Anisotropic Phonon Recoil in Pristine and Hydrogenated Graphene

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Outline

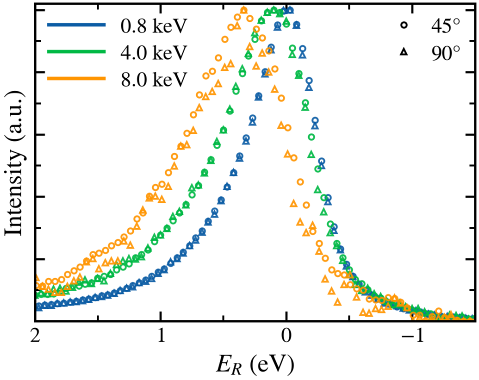
Why Hard X-rays?

At multi-keV photon energies the photoelectron carries enough momentum to kick the emitting nucleus:

$$E_{\mathrm{R}} = \frac{m_e}{M_{\mathrm{C}}} E_{\mathrm{kin}}$$

- $E_{\mathrm{R}} \sim$ 20 meV at 0.8 keV $\longrightarrow$ negligible
- $E_{\mathrm{R}} \sim$ 147 meV at 4 keV
- $E_{\mathrm{R}} \sim$ 332 meV at 8 keV

Recoil **shifts**, **broadens**, and **distorts** the C 1*s* spectrum in a geometry-dependent way.



Anisotropic Vibrational Model

Graphene phonons split into two channels:

In-plane (stretching)

$\omega \propto q \;\Rightarrow\; D_s(\omega) = 2\omega/\omega_s^2, \quad \hbar\omega_s \simeq 160$ meV

Out-of-plane (bending)

$\omega \propto q^2 \;\Rightarrow\; D_b(\omega) = 1/\omega_b, \quad \hbar\omega_b \simeq 66$ meV

1. Each normalised DOS $D_\lambda(\omega)$ builds a channel-resolved spectral density:

$$J_\lambda(\omega) = \frac{E_{\mathrm{R}}}{\hbar\omega} D_\lambda(|\omega|) \left\{ \left[n(|\omega|) + 1 \right] \Theta(\omega) + n(|\omega|)\, \Theta(-\omega) \right\}$$

(phonon emission $\omega > 0$ and absorption $\omega < 0$; $n(\omega) = [e^{\hbar\omega/k_B T} - 1]^{-1}$; strength $\propto E_{\mathrm{R}} \propto E_{\mathrm{kin}}$)

2. The cumulant $G(t)$ encodes both channels with their angular weights:

$$G(t) = \int_{-\infty}^{+\infty} \mathrm{d}\omega \, \left(e^{i\omega t} - 1 \right) \left[J_s(\omega) \cos^2\theta + J_b(\omega) \sin^2\theta \right]$$

3. The phonon recoil kernel follows from the generating function:

$$F(t) = \left\langle e^{i\mathrm{k}\cdot\mathrm{u}(t)}\, e^{-i\mathrm{k}\cdot\mathrm{u}(0)} \right\rangle_\beta = e^{G(t)} \qquad \Longrightarrow \qquad I_{\mathrm{ph}}(E) \propto \int_{-\infty}^{+\infty} \mathrm{d}t \; e^{-iEt/\hbar} F(t)$$

($\langle \cdots \rangle_\beta$: canonical thermal average; equality holds exactly in the harmonic approximation)

Baseline Recoil Model

Replace electronic effects with a symmetric Lorentzian ($\Gamma = 0.16$ eV):

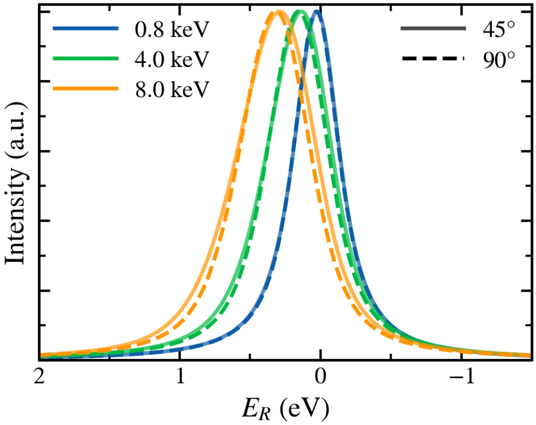
$$I_{\mathrm{FT}}(E) \propto \int \mathrm{d}t \; e^{-iEt/\hbar} \, e^{-\Gamma|t|/\hbar} \, F(t)$$

What the model gets right:

- Recoil shift $\propto E_{\mathrm{R}}$
- Progressive broadening
- Angular anisotropy

What it misses:

- The pronounced asymmetric tail on the high-binding-energy side



Explicit Electronic Convolution Model

Key idea

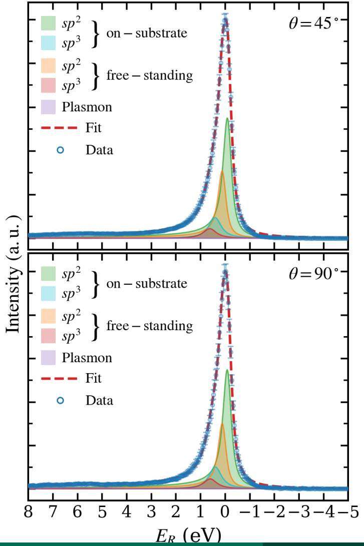
Separate the **intrinsic electronic** spectrum from the **phonon recoil** kernel — justified by the Born–Oppenheimer timescale separation (10^{-16} s vs. 10^{-13} s).

$$\boxed{I_{\mathrm{model}}(E) = \left[\, I_{\mathrm{el}}(E) \, * \, I_{\mathrm{ph}}(E) \right] \, * \, R(E)}$$

- $I_{\mathrm{el}}(E)$ Intrinsic electronic line shape — extracted **once** from 0.8 keV data (Doniach–Šunjić components + Gaussian plasmon loss)
- $I_{\mathrm{ph}}(E)$ Phonon recoil kernel — carries **all** $(h\nu,\ \theta,\ T)$ dependence
- $R(E)$ Gaussian instrumental resolution (fixed by Au Fermi edge)

No free parameters at 4 and 8 keV — only E_{R} is updated.

Electronic Line Shape from the 0.8 keV Reference



At 0.8 keV $E_\mathrm{R} \simeq 20$ meV $\ll$ linewidth $\Longrightarrow$ recoil is negligible, spectrum is dominated by **electronic** contributions.

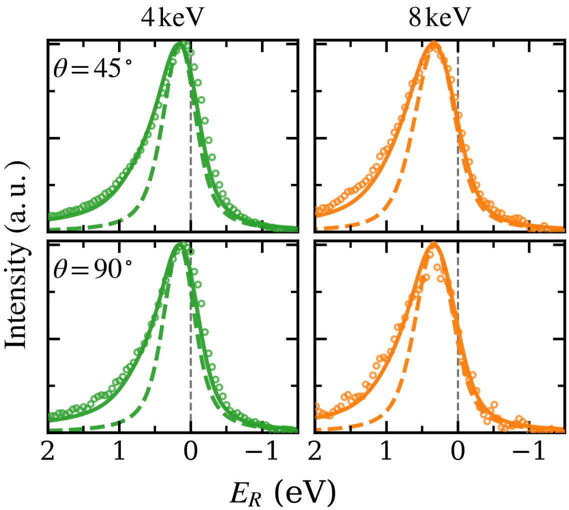
Fit with 4 Doniach–Šunjić peaks + plasmon Gaussian:

- *sp*^{2}: $\alpha \simeq 0.10$ (asymmetric)
- *sp*^{3}: $\alpha = 0$ (Lorentzian limit)
- Parameters stable across θ

$\chi^2_\nu = 1.18$ (45), 1.12 (90)

$\Longrightarrow$ **single angle-independent** $I_\mathrm{el}(E)$ is validated.

Pristine Graphene: Model vs. Experiment



- Convolution model: ∼5–10 meV accuracy at 8 keV
- Baseline underestimates by tens of meV
- Asymmetric tail reproduced without refitting

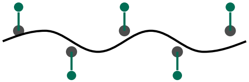
From sp^2 to sp^3: What Changes?

Pristine graphene

flat sp^2 network

2 phonon channels:
stretching + bending
$\hbar\omega_{\mathrm{max}} \sim 160\,\mathrm{meV}$

Hydrogenated (graphane)



buckled sp^3 + C–H

3 phonon channels:
stretching + bending + **C–H stretch**
$\hbar\omega_{\mathrm{CH}} \sim 360\,\mathrm{meV}$

The C–H stretching frequency is **comparable to** E_{R} at 8 keV $\Longrightarrow$ single-phonon C–H emission becomes accessible!

Three-Channel Vibrational Model

Channel	DOS form	Cutoff	Coupling	Weight w_λ
Stretching (s)	$2\omega/\omega_s^2$	140 meV	$\cos^2\theta$	1
Bending (b)	$1/\omega_b$	100 meV	$\sin^2\theta$	$M_\mathrm{C}/(M_\mathrm{C}+M_\mathrm{H}) = 12/13$
C–H stretch	flat, 350–375 meV	—	$\sin^2\theta$	$M_\mathrm{H}/(M_\mathrm{C}+M_\mathrm{H}) = 1/13$

Out-of-plane spectral density: $J_\perp = w_b\, J_b + w_\mathrm{CH}\, J_\mathrm{CH}$

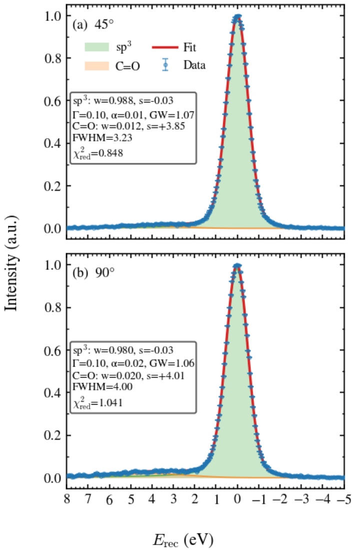
Recoil-energy conservation at every angle

$$\langle E_\mathrm{rec}\rangle = E_\mathrm{R}\cos^2\theta + E_\mathrm{R}\sin^2\theta = E_\mathrm{R}$$

guaranteed by $w_b + w_\mathrm{CH} = 1$ — follows from phonon eigenvector completeness.

Weights w_b, w_CH are **not fitting parameters**: they are fixed by the carbon eigenvector components of the ZA/ZO and C–H branches.

Electronic Line Shape: Hydrogenated Reference



Hydrogenation simplifies I_{el}:

- Single sp^3 peak ($>$ 98% weight)
- DS asymmetry $\alpha \lesssim 0.02 \approx$ zero (no metallic π-band screening)
- Minor C=O contamination at +4 eV ($<$ 2%)

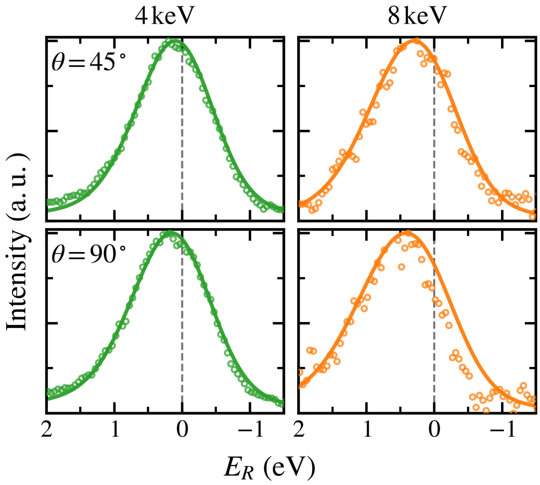
Contrast with pristine graphene:

sp^2: $\alpha \simeq 0.10$ (finite asymmetry)

sp^3: $\alpha \simeq 0$ (symmetric)

Fit stable between 45 and 90
$\Longrightarrow$ angle-independent I_{el} validated.

Hydrogenated Graphene: Theory vs. Experiment



I_{el} fixed from 0.8 keV; only E_{R} is updated via E_{kin} at each photon energy.

Quantitative agreement at both angles and both photon energies:

- Recoil-induced peak shifts and broadenings correctly reproduced
- Angular splitting (45 vs 90) captured by the three-channel kernel
- No refitting of electronic parameters

Summary and Outlook

1. **Pristine graphene** — the explicit electronic convolution model separates the DS asymmetry from anisotropic phonon recoil, yielding parameter-free predictions at 4 and 8 keV (∼5–10 meV accuracy on peak shifts).
2. **Hydrogenated graphene** — a single additional channel (C–H stretching) introduces a mode-selective angular fingerprint via $\sin^2\theta$.

Outlook: the convolution strategy is directly transferable to other functionalised 2D materials (fluorographene, BN, oxidised graphene. . .) wherever the Born–Oppenheimer factorisation and a near-recoilless reference are available.

Thank you!

Questions?

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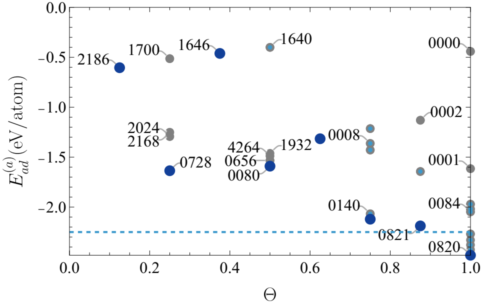
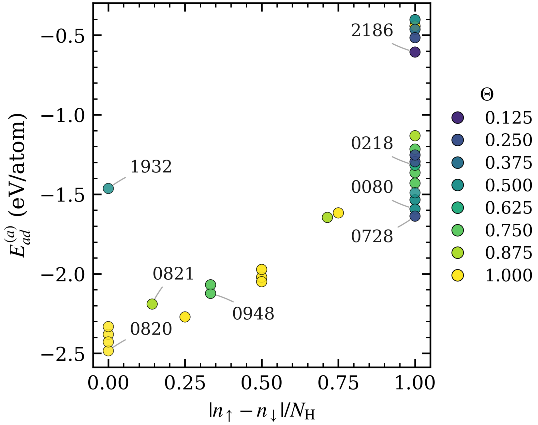
Why Thermodynamics?

So far: *how* does the recoil line shape look?
Now: *when* is hydrogenated graphene **stable**?

- DFT energetics (Sluiter & Kawazoe 2003): systematic enumeration of two-sided H patterns on graphene
- Coverage $\Theta = N_\mathrm{H}/N_\mathrm{C}$: from 0 (pristine) to 1 (chair graphane)
- At $T = 0$: phase separation into the two endpoints is energetically favoured (positive tie-line excess for all intermediate Θ)



Configurational Landscape: Two-Sided Imbalance



Key structural discriminator:
imbalance $= |n_\uparrow - n_\downarrow| / N_\mathrm{H}$

- One-sided adsorption → membrane bending
  → elastic penalty $\propto \kappa^2$
- Balanced two-sided → local puckering
  → no net curvature

⟹ High imbalance correlates with less favourable adsorption energy

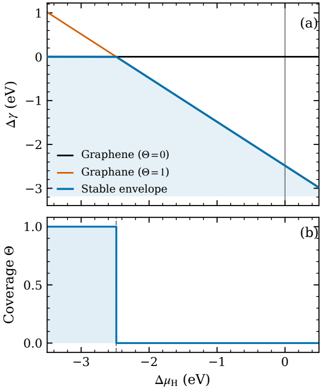
* Several balanced configurations are *missing* from the original dataset: true ground states at intermediate Θ may be even lower.

Grand-Canonical Phase Diagram

Stability functional per site:

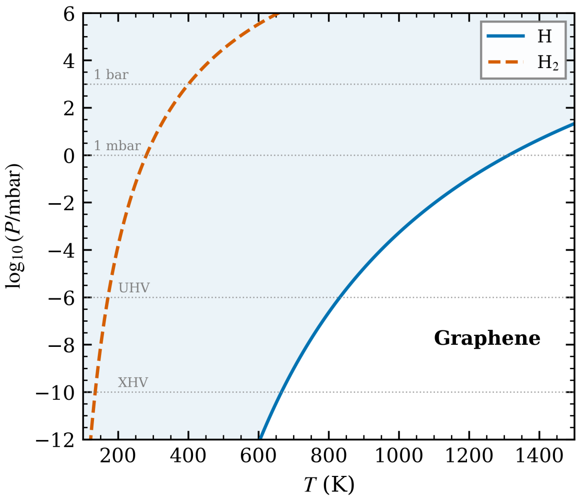
$$\Delta\gamma(\Theta;\ T,P) = \Theta\left[\,E_{\mathrm{ad}}(\Theta) - \Delta\mu_{\mathrm{H}}(T,P)\,\right]$$

Minimize over Θ at fixed (T,P) $\longrightarrow$ equilibrium coverage.



- Miscibility gap: **no stable intermediate coverages**
- Sharp transition at $\Delta\mu_{\mathrm{H}} = E^{(a)}_{\mathrm{ad}}(\Theta{=}1)$
- Maps to a line in the (T,P) plane via gas-phase thermochemistry

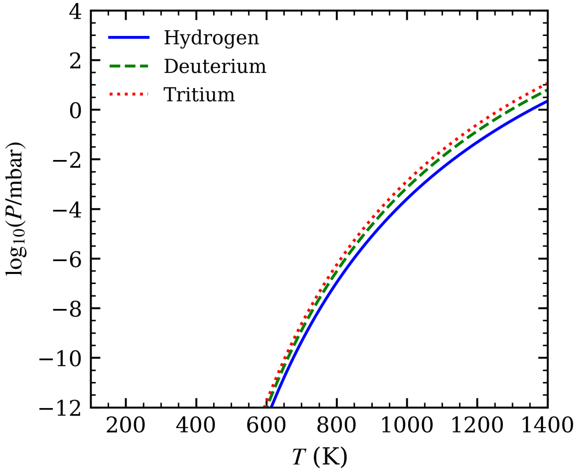
Phase Boundary: Atomic vs. Molecular Hydrogen



Under UHV (10^{-10}–10^{-6} mbar):

- **Atomic H:** boundary at $T <$ 600–700 K $\implies$ graphane thermodynamically favoured
- **Molecular H_2:** boundary far outside any experimental window

Isotope Effects and the PTOLEMY Connection



Relevance: the PTOLEMY project proposes tritium on graphene for cosmic relic neutrino detection.