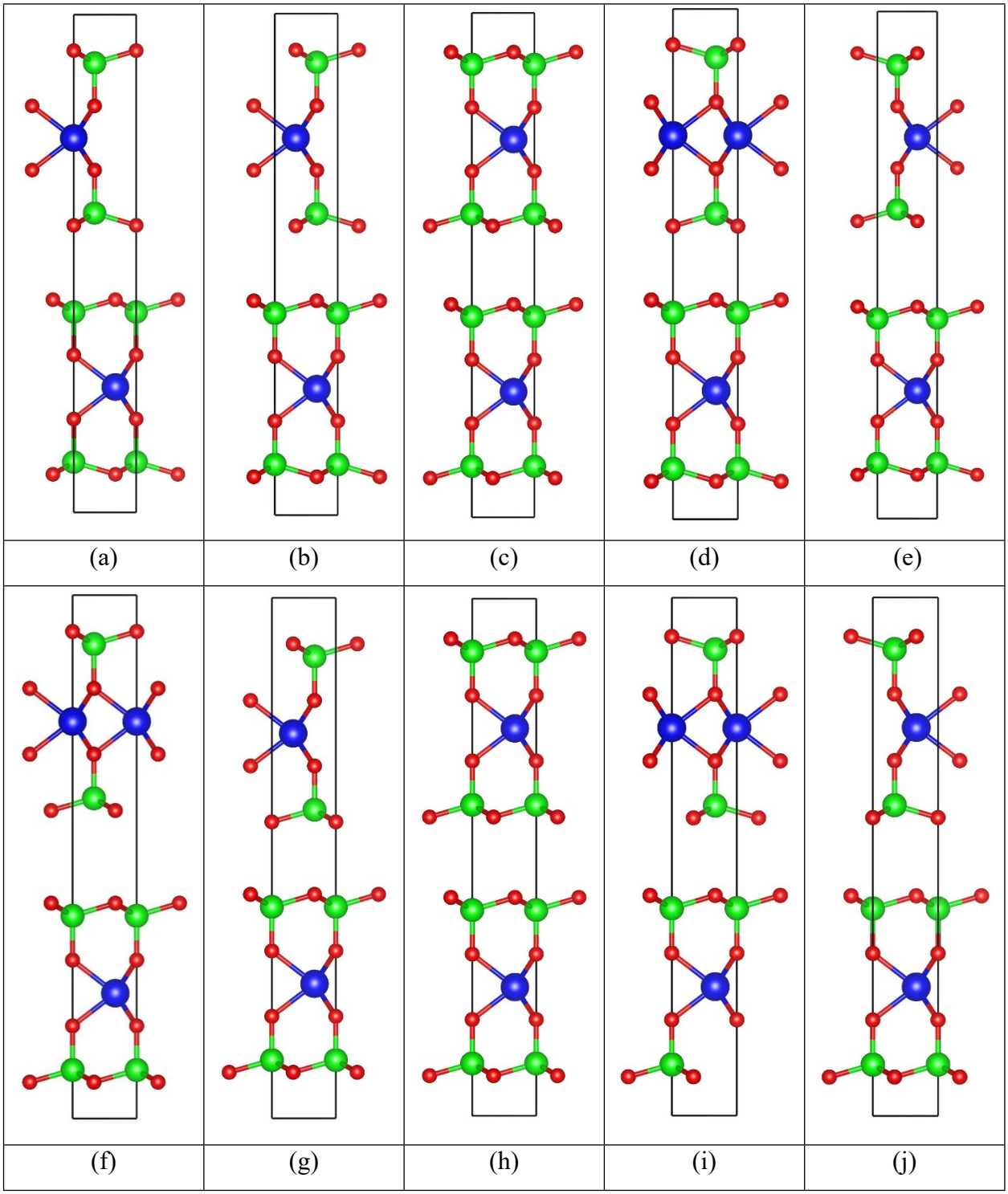
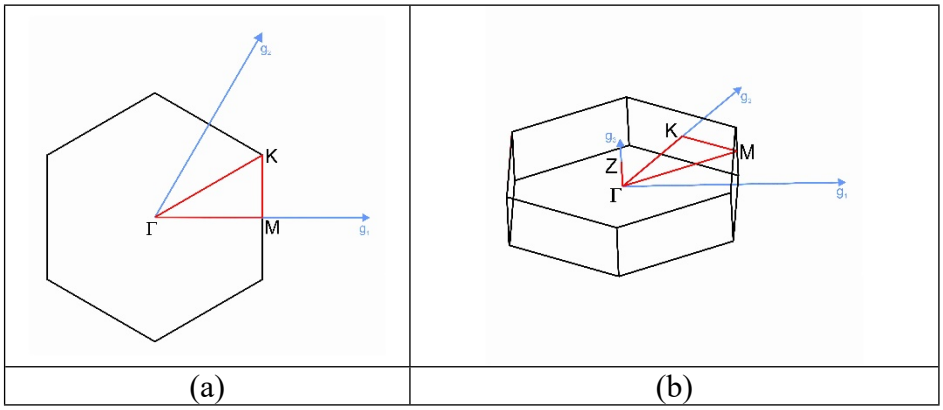
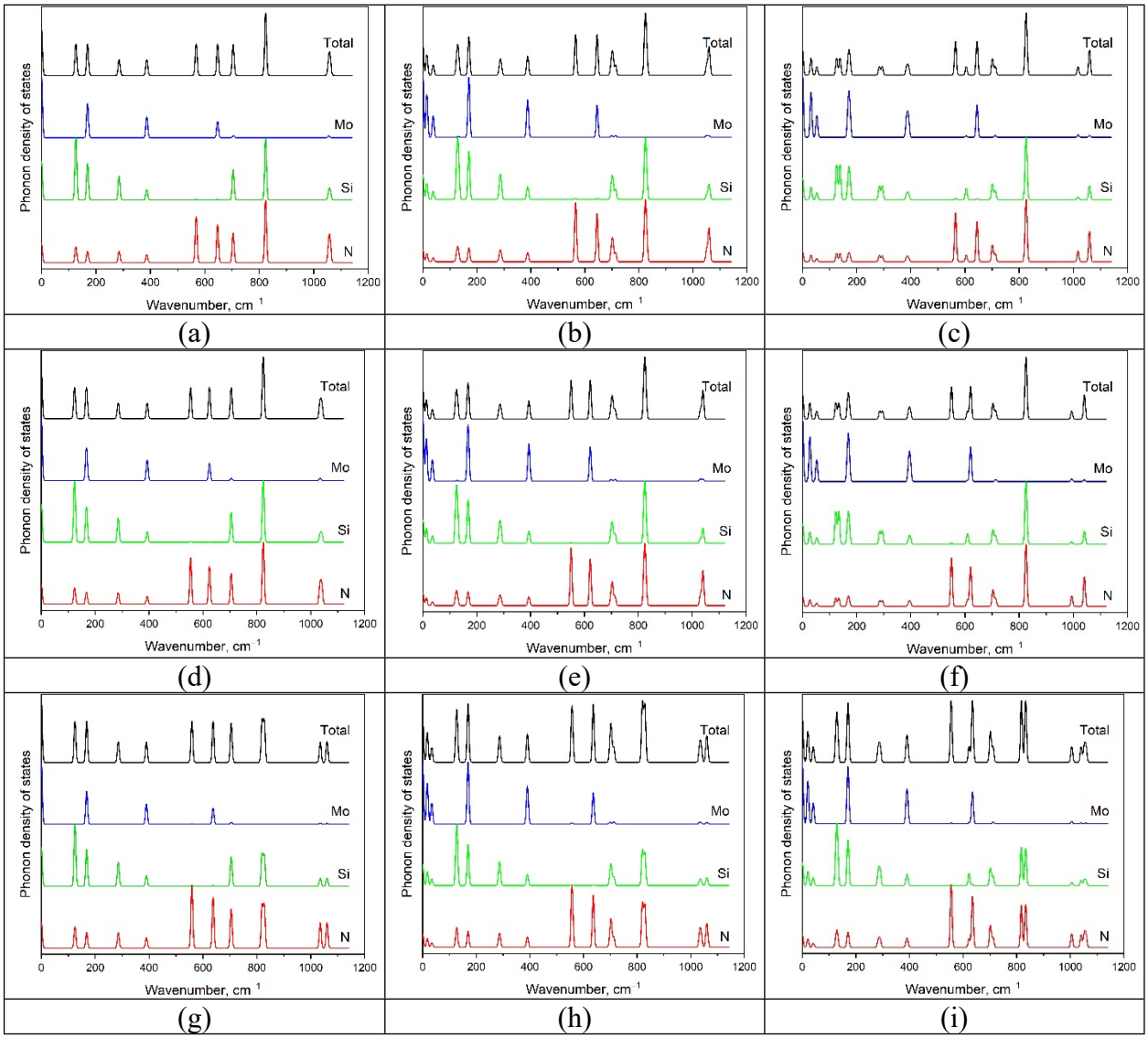



Figure S1. Proposed layer stacking patterns (a) AB, (b) AC, (c) AA, (d) AB*, (e) AC* and (f) AB, (g) AC, (h) AA, (i) AB*, (j) AC* for potentially plausible α2 and α3 structures of $MoSi_2N_4$, correspondingly.




(a) (b)

Figure S2. Schemes of Brillouin zone for single layer, double layer (a) and bulk (b) $MoSi_2N_4$.




(a) (b) (c)

(d) (e) (f)

(g) (h) (i)

Figure S3. Total and partial phonon density of states for 1 layer, 2 layers and bulk structures of α1 (a, b, c), α2 (d, e, f) and α3 (g, h, i) $MoSi_2N_4$ configurations.

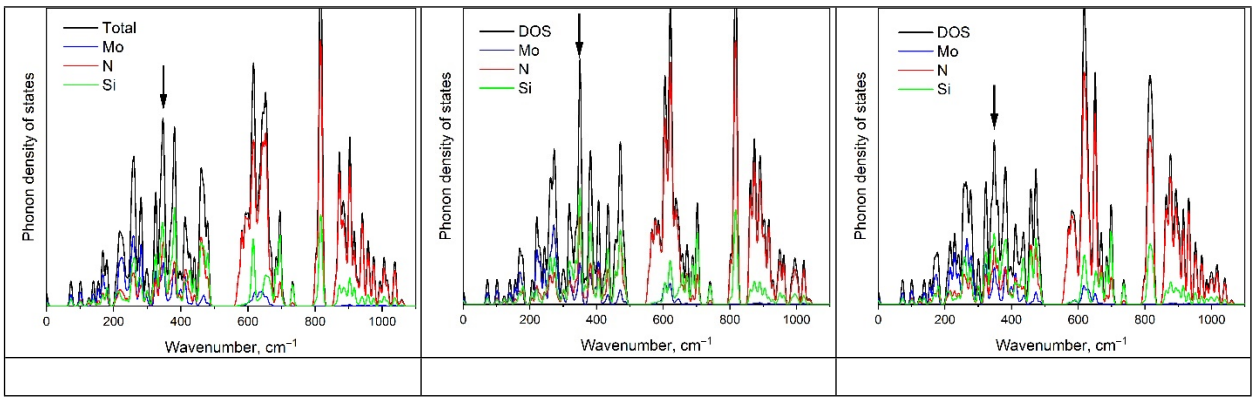



Figure S4. Phonon density of states simulated for α1 (a), α2 (b) and α3 (c) monolayers.