

Supplemental Material

Rigid Unit Modes in sp - sp^2 Hybridized Carbon Systems: Origin of Negative Thermal Expansion

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We further searched for other rigid unit modes (RUMs) that contribute to negative thermal expansion by evaluate the mode Grüneisen parameters of all phonon modes using Eq. (3) in the main article. Fig. S1 shows a few in-plane phonon modes that can be classified as rigid unit modes (RUMs) or quasi RUMs. The evaluated mode Grüneisen parameters of these in-plane modes as well as flexural modes are negative as displayed in Fig. S2.

The libration angle φ of the RUMs depicted in Fig. 5(a-c), and the resulting area reduction $\Delta A/A_0$ due to the RUMs estimated from Fig. 5(d-f) at two different temperatures $T \approx 600$ and 900 K corresponding to $\Delta E \approx 52$ and 78 meV/atom.

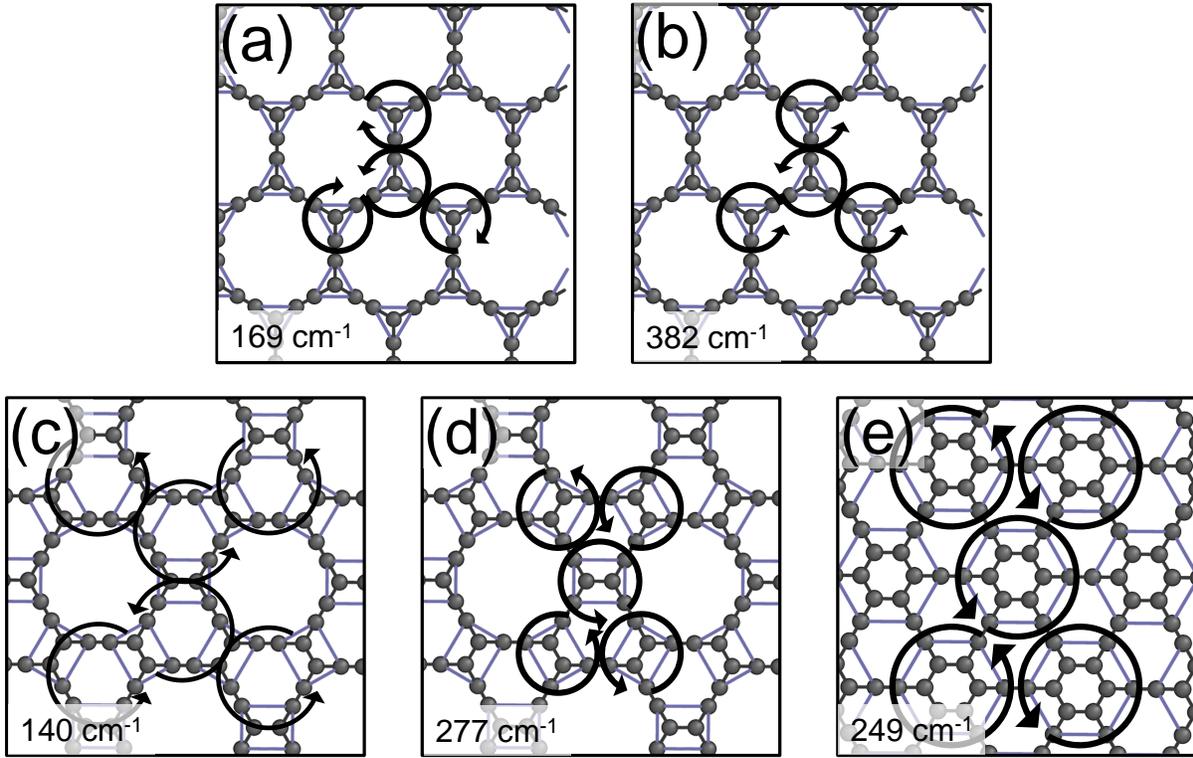


FIG. S1. In-plane phonon modes with negative Grüneisen parameters that can be classified as RUMs or quasi RUMs of (a, b) α -, (c, d) β - and (e) γ -graphyne. Their respective frequencies are given. The modes shown in (b), (d), and (e) are also shown in Fig. 5 (a-c). The black rounded arrows indicate the relative rotation of neighboring local rigid or quasi rigid units.

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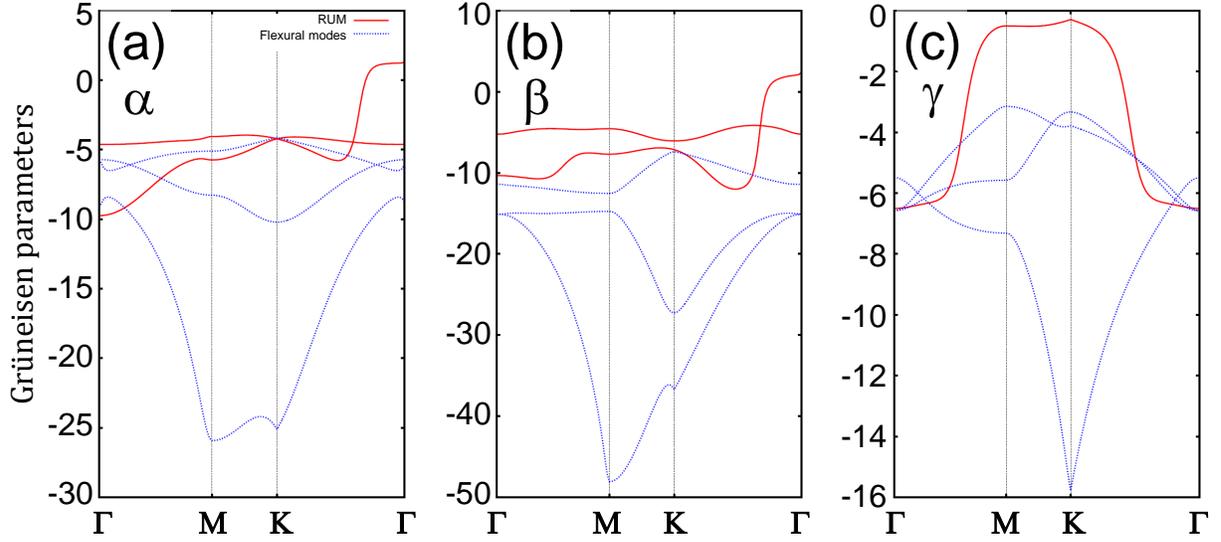


FIG. S2. Mode Grüneisen parameters for a few selected in-plane modes (red solid lines) shown in Fig. S1, and a few flexural modes (blue dotted lines) observed in the (a) α -, (b) β - and (c) γ -graphyne along the high symmetry lines in 2D hexagonal Brillouin zones (BZ). The values are significantly negative mostly over the whole BZ. It turns out, on the other hand, that those for the other phonon modes (not shown) have negligibly small negative values or positive values.

TABLE S1. Libration angle φ of the rigid unit mode (RUM) of each type of graphyne depicted in Fig. 5 (a), (b), or (c), and the resulting area reduction $\Delta A/A_0$ due to the RUM estimated from Fig. 5 (d), (e), or (f) at two different temperatures $T \approx 600$ and 900 K corresponding to $\Delta E \approx 52$ and 78 meV/atom.

		α	β	γ
$T \approx 600$ K	φ	5.8°	5.5°	4.2°
	$\Delta A/A_0$	-1.8%	-2.0%	-2.0%
$T \approx 900$ K	φ	7.0°	6.5°	5.0°
	$\Delta A/A_0$	-2.7%	-2.9%	-2.9%