Stability and Phonon Anharmonicity of Black (BP) and Blue (bP) Phosphorus

Damien Tristant,* Andrew Cupo & Vincent Meunier

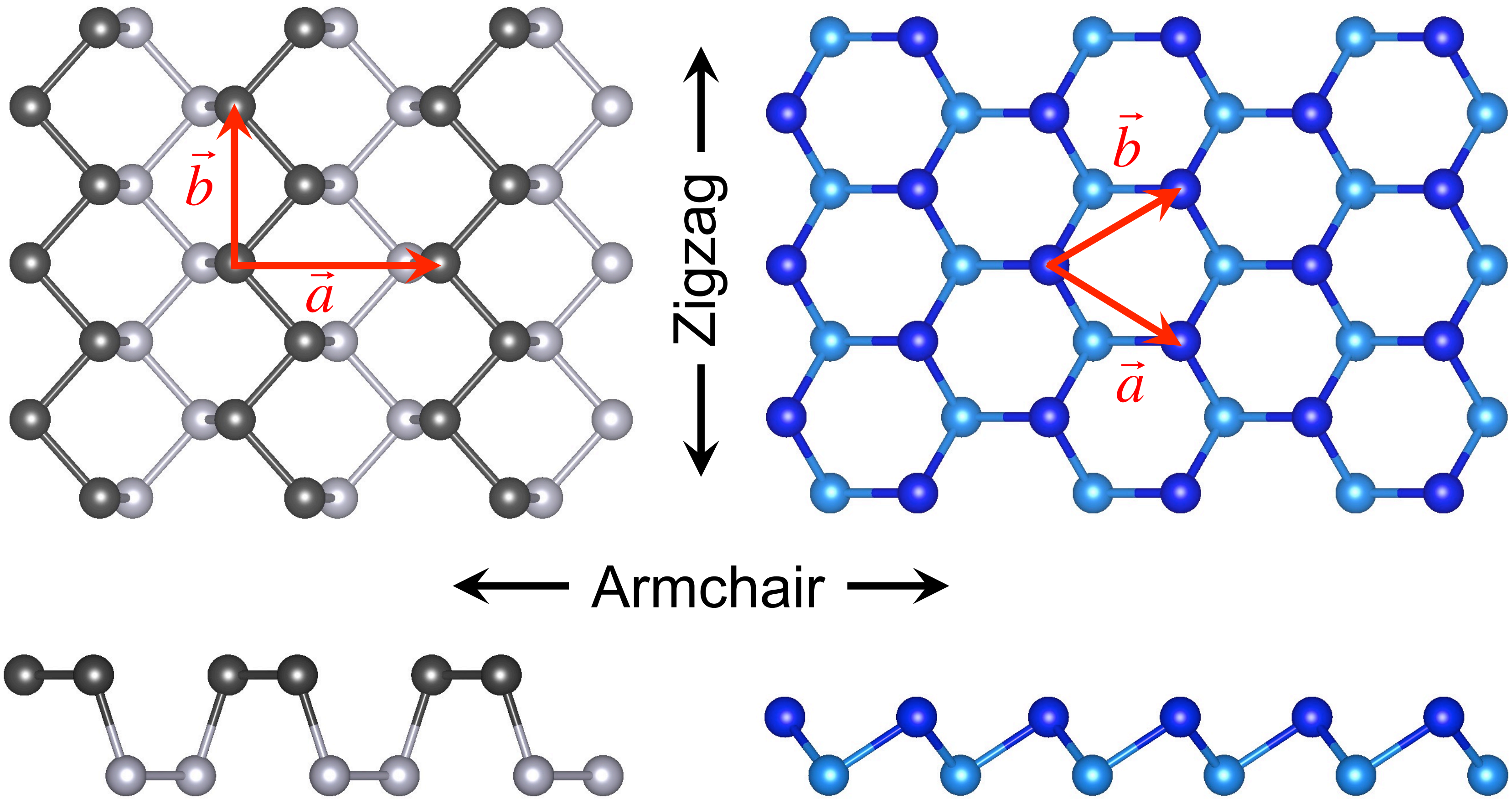
Department of Physics, Applied Physics and Astronomy,
RPI, Troy, New York, USA

*tristd@rpi.edu

Benasque, Spain

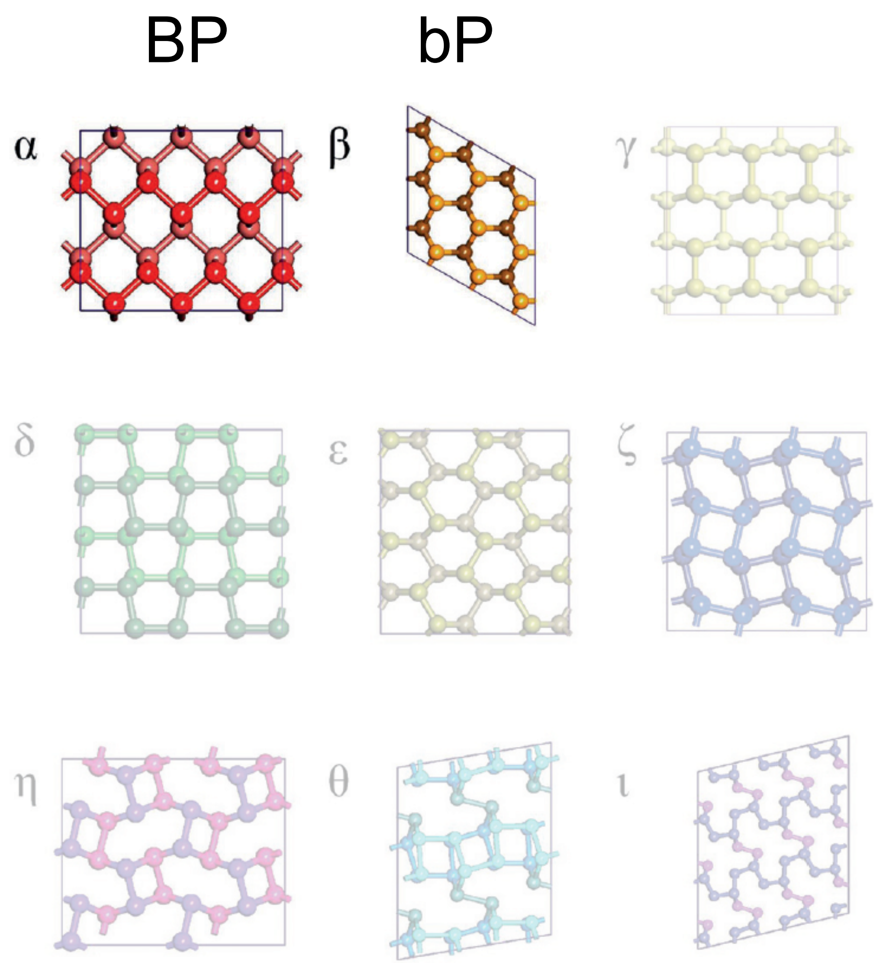
Tuesday, December 12th, 2017

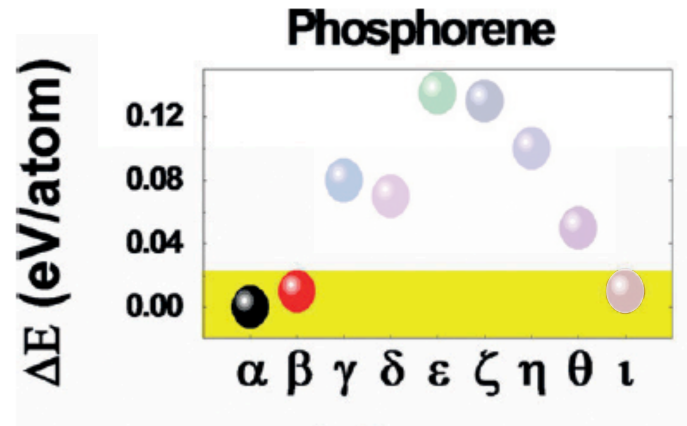
Single-Layer BP and bP

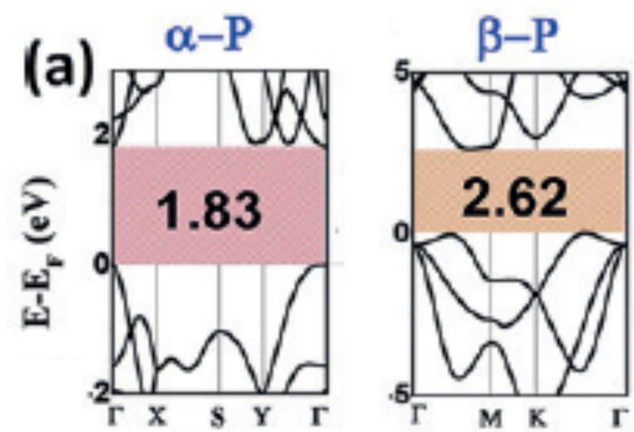


van der Waals (vdW) interactions

Many Allotropes

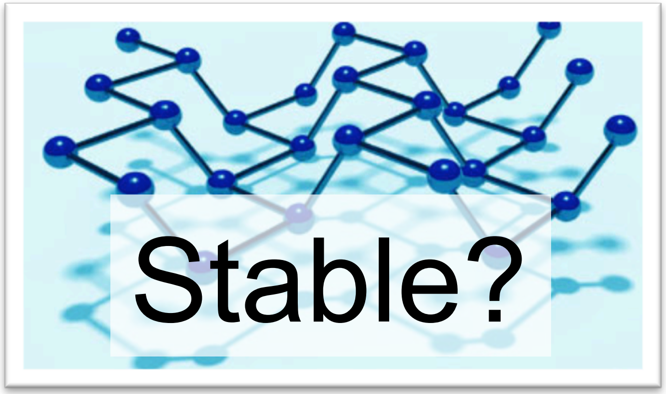




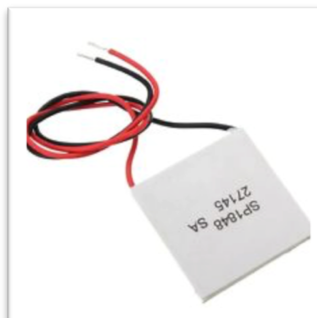


S. Zhang *et al.*, *Angew. Chem.* 128 1698 (2016)

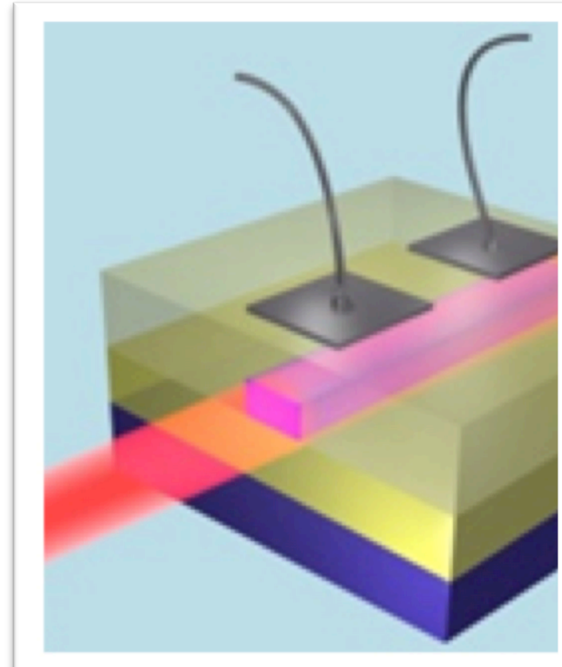
BP *vs* Graphene



Electron mobility 4.4 weaker [1]



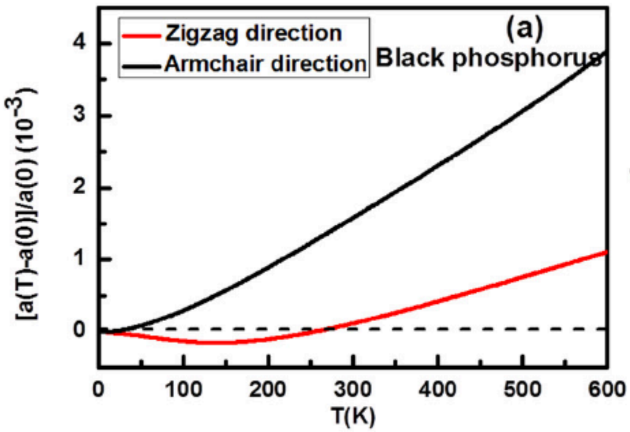
Low thermal conductivity [2]

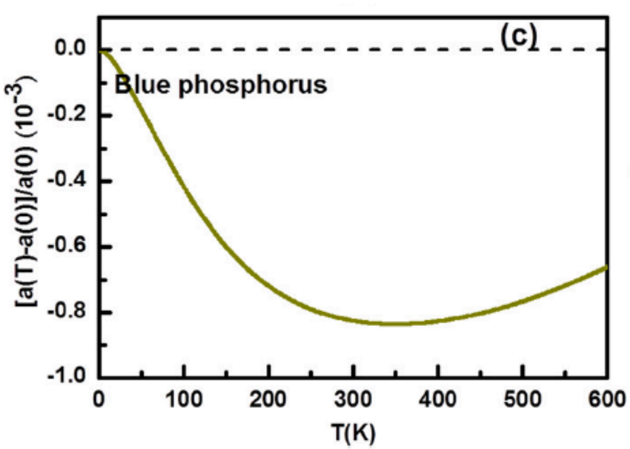


Tunable band gap [3]

[1] G. Long, *Nano Lett.,* 16 (12) 7768 (2016) / [2] R. Fei, *Nano Lett.,* 14 6393 (2014) / [3] V. Tran, *Phys. Rev. B: Condens. Matter. Mater. Phys.,* 89 235319 (2014)

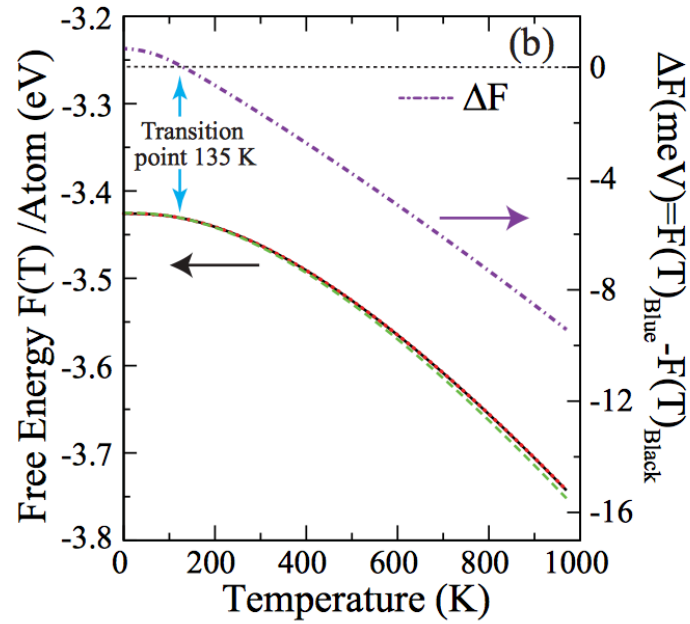
Previous Research on Single-Layer

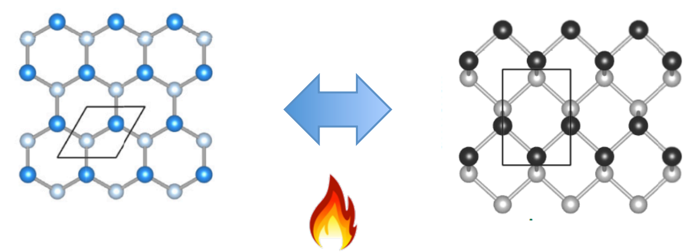




H. Sun, *Phys. Lett.A,* 380 2098 (2016)

$\vec{F}_{vdW}$

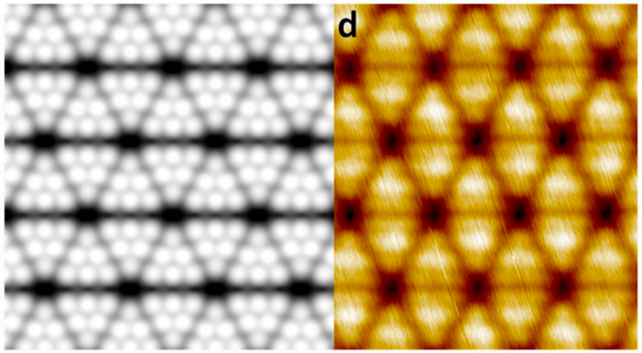




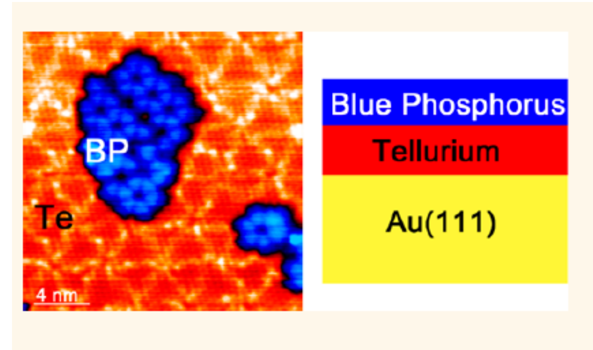
Y. Aierken, *Phys. Rev. B,* 92 081408 (2015)

Not observed experimentally!

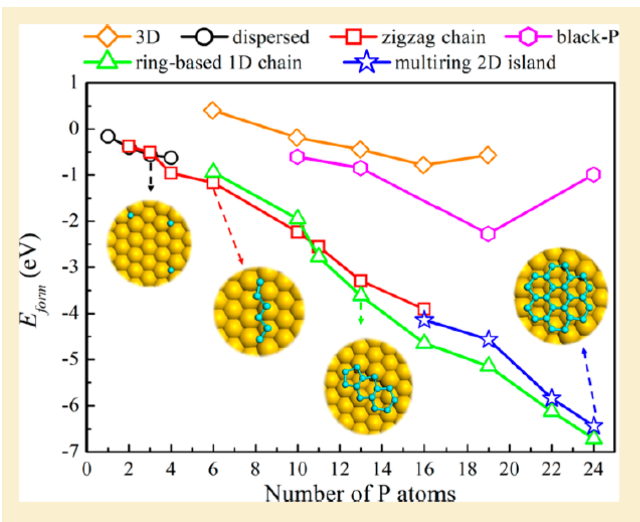
Previous Research on Substrates



J. L. Zhang, *Nano Lett.,* 16 4903 (2016)



C. Gu, *ACS Nano,* 11 4943 (2017)



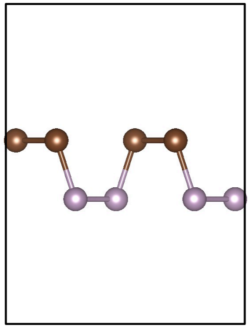
N. Hang, *J. Phys. Chem.,* 121 (33) 17893 (2017)

		BAs	BP	Cu	Au	GaN
	a_0 (Å)	3.41	3.22	2.56	2.95	3.25
BlackP	δ_a (%)	4.35	−1.65	−1.78	−2.25	−0.60
	δ_b (%)	3.07	−2.86	3.42	2.99	−1.82
	$E_{b\text{-D2}}$ (eV)	0.42	0.56	0.69	0.76	0.71
	$E_{b\text{-TS}}$ (eV)	0.20	0.27	0.37	0.33	0.42
	$E_{b\text{-DF2}}$ (eV)	0.18	0.29	0.30	0.31	0.41
BlueP	δ (%)	3.70	−2.27	2.23	1.75	−1.22
	$E_{b\text{-D2}}$ (eV)	0.49	0.58	0.86	0.88	0.88
	$E_{b\text{-TS}}$ (eV)	0.23	0.32	0.53	0.37	0.49
	$E_{b\text{-DF2}}$ (eV)	0.20	0.31	0.44	0.33	0.45

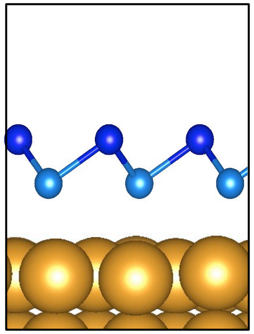
J. Zeng, *Phys. Rev. Lett.*, 118 046101 (2017)

bP is more stable than BP on different substrates

Questions



➢ Is it reasonable to neglect vdW interactions?



➢ Why is bP more stable than BP?

➢ Is it always the case at high temperature?

Outline

- Methods:

  Helmholtz free energy w/ & w/o anharmonic effects

- Comparison between single-layers of BP & bP:

  Structural & energetic properties w/ & w/o vdW interactions

- Comparison between BP & bP on Au(111):

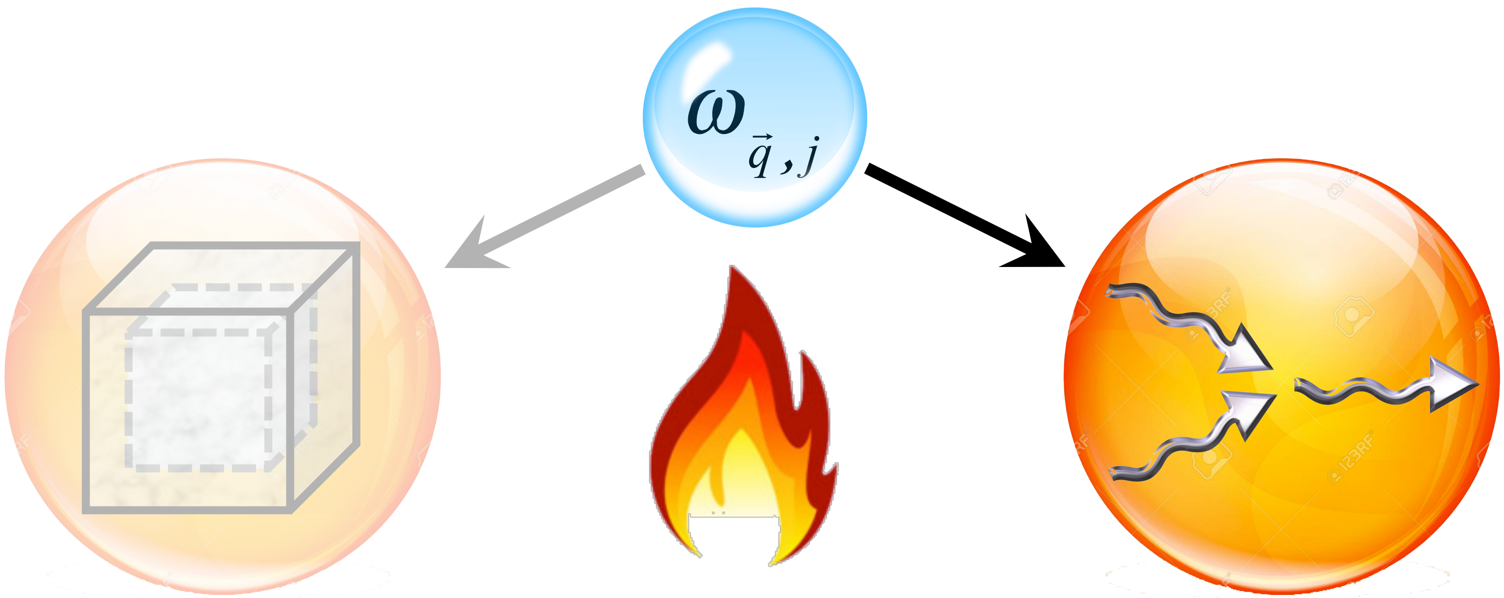
  Vibrational properties including interface interactions

- Conclusions & Outlook

Helmholtz Free Energy

$$F\left(a,b,T\right)=E\left(a,b\right)+\sum_{\vec{q}\in \mathrm{BZ},j}\frac{\hbar\omega_{\vec{q},j}}{2}+k_{\mathrm{B}}T\sum_{\vec{q}\in \mathrm{BZ},j}\ln\left(1-\exp\left(-\frac{\hbar\omega_{\vec{q},j}}{k_{\mathrm{B}}T}\right)\right)$$

Ground energy — Zero-point energy — Vibrational energy

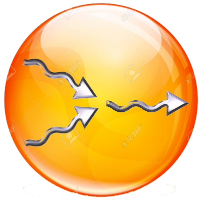


Thermal expansion

Phonon-Phonon coupling

C. Sevik, *Phys. Rev. B* 89 (3) 035422 (2014)

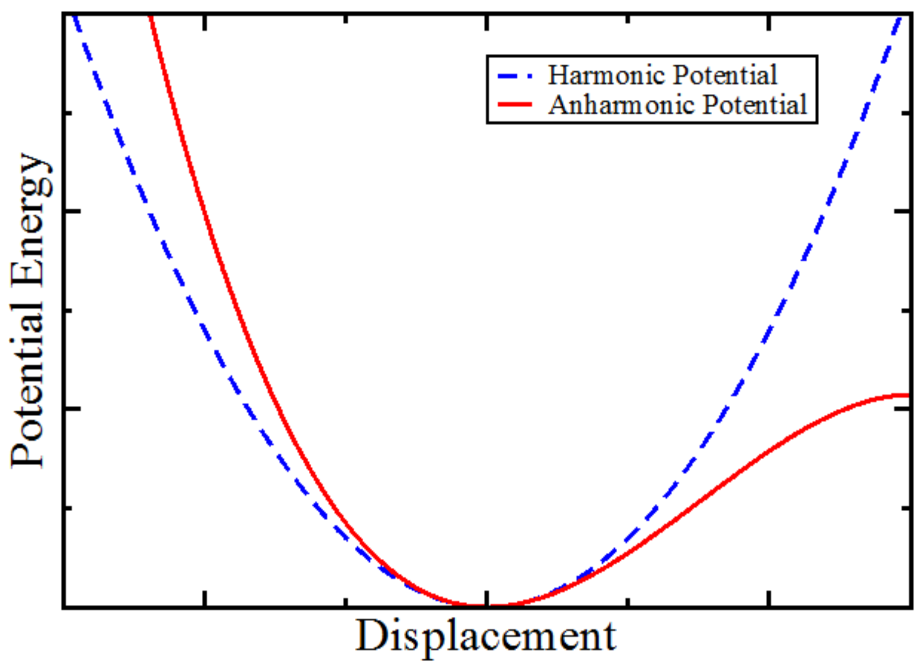
Anharmonic Effect

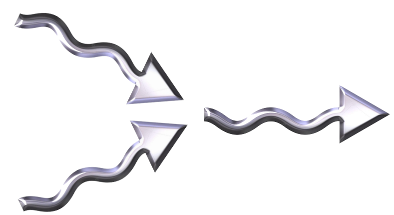


$n > 2$

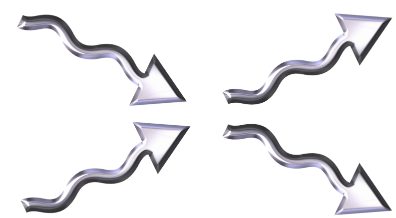
$$V = V_{\text{eq}} + \sum_{n=2}^{\infty} \frac{1}{n!} \sum_{\vec{R}_1 \ldots \vec{R}_n} \sum_{\alpha_1 \ldots \alpha_n} \Phi^{(n)}_{\alpha_1 \ldots \alpha_n}\left(\vec{R}_1 \ldots \vec{R}_n\right) u_{\alpha_1}\left(\vec{R}_1\right) \ldots u_{\alpha_n}\left(\vec{R}_n\right)$$

Interatomic force constants





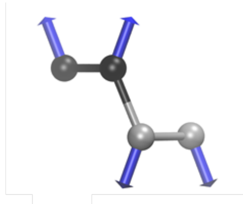
n = 3 phonon process



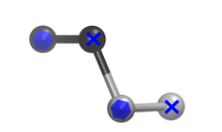
n = 4 phonon process

Anharmonic Effect (Γ point)

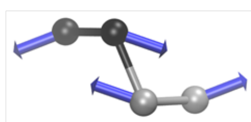
A_g^1

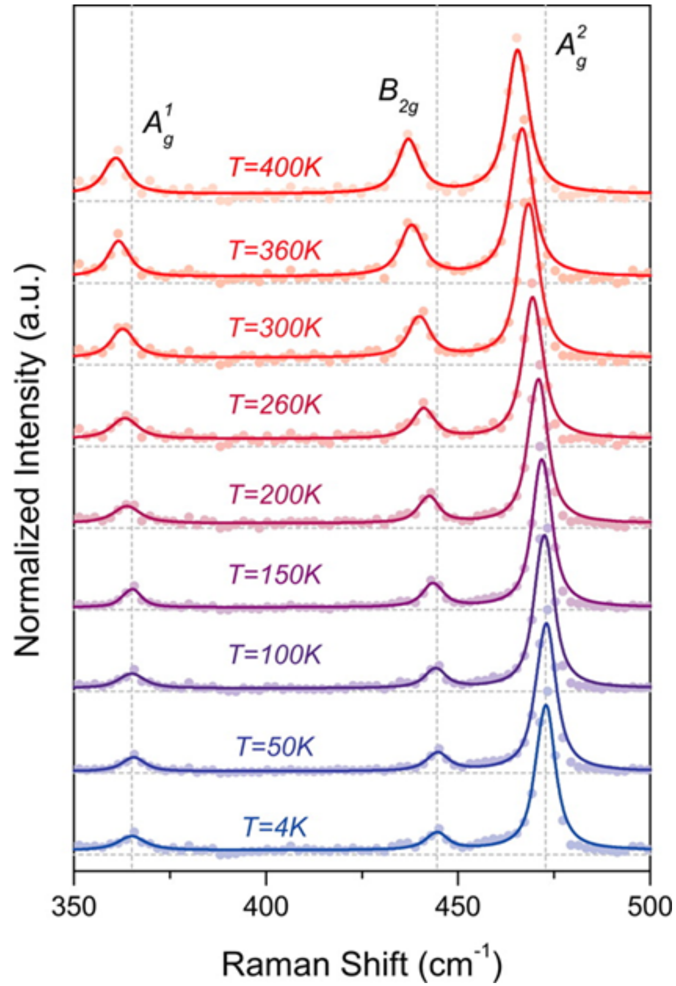


B_{2g}



A_g^2





Frequency downshifts with increased temperature

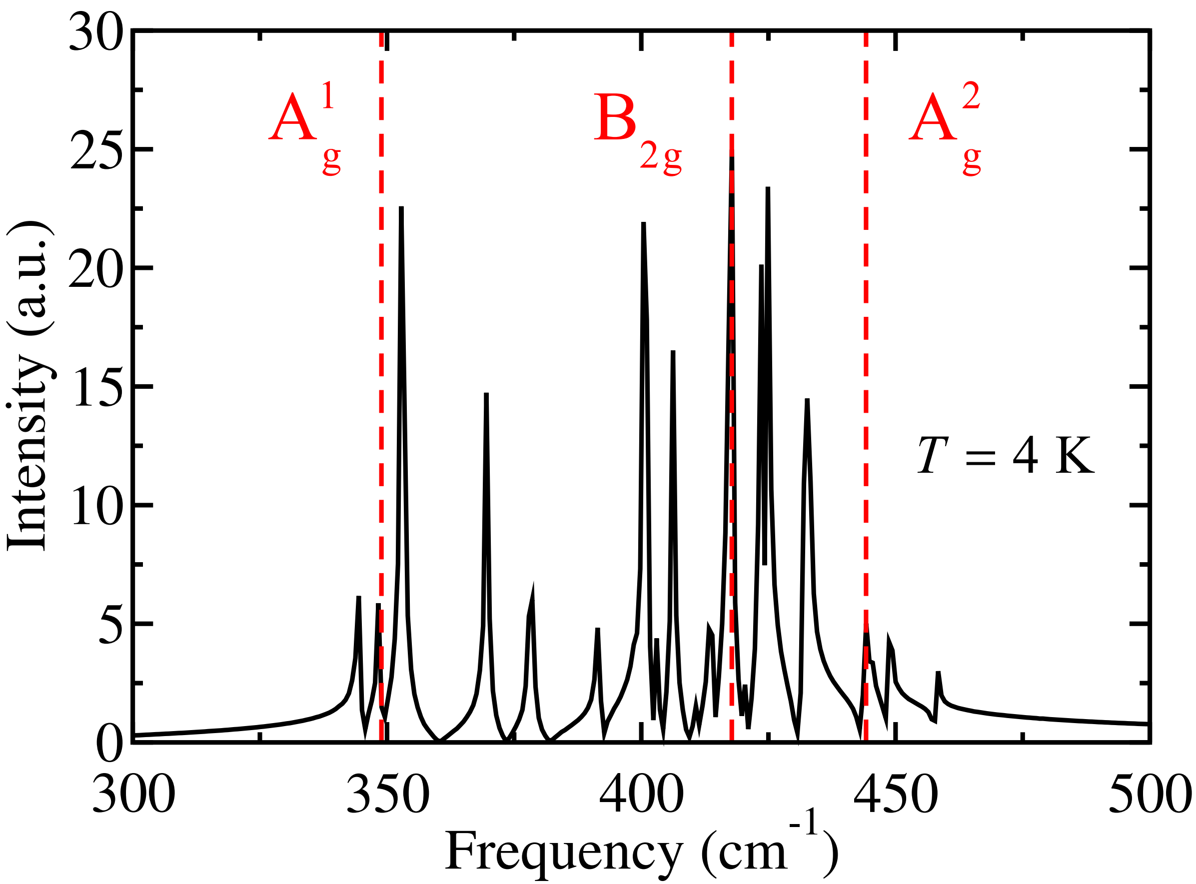
A. Łapińska, *J. Phys. Chem. C*, (9), 5265 (2016)

Anharmonic Effect (Γ point)

- *Ab initio* molecular dynamics simulations (60 ps):[1]

$$P(\omega) = \left| FT_\tau \left\{ \sum_{N=1}^{N_{\text{atoms}}} \int_{-\infty}^{\infty} \mathrm{d}t \, \overrightarrow{v_N}(t) \cdot \overrightarrow{v_N}(t+\tau) \right\}(\omega) \right|$$

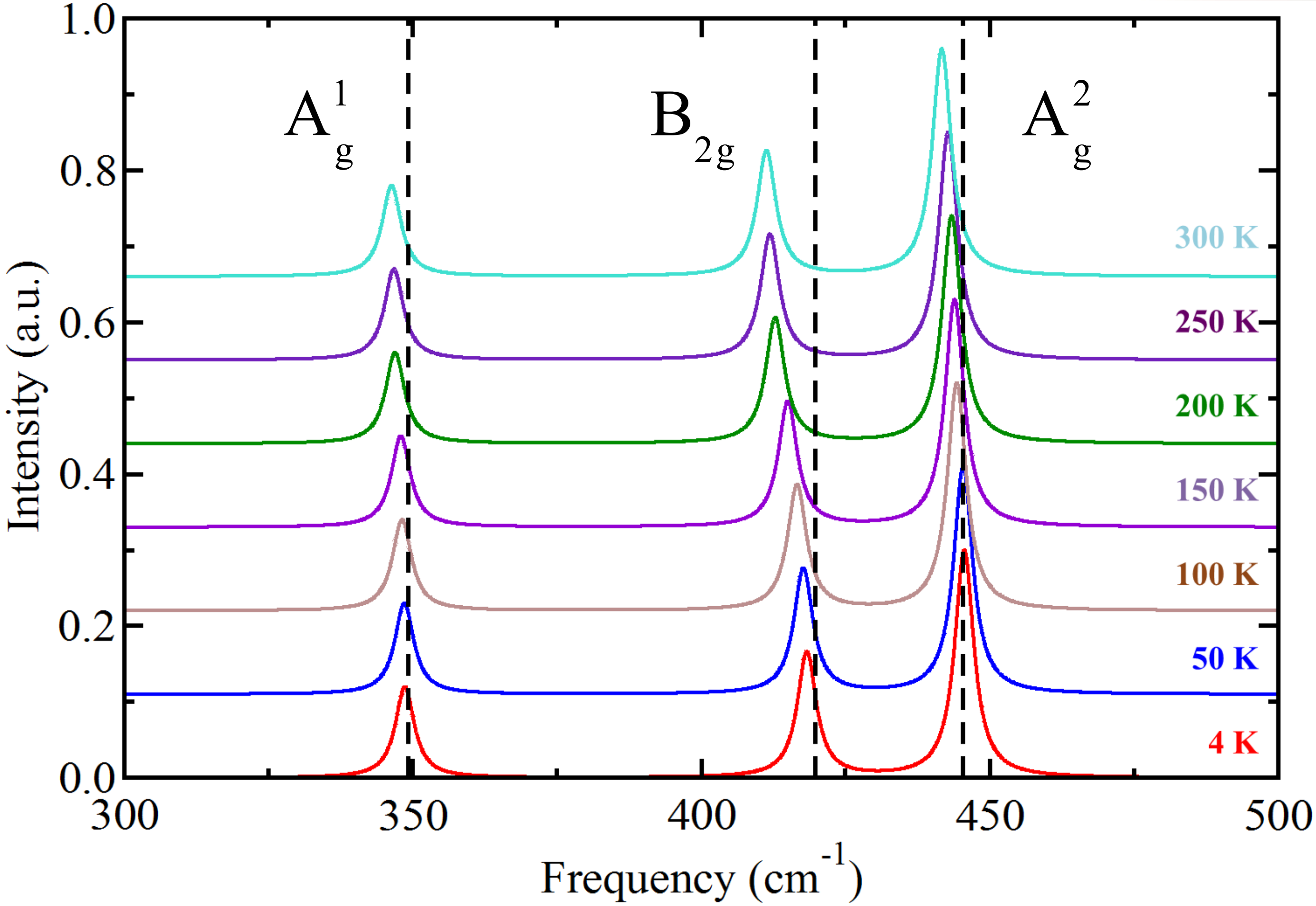
Poster Session



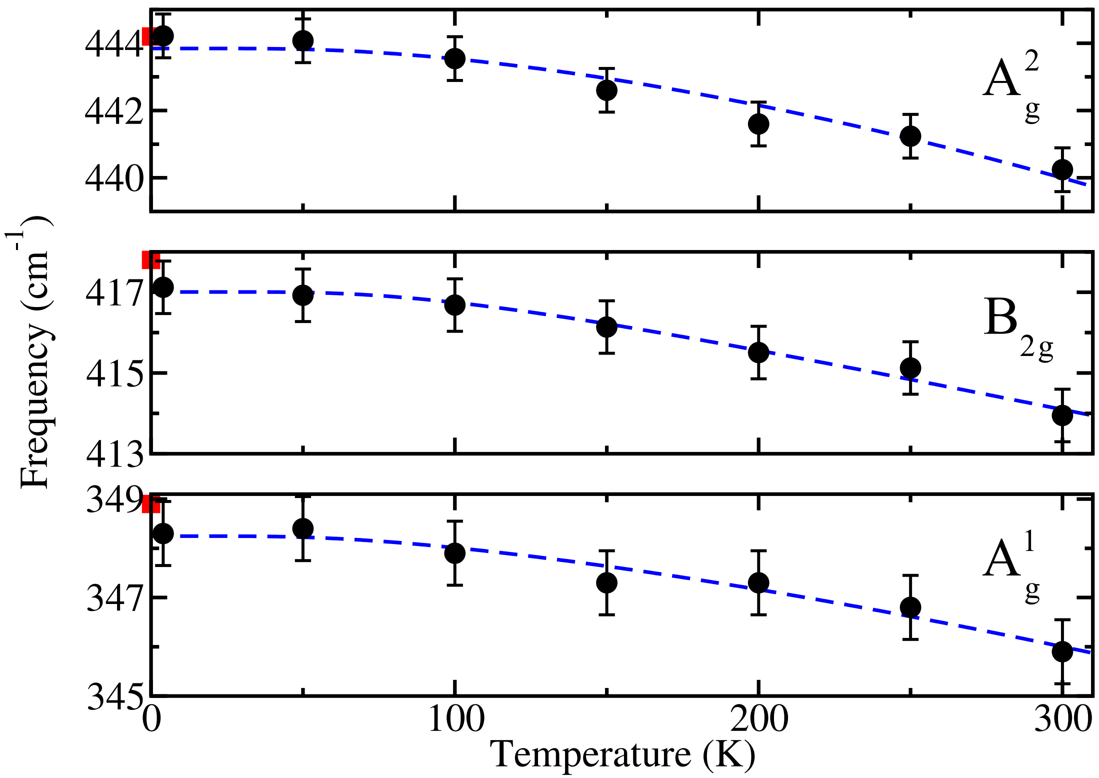
[1] K. Wendler, *J. Chem. Theory Comput.*, 8 (5), 1570 (2012)

Anharmonic Effect (Γ point)

$$\text{Filter} \propto C_n \operatorname{sinc}(\omega - \omega_n)$$



Anharmonic Effect (Γ point)



Balkanski's model: $$\omega(T) = \omega_0 + A\left[1 + \frac{2}{e^x - 1}\right] + B\left[1 + \frac{3}{e^y - 1} + \frac{3}{\left(e^y - 1\right)^2}\right]$$

$$x = \hbar\omega_0 / 2k_B T, \quad y = \hbar\omega_0 / 3k_B T$$

M. Balkanski, *Phys. Rev. B,* 28 (4), 1928 (1983)

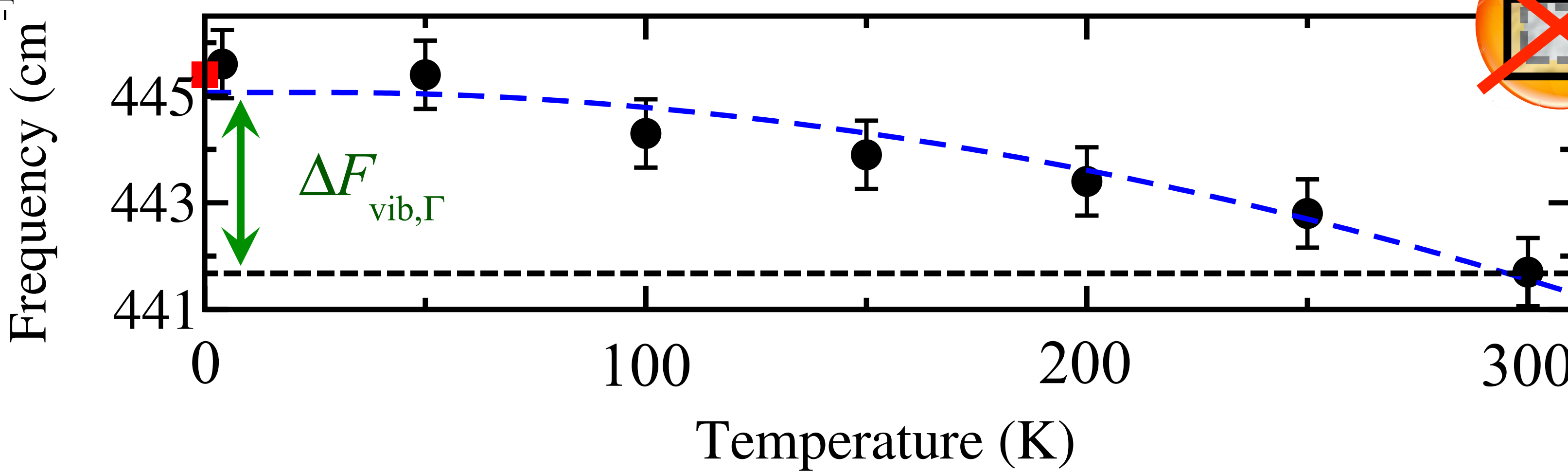
Anharmonic Effect (Γ point)

Mode	*A* (cm^{-1})	*B* (cm^{-1})
	Theo. / Exp.[1]	Theo. / Exp.[1]
A^1_g	-0.85 / -0.81 ± 0.20	-0.10 / -0.18 ± 0.03
B_{2g}	-2.73 / -4.21 ± 0.40	0.04 / -0.06 ± 0.02
A^2_g	-1.08 / -3.26 ± 0.28	-0.48 / -0.28 ± 0.05

A & *B*: qualitative agreement with experiment

[1] A. Lapinska, *J. Phys. Chem. C,* 120 (9), 5265 (2016)

From Anharmonic to Harmonic Effect



$$\Delta F_{vib,\Gamma} = F_{vib,\Gamma}\left(\text{harmonic}\right) - F_{vib,\Gamma}\left(\text{anharmonic, 300 K}\right) \approx 0.02\ \text{eV}$$

Anharmonic interactions in graphite and diamond:
neglect up to 1000 K

N. Mounet, *Phys. Rev. B,* 71, 205214 (2005)

Harmonic Effect

$n = 2$

$$V = V_{\mathrm{eq}} + \sum_{n=2}^{\infty} \frac{1}{n!} \sum_{\vec{R}_1 \ldots \vec{R}_n} \sum_{\alpha_1 \ldots \alpha_n} \Phi^{(n)}_{\alpha_1 \ldots \alpha_n}\left(\vec{R}_1 \ldots \vec{R}_n\right) u_{\alpha_1}\left(\vec{R}_1\right) \ldots u_{\alpha_n}\left(\vec{R}_n\right)$$

Interatomic force constants

$$\omega^2(\vec{q})\, U_{\alpha_j} = \sum_{\alpha_n} D_{\alpha_j \alpha_n}(\vec{q})\, U_{\alpha_n}$$

with

$$D_{\alpha_j \alpha_n}(\vec{q}) = \sum_{\vec{R}} \frac{\Phi_{\alpha_j \alpha_n}\left(\vec{R}\right)}{\sqrt{M_{\alpha_j} M_{\alpha_n}}} e^{i\vec{q}\cdot\vec{R}}$$

Dynamical matrix (DM)

Obtain DM: finite-displacement & supercell methods

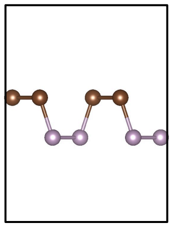
Dynamical Matrix

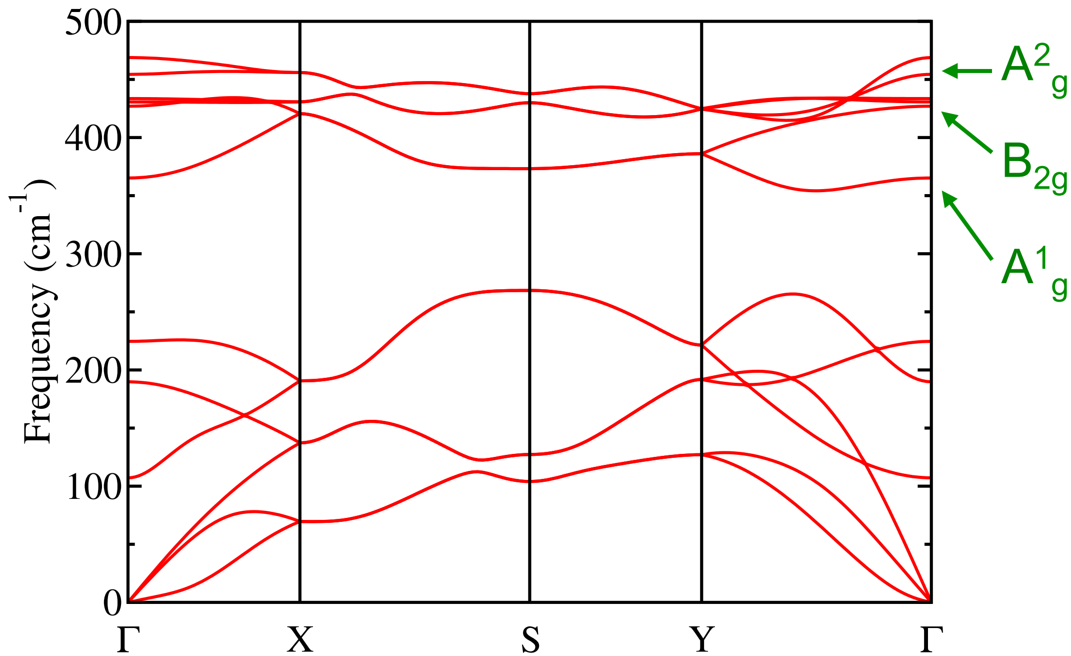
$$
\begin{pmatrix}
D_{x_1x_1} & D_{x_1y_1} & D_{x_1z_1} & & D_{x_1x_N} & D_{x_1y_N} & D_{x_1z_N} \\
D_{y_1x_1} & D_{y_1y_1} & D_{y_1z_1} & \cdots & D_{y_1x_N} & D_{y_1y_N} & D_{y_1z_N} \\
D_{z_1x_1} & D_{z_1y_1} & D_{z_1z_1} & & D_{z_1x_N} & D_{z_1y_N} & D_{z_1z_N} \\
 & \vdots & & \ddots & & \vdots & \\
D_{x_Nx_1} & D_{x_Ny_1} & D_{x_Nz_1} & & D_{x_Nx_N} & D_{x_Ny_N} & D_{x_Nz_N} \\
D_{y_Nx_1} & D_{y_Ny_1} & D_{y_Nz_1} & \cdots & D_{y_Nx_N} & D_{y_Ny_N} & D_{y_Nz_N} \\
D_{z_Nx_1} & D_{z_Ny_1} & D_{z_Nz_1} & & D_{z_Nx_N} & D_{z_Ny_N} & D_{z_Nz_N}
\end{pmatrix}
$$

$$
\begin{pmatrix}
F_{A_1}^{\rightarrow A_1} & \cdots & F_{A_N}^{\rightarrow A_1} \\
\vdots & \ddots & \vdots \\
F_{A_1}^{\rightarrow A_N} & \cdots & F_{A_N}^{\rightarrow A_N}
\end{pmatrix}
$$

Diagonalized: obtaining eigenvalues and eigenvectors

Phonon Dispersion



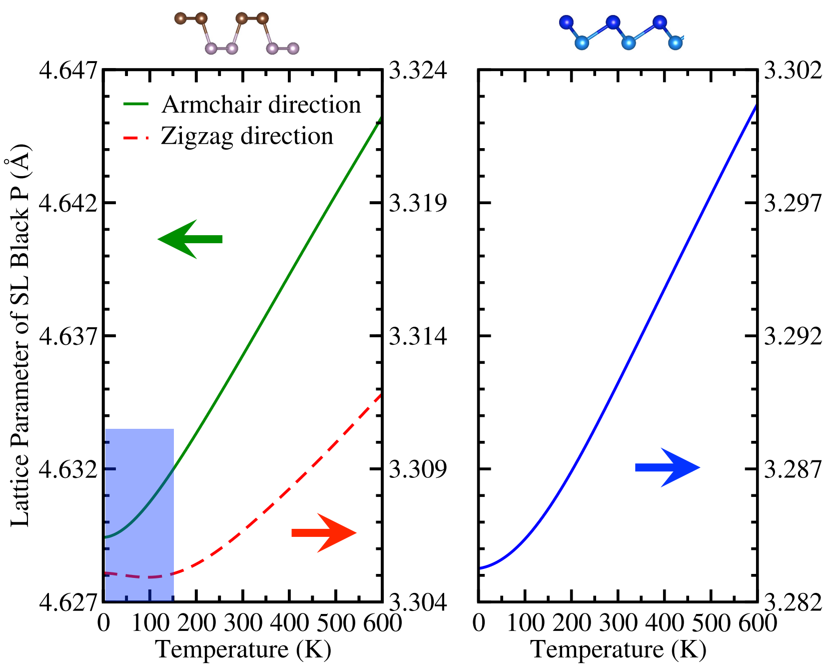


Quasi-Harmonic Approximation

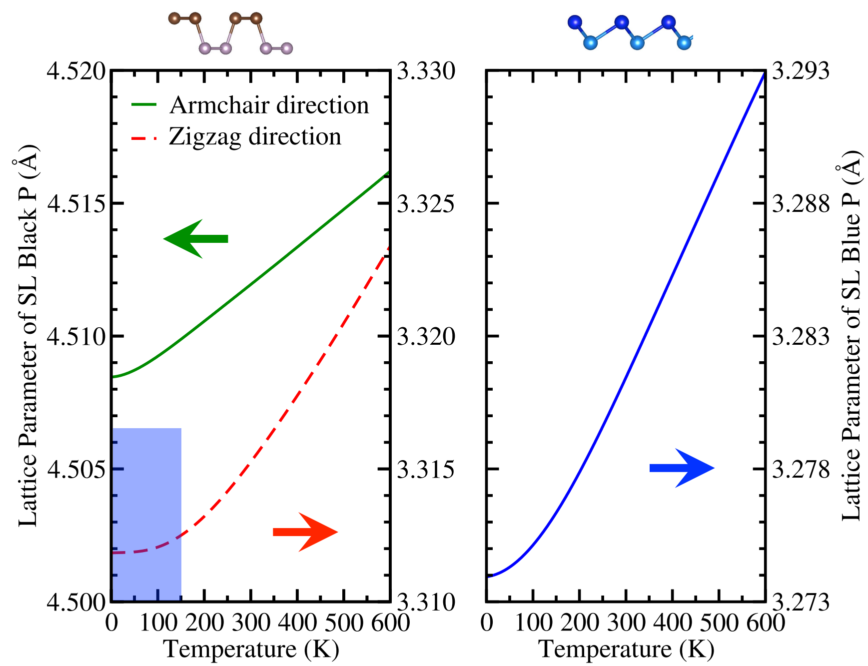
$$F\left(a,b,T\right)=E\left(a,b\right)+\sum_{\vec{q}\in \mathrm{BZ},j}\frac{\hbar\omega_{\vec{q},j}(a,b)}{2}+k_{\mathrm{B}}T\sum_{\vec{q}\in \mathrm{BZ},j}\ln\left(1-\exp\left(-\frac{\hbar\omega_{\vec{q},j}(a,b)}{k_{\mathrm{B}}T}\right)\right)$$

Temperature Dependent Lattice Constants

~~$\vec{F}_{\mathrm{vdW}}$~~



$\vec{F}_{\mathrm{vdW}}$



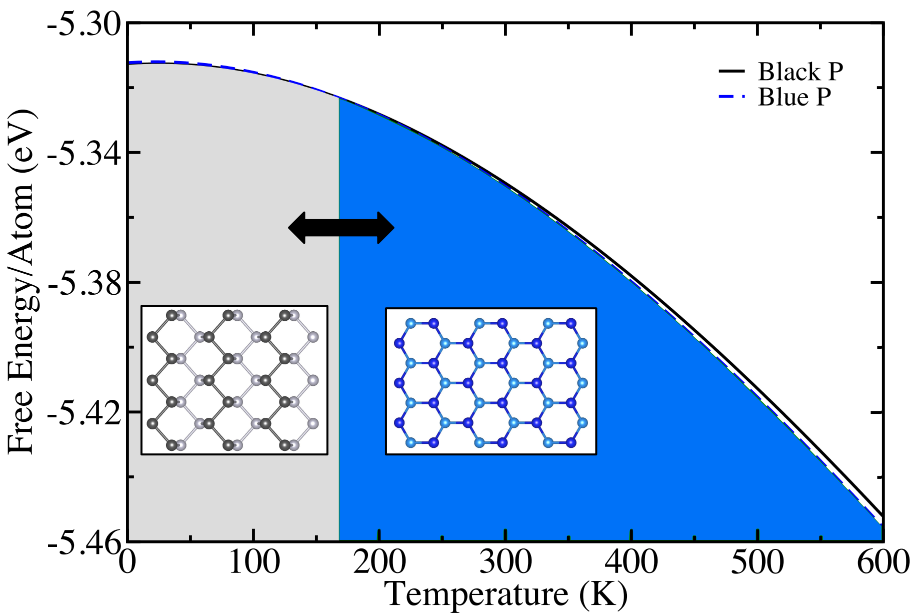
Contraction of BP along zigzag direction until 168 K

$\neq$

Expansion of BP along zigzag direction at any temperature

Temperature Dependent Free Energy

~~$\vec{F}_{vdW}$~~

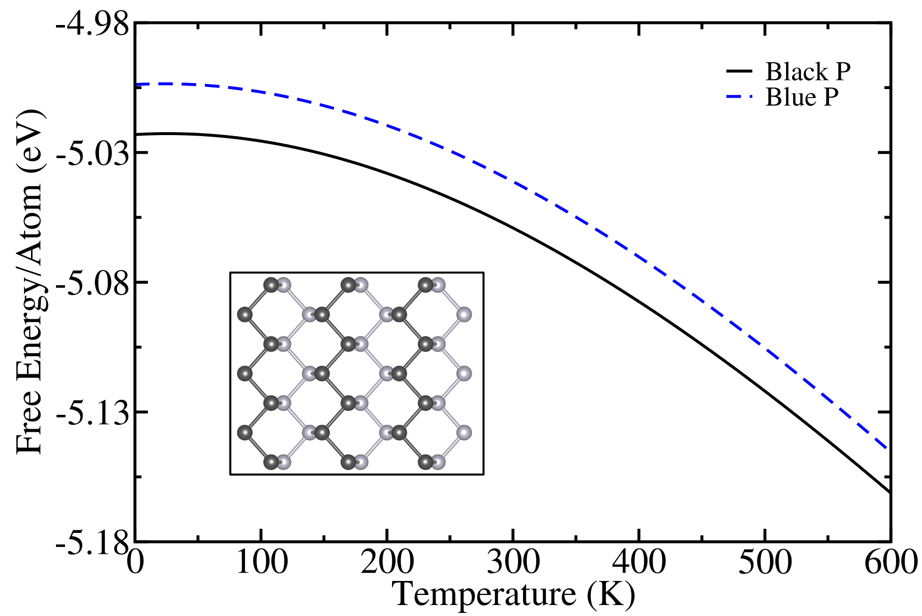


Phase transition ~168 K

Not observed experimentally

≠

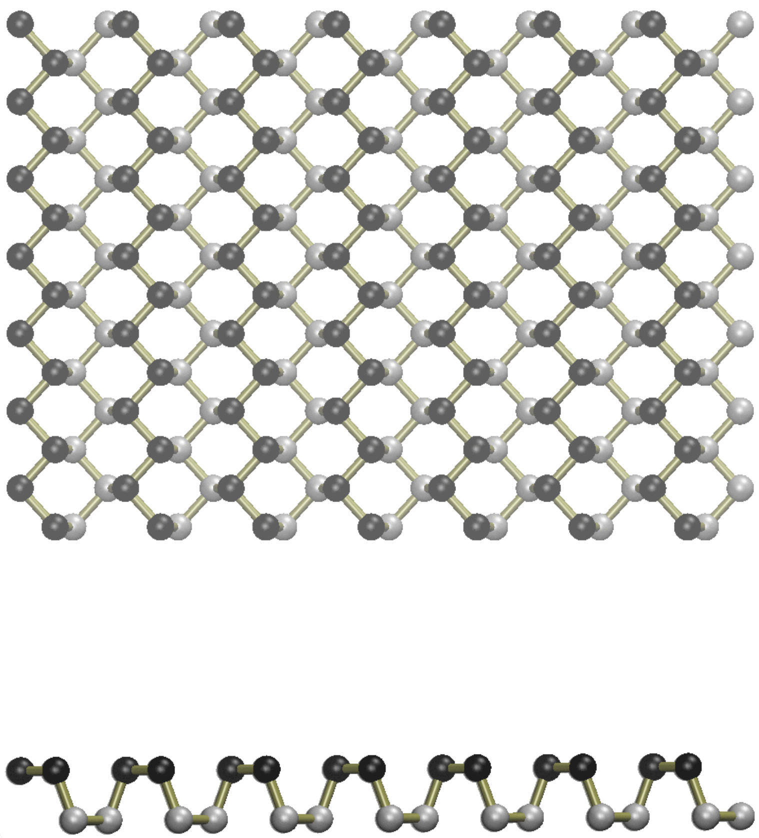
$\vec{F}_{vdW}$



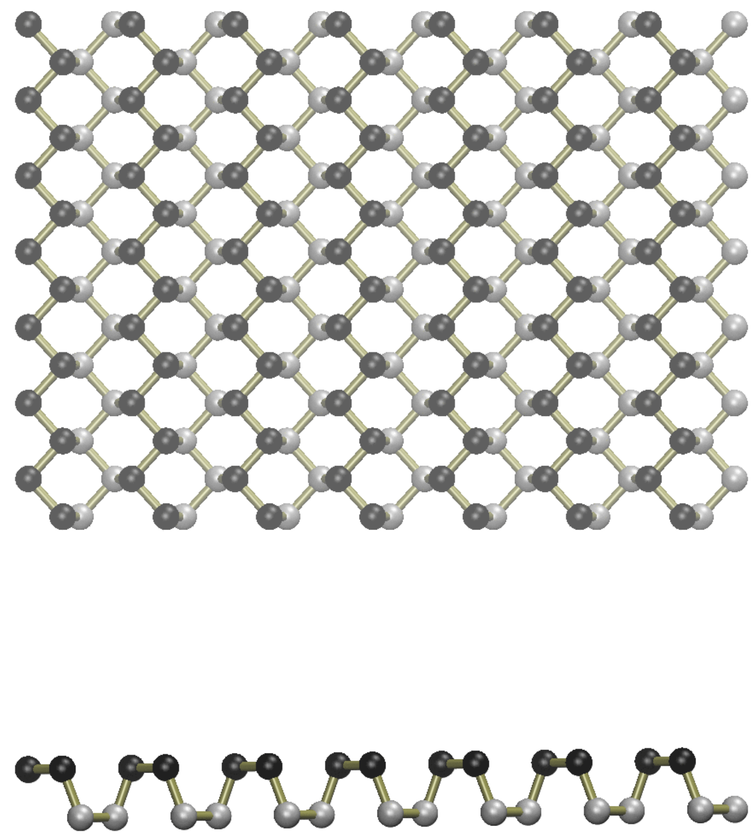
No phase transition

Energy Barrier Between BP and bP

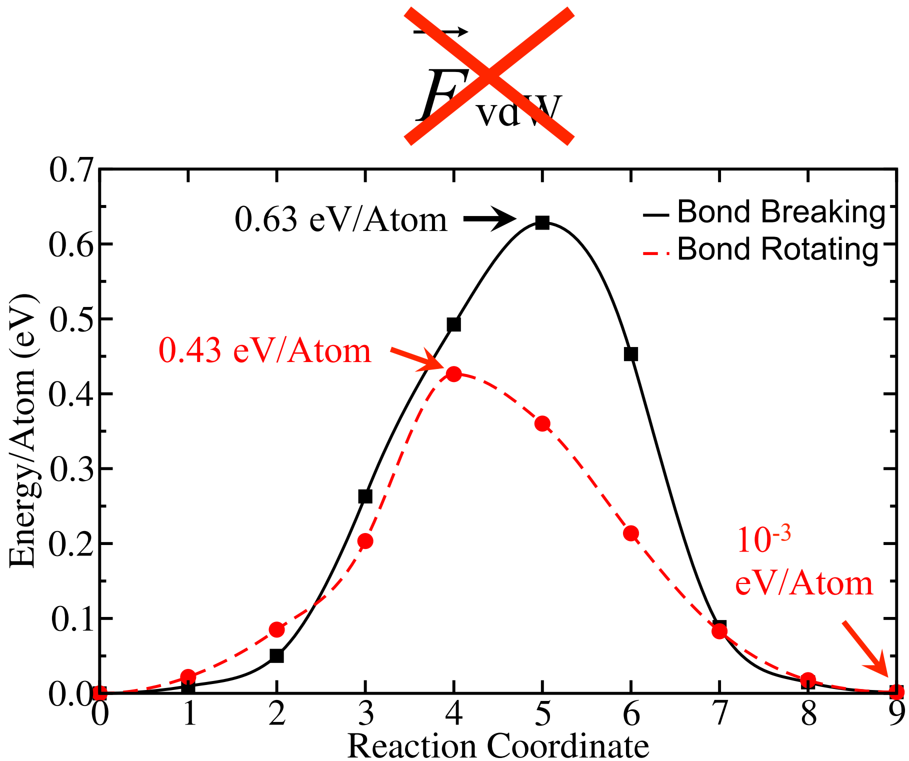
Path-1: Bond Breaking

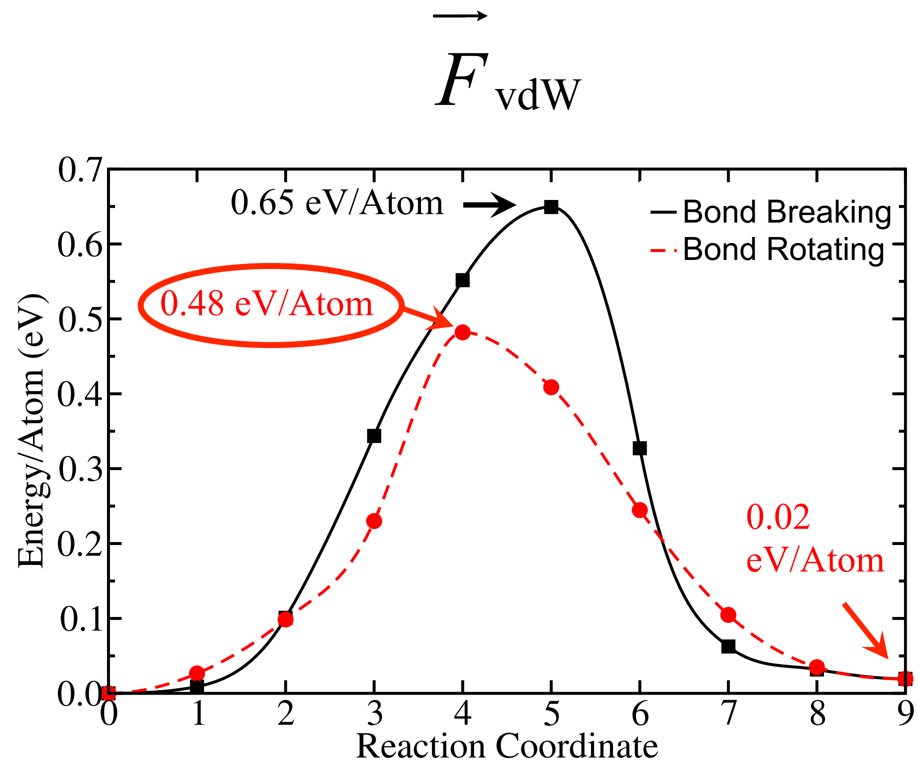


Path-2: Bond Rotating

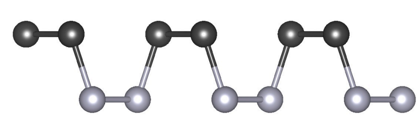


Nudged Elastic Band (NEB)

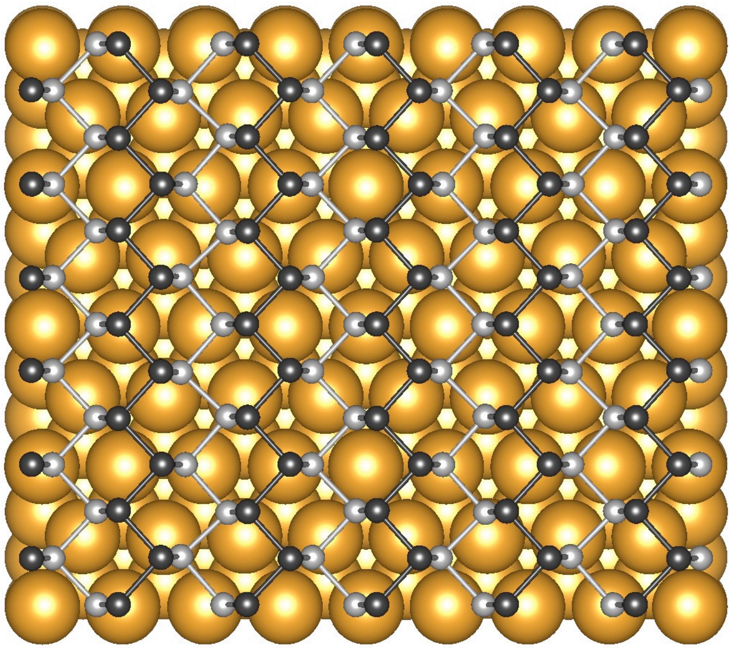


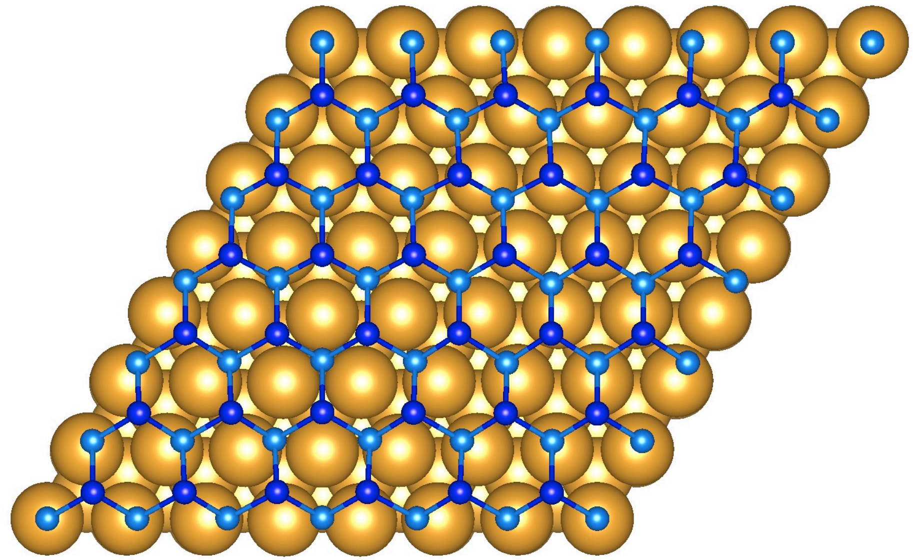


Energy barrier is 10% higher including vdW interactions

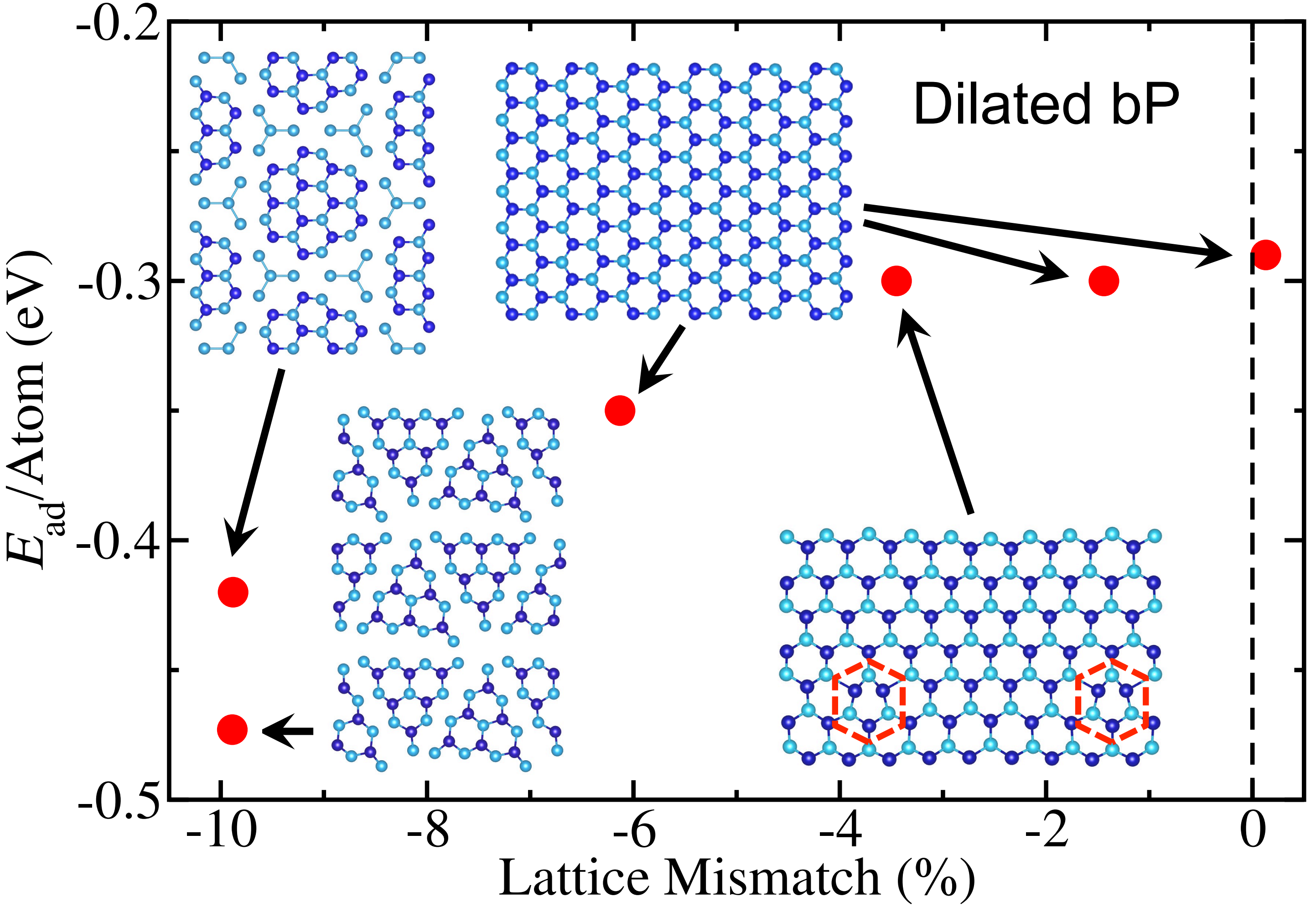


BP and bP Adsorbed on Au(111)



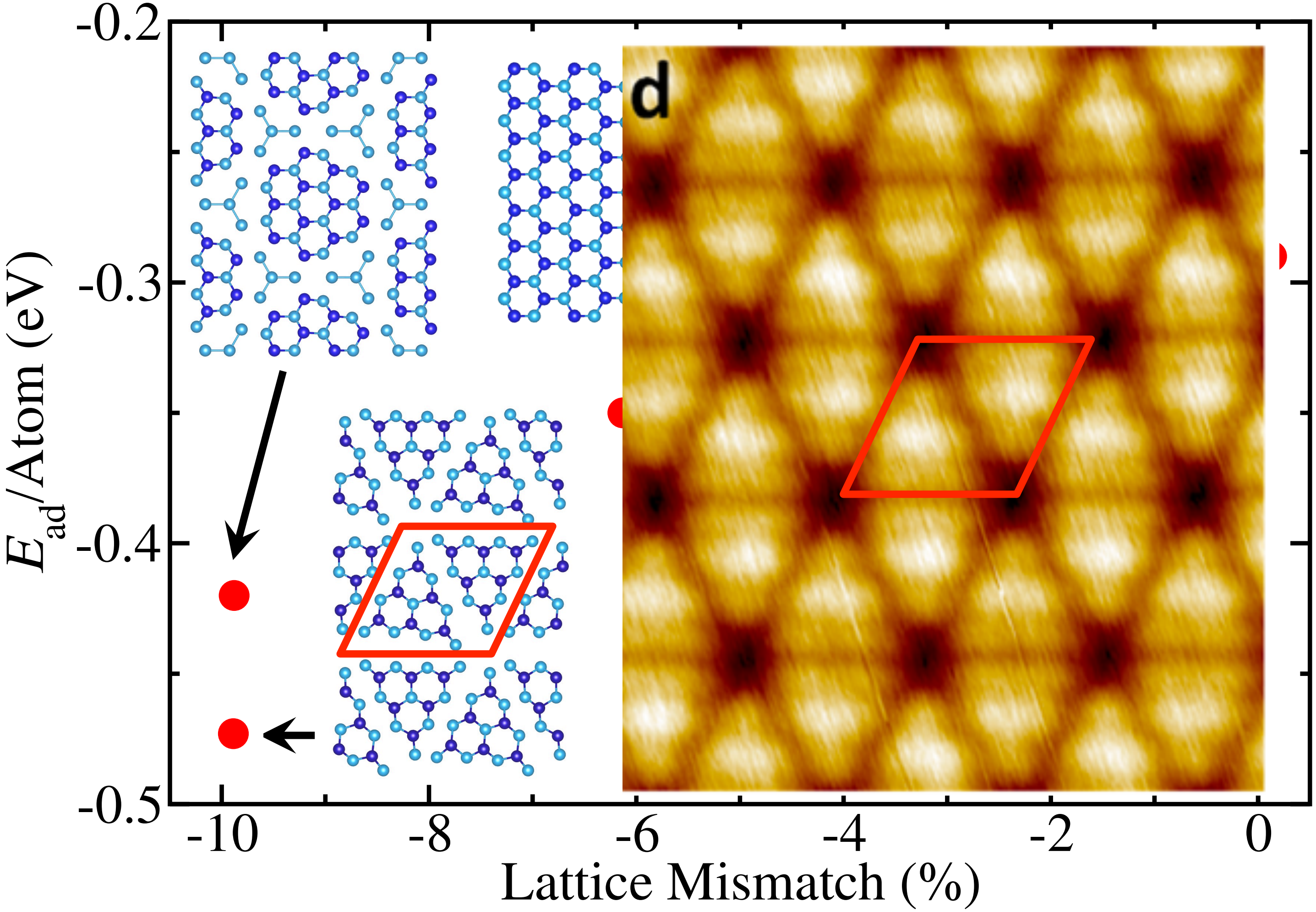


bP Adsorbed on Au(111)



bP's structure: distorted

bP Adsorbed on Au(111)

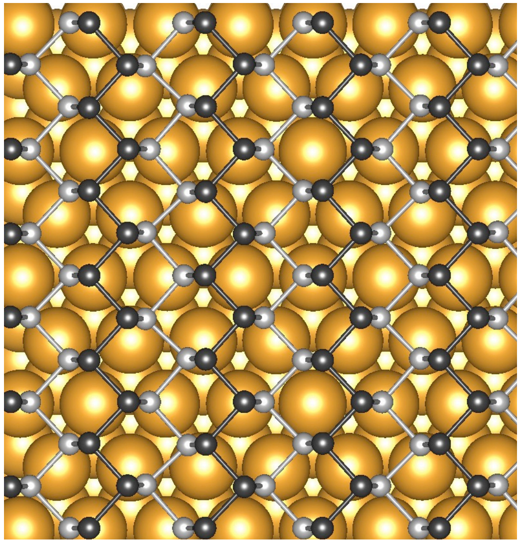


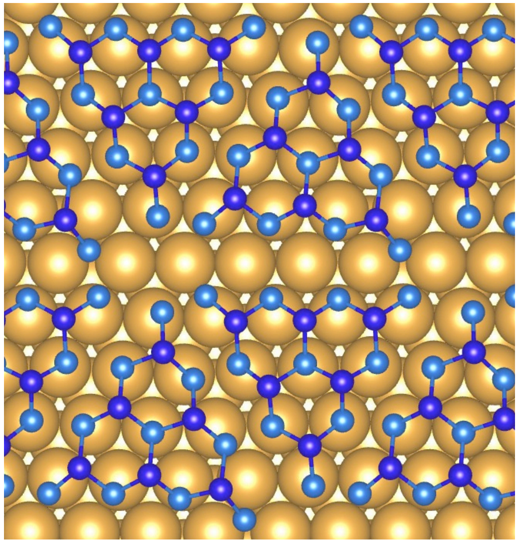
bP's structure: distorted

J. L. Zang, *Nano Lett., 16*, 4903 (2016)

BP and bP Adsorbed on Au(111)

$E_f = -5.60$ eV/Atom $>$ $E_f = -5.66$ eV/Atom





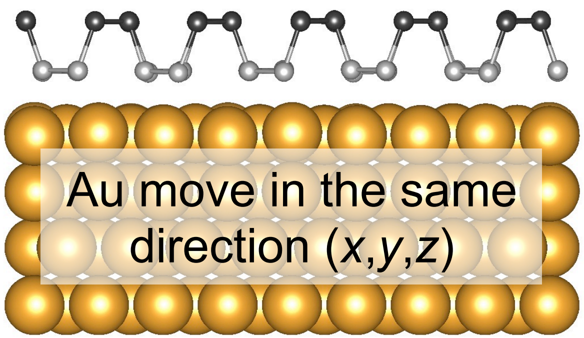
$$\omega_{\vec{q},j} = \omega_{\vec{q},j}\left(\mathrm{P@Au(111)}\right) + \omega_{\vec{q},j}\left(\mathrm{P}\right) + \omega_{\vec{q},j}\left(\mathrm{Au(111)}\right)$$

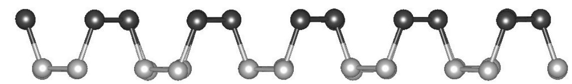
Include the interface interactions

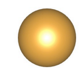
Phonons Including Interface Interactions

Force calculations

Phonon calculations





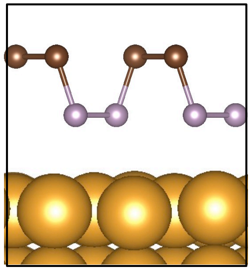


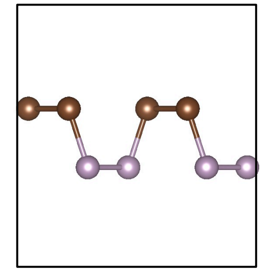
$$\sum_{i=1}^{i=M}\left(m_{\mathrm{Au}_i}, F_{\mathrm{Au}_i}\right)$$

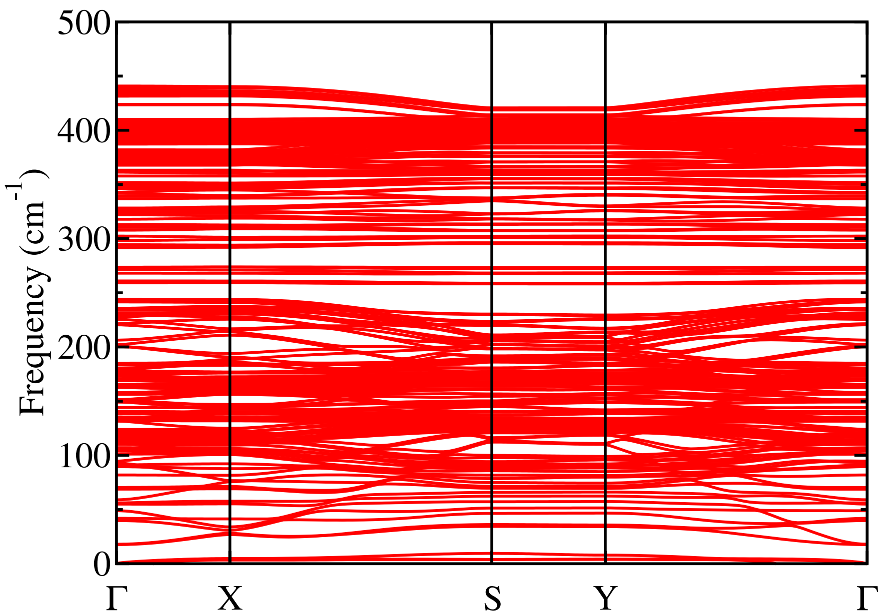
$$\begin{pmatrix} F_{\mathrm{P}_N}^{\to \mathrm{P}_N} & F_{\mathrm{Au}_1}^{\to \mathrm{P}_N} & \cdots & F_{\mathrm{Au}_M}^{\to \mathrm{P}_N} \\ F_{\mathrm{P}_N}^{\to \mathrm{Au}_1} & F_{\mathrm{Au}_1}^{\to \mathrm{Au}_1} & & \\ \vdots & & \ddots & \\ F_{\mathrm{P}_N}^{\to \mathrm{Au}_M} & & \cdots & F_{\mathrm{Au}_M}^{\to \mathrm{Au}_M} \end{pmatrix} \rightarrow \begin{pmatrix} F_{\mathrm{P}_N}^{\to \mathrm{P}_N} & F_{\mathrm{Au}_1}^{\to \mathrm{P}_N} & \cdots & 0 \\ F_{\mathrm{P}_N}^{\to \mathrm{Au}_1} & F_{\mathrm{Au}_1}^{\to \mathrm{Au}_1} & & \\ \vdots & & \ddots & \\ 0 & & \cdots & 0 \end{pmatrix}$$

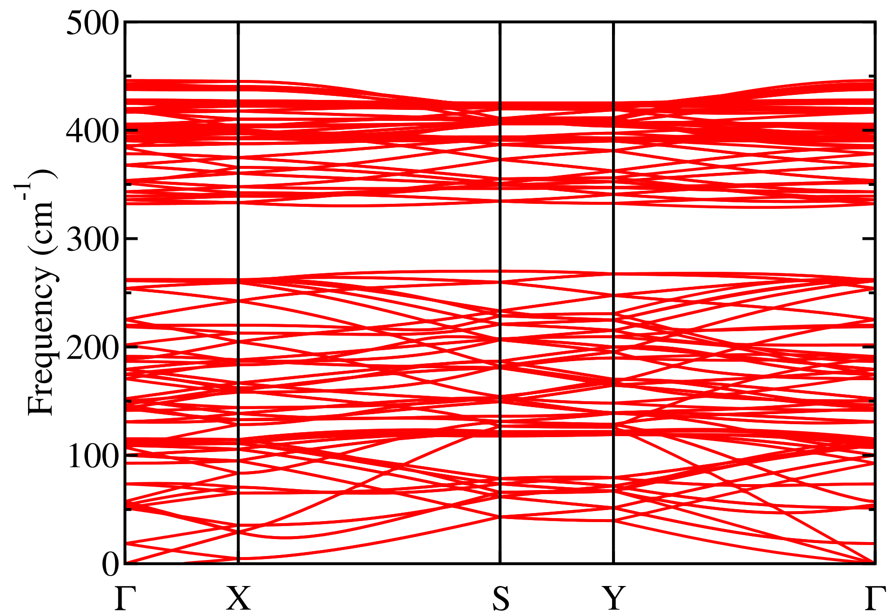
Reduce the size of the system

Phonons Including Interface Interactions



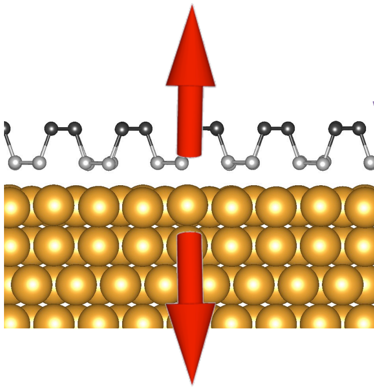




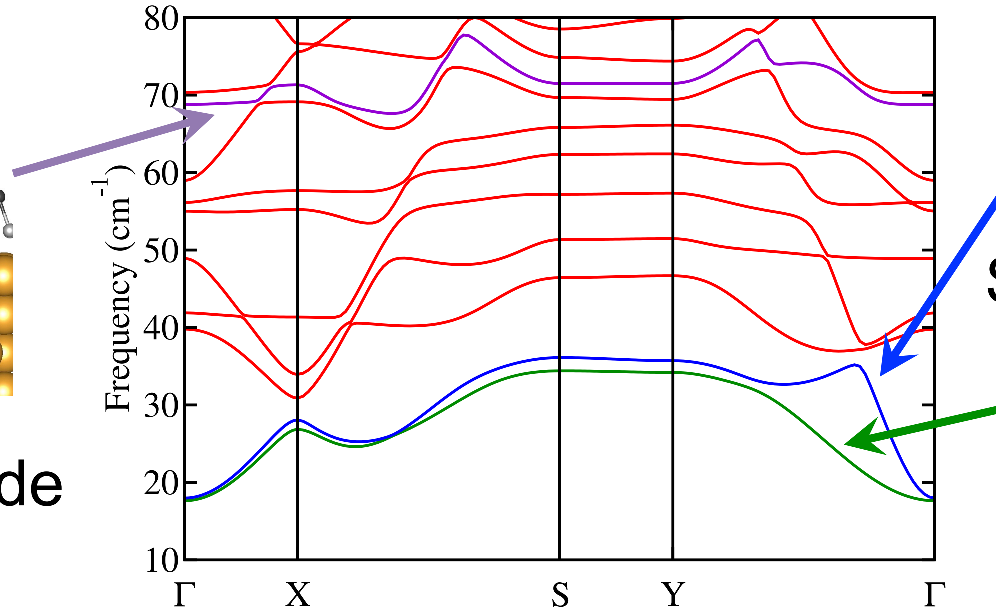


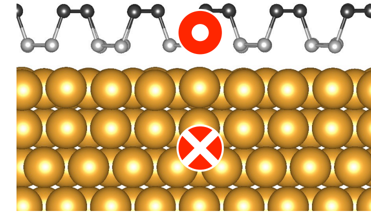
Phonon modes: continuous surface in interaction with a substrate

Emergence of New Modes

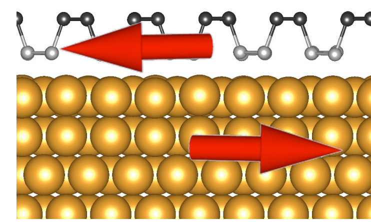


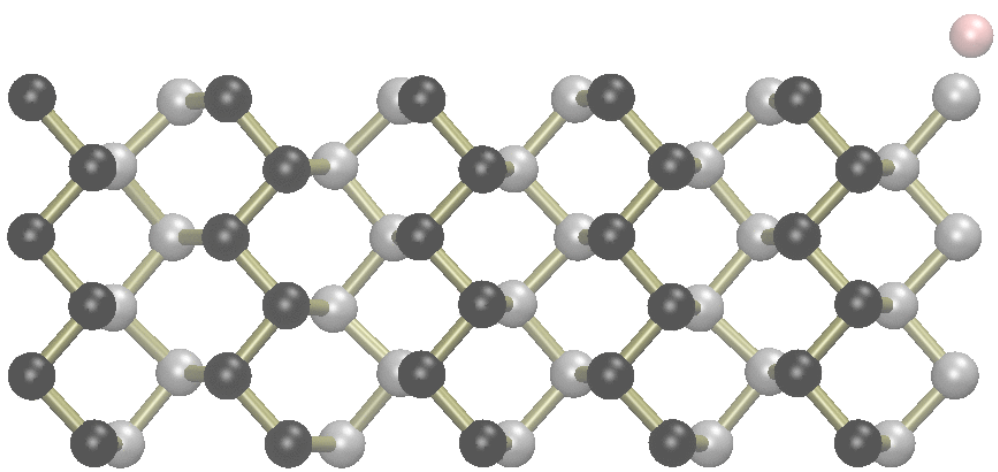
Breathing mode



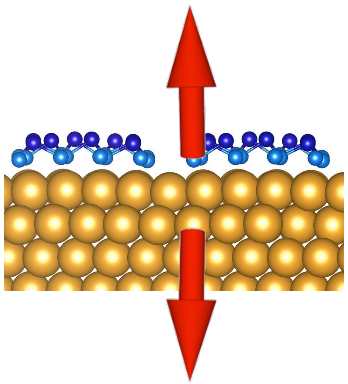


Shearing modes

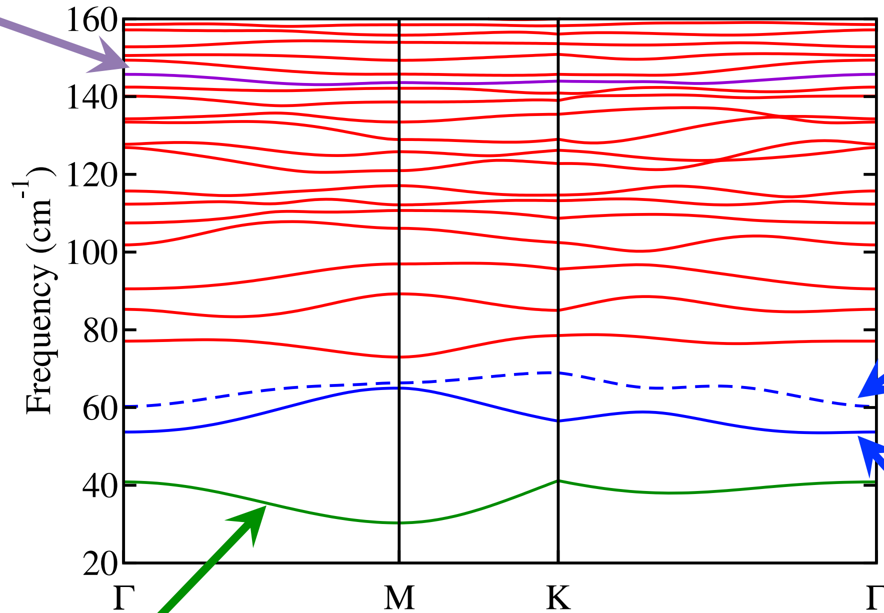


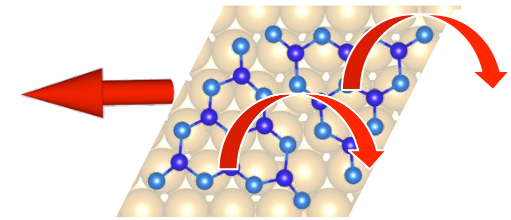


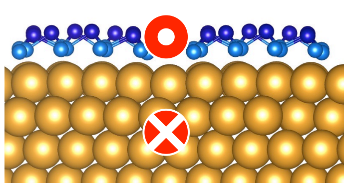
Emergence of New Modes

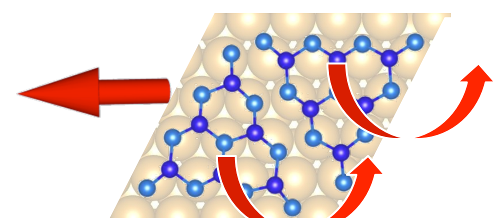


Breathing mode



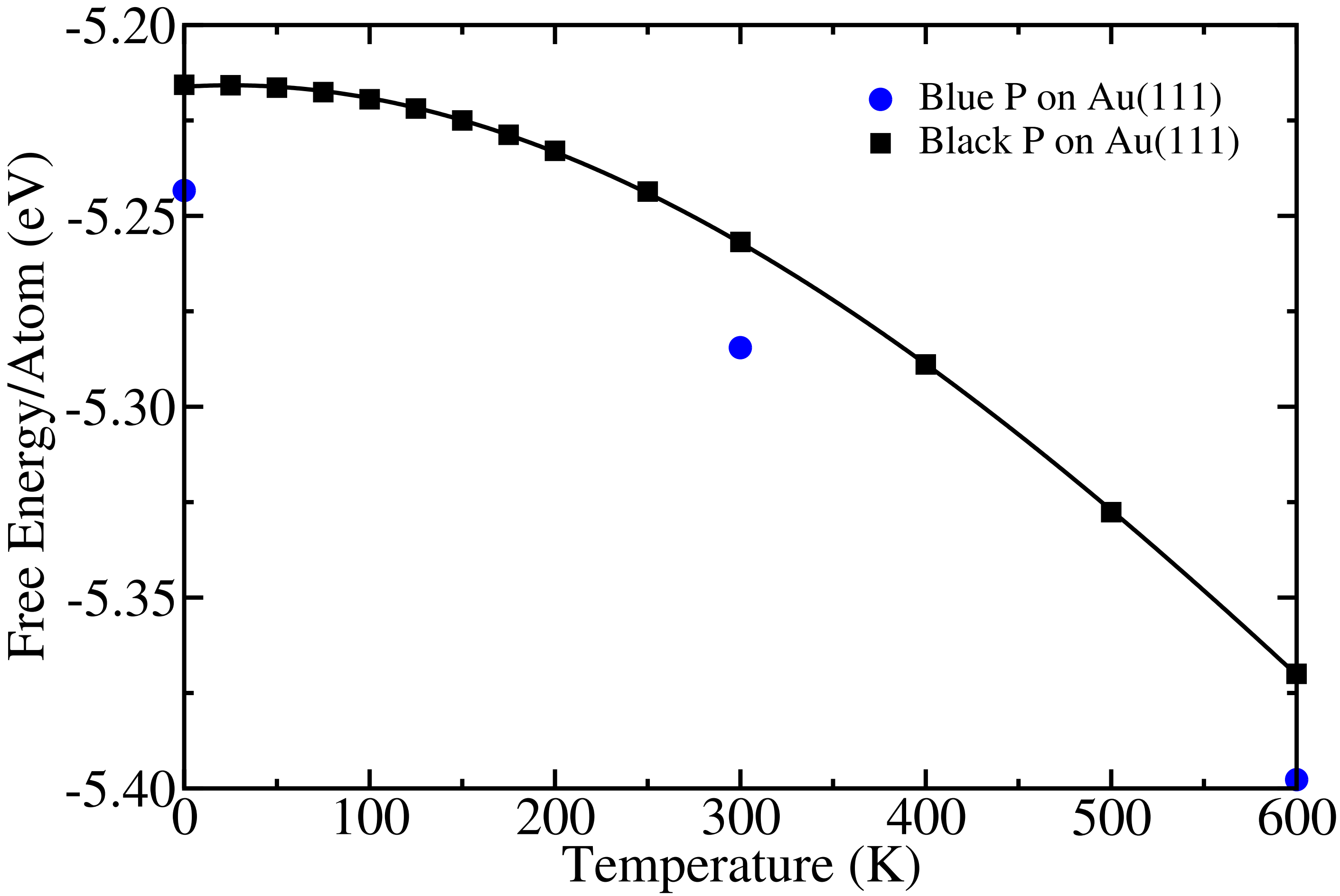


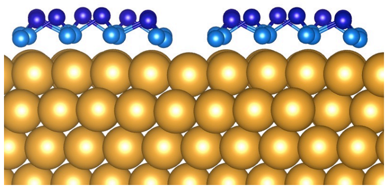




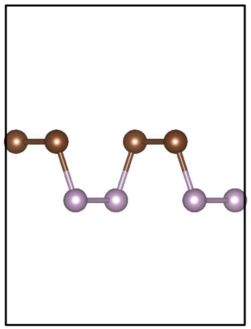
Shearing modes

Temperature Dependent Free Energy

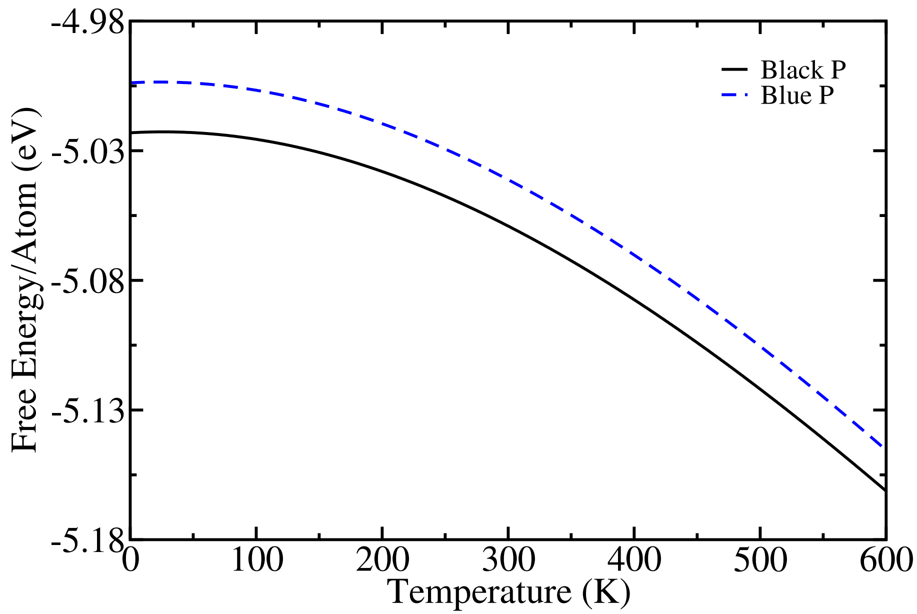




Conclusions



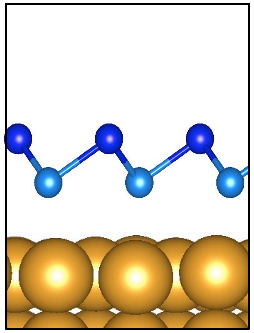
- Is it reasonable to neglect vdW interactions?



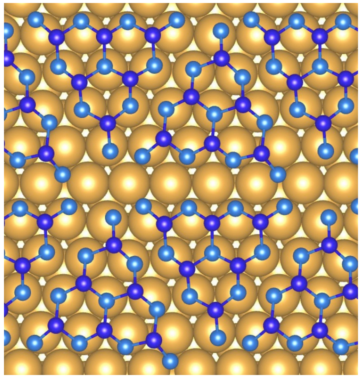
$\vec{F}_{\mathrm{vdW}}$

No phase transition

Conclusions

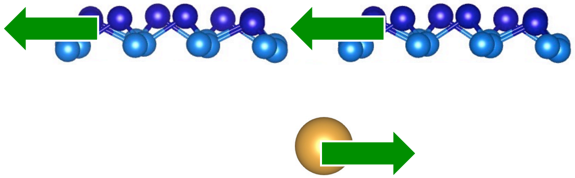


- Why is bP more stable than BP?

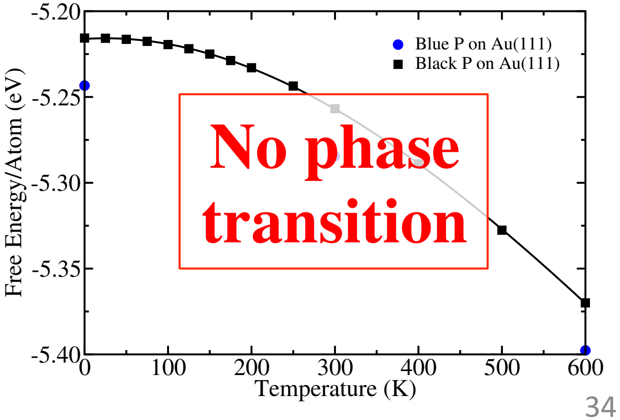


Modified structure

- Is it always the case at high temperature?



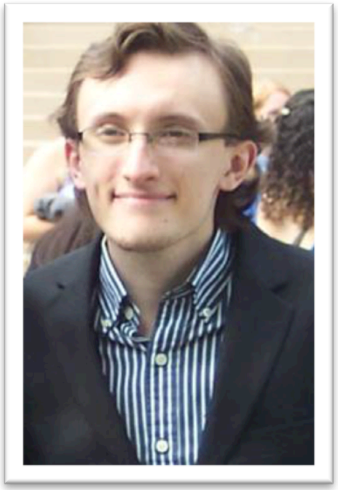
New method
Emergence of modes



No phase transition

Acknowledgments

- PhD Student: Andrew Cupo
- Prof. Vincent Meunier



- Supercomputer Blue Gene, New York State, USA