VIBRATION SPECTRA OF $\gamma$-P AND $\delta$-P

Independent of its cohesive energy, a structure may only be considered stable if it does not spontaneously change. A tendency for spontaneous structural change is indicated by the presence of soft modes (or imaginary frequency values) in the vibration spectrum. To demonstrate the stability and structural rigidity of $\gamma$- and $\delta$-P, we present the vibration spectra of these phases in Figs. S1(a) and S1(b). Absence of soft modes in these spectra indicates that $\gamma$- and $\delta$-P are stable. We compare the vibration spectra with those of $\alpha$-P and $\beta$-P monolayers in our previous study [1] and find them to be rather similar, reflecting similar bonding character in all four phosphorene allotropes. The hardest optical mode frequency in $\gamma$-P near 500 cm$^{-1}$ at $\Gamma$ lies very close to that of $\beta$-P due to the close relationship of the two structures. Similar to $\beta$-P, the vibration spectrum of $\gamma$-P is nearly isotropic. This can be explained by a close inspection of the structural differences, which indicate that the level of buckling in $\gamma$-P is much smaller than in $\alpha$-P and $\delta$-P. The vibration spectrum of $\delta$-P best matches that of $\alpha$-P in terms of the hardest mode frequency and the anisotropy of the longitudinal acoustic modes. The differences in the vibration spectra bear promise to identify the presence of $\gamma$-P and $\delta$-P in the experiment using Raman or infrared spectroscopy.

STABILITY OF $\gamma$-P AND $\delta$-P AT HIGH TEMPERATURES

Structural stability at $T = 0$, evidenced in the vibration spectra, says little about stability at high temperatures, where thermally activated structural changes may take place. As discussed in the main manuscript, $\alpha$-P, $\beta$-P, $\gamma$-P and $\delta$-P are structurally related by different ways to connect tetrahedrally coordinated P atoms in a 2D lattice. Local structural changes may be achieved by flipping bonds in a bi-stable configuration at an energy cost of $\lesssim 0.5$ eV/atom, identified in the $\alpha$-P$\rightarrow$ $\beta$-P transition [1]. The relatively high activation energy value suggests that structural changes may rarely occur before the system melts.

A more direct way to probe the stability of $\gamma$-P and $\delta$-P at high temperatures is by performing molecular dynamics (MD) simulations. Results of our canonical MD simulations are presented as structural snap shots of infinite $\gamma$-P and $\delta$-P monolayers at $T = 300$ K and $T = 1,000$ K in Fig. S2. To avoid artifacts associated with constraints imposed by finite-size unit cells, we used very large supercells containing 96 atoms for $\gamma$-P and 128 atoms for $\delta$-P. Due to the large unit cell size, we needed to limit the simulation time to 1.6 ps for $\gamma$-P and 0.6 ps for $\delta$-P when using 1 fs time steps. This simulation time still covers
about 10 vibration periods of the optical modes and thus should indicate the propensity to structural changes.

At room temperature, we find the structural changes in the layers to be minimal. More significant changes are expected at \( T = 1,000 \) K, which lies well above \( T_M = 863 \) K, the melting point of red phosphorus [2]. Even though the changes are larger in this case, they resemble more the onset of a melting process than a concerted structural change. We also expect that few-layer structures may convert to an amorphous structure resembling red phosphorus above the melting point.

Our high-temperature MD simulations suggest that \( \gamma \)-P and \( \delta \)-P should display a similar thermal stability as previously found [1] for \( \alpha \)-P and \( \beta \)-P. In view of cohesive energy differences between the structures not exceeding 0.1 eV per atom, we expect the four phosphorene allotropes to coexists under experimental conditions.

The following movies, which illustrate the dynamics at high temperatures better than structural snapshots, are part of the Supplemental Information:

- \texttt{gamma-300K-top.avi} represents the infinite \( \gamma \)-P monolayer at \( T = 300 \) K in top view;
- \texttt{gamma-300K-side.avi} represents the infinite \( \gamma \)-P monolayer at \( T = 300 \) K in side view;
- \texttt{gamma-1000K-top.avi} represents the infinite \( \gamma \)-P monolayer at \( T = 1,000 \) K in top view;
- \texttt{gamma-1000K-side.avi} represents the infinite \( \gamma \)-P monolayer at \( T = 1,000 \) K in side view;
- \texttt{delta-300K-top.avi} represents the infinite \( \delta \)-P monolayer at \( T = 300 \) K in top view;
- \texttt{delta-300K-side.avi} represents the infinite \( \delta \)-P monolayer at \( T = 300 \) K in side view;
- \texttt{delta-1000K-top.avi} represents the infinite \( \delta \)-P monolayer at \( T = 1,000 \) K in top view;
- \texttt{delta-1000K-side.avi} represents the infinite \( \delta \)-P monolayer at \( T = 1,000 \) K in side view.