Supplementary Information

DERIVATION OF EQ. 1

The electronic Hamiltonian for the π,π^* basis can be written as a 2×2 matrix:

$$H(\mathbf{k},\mathbf{0}) = \begin{pmatrix} \hbar v_F k & 0 \\ 0 & -\hbar v_F k \end{pmatrix}, \tag{S-1}$$

where $\mathbf{k}$ is a small in plane wave-vector and $\mathbf{K}+\mathbf{k}$ is the electronic momentum. Let us consider a distortion of the lattice according to a $\mathbf{\Gamma} - E_{2g}$ phonon pattern (note that the $\mathbf{\Gamma} - E_{2g}$ phonon is doubly degenerate). At the lowest order the π-bands Hamiltonian changes as

$$H(\mathbf{k},\mathbf{u}) = H(\mathbf{k},\mathbf{0}) + \frac{\partial H(\mathbf{k},\mathbf{0})}{\partial u} u \tag{S-2}$$

where u is the phonon normal coordinate (the two atoms in the unit-cell are displaced by $\pm u/\sqrt{2}$ along a given direction in the plane). $\partial H/(\partial u)$ can be obtained from the ab-initio deformation potential matrix elements. Following Ref. 1 (Eq.6 and note 24) and Ref. 2, for the E_{2g} phonon mode and for a small $\mathbf{k}$

$$\left|\langle \mathbf{k}\pi^* | \frac{\partial H}{\partial u} | \mathbf{k}\pi^* \rangle\right|^2 = \left|\langle \mathbf{k}\pi | \frac{\partial H}{\partial u} | \mathbf{k}\pi \rangle\right|^2 = \langle D^2_{\mathbf{\Gamma}} \rangle_F [1 + \cos(2\theta)] \tag{S-3}$$

$$\left|\langle \mathbf{k}\pi^* | \frac{\partial H}{\partial u} | \mathbf{k}\pi \rangle\right|^2 = \langle D^2_{\mathbf{\Gamma}} \rangle_F [1 - \cos(2\theta)], \tag{S-4}$$

where $|\mathbf{k}\pi/\pi^*\rangle$ are the electronic states with momentum $\mathbf{K}+\mathbf{k}$ and θ is the angle between $\mathbf{k}$ and the direction perpendicular to the atomic vibration. Taking the square root of Eqs. S-3, S-4 and inserting them into Eq. S-2

$$H(\mathbf{k},\mathbf{u}) = \begin{pmatrix} \hbar v_F k & 0 \\ 0 & -\hbar v_F k \end{pmatrix} + \sqrt{2\langle D^2_{\mathbf{\Gamma}} \rangle_F} \begin{pmatrix} \cos(\theta) & \sin(\theta) \\ \sin(\theta) & -\cos(\theta) \end{pmatrix} u. \tag{S-5}$$

The eigenvalues of Eq. S-5 are then

$$\epsilon = \pm \hbar v_F \sqrt{k^2 + s^2 + 2ks\cos(\theta)} = \pm \hbar v_F |\mathbf{k} - \mathbf{s}(\mathbf{u})|, \tag{S-6}$$

where $\mathbf{s}$ is defined in the main text.

DERIVATION OF EQ. 4

Considering the Taylor expansion of $\Delta E(u)$ in u, Eq. 4 is equivalent to:

$$\frac{d^2}{(du)^2}\Delta E(u) = \frac{d^2}{(du)^2}\left\{\frac{4A}{(2\pi)^2}\int_{\epsilon(\mathbf{k},\pi^*,\mathbf{0})<\epsilon_F} \epsilon(\mathbf{k},\pi^*,\mathbf{u})\ d^2k\right\}. \tag{S-7}$$

In this section, we will demonstrate that

$$\hbar\Delta\omega = \frac{\hbar}{2M\omega_0}\frac{d^2}{(du)^2}\left\{\frac{4A}{(2\pi)^2}\int_{\epsilon(\mathbf{k},\pi^*,\mathbf{0})<\epsilon_F} \epsilon(\mathbf{k},\pi^*,\mathbf{u})\ d^2k\right\}, \tag{S-8}$$

at $T = 0$ and under the condition

$$\epsilon_F \gg \hbar\omega_0/2. \tag{S-9}$$

Using Eq. 2, Eq. 4 will then immediately follow.

Within time dependent perturbation theory, $\hbar\Delta\omega$ is (see Eq. 10 of Ref. 3):

$$\hbar\Delta\omega = \frac{\hbar}{2M\omega_0}[F_{\mathbf{0}}^{\epsilon_F}(\omega_0) - F_{\mathbf{0}}^{0}(\omega_0)]. \tag{S-10}$$

were at $T = 0$,

$$F_{\mathbf{0}}^{\epsilon_F}(\omega_0) = \frac{2}{N_{\mathbf{k}}}\sum_{\mathbf{k},o,e}|D_{\mathbf{k}o,\mathbf{k}e}|^2\left\{\frac{1}{\epsilon_{\mathbf{k}o}-\epsilon_{\mathbf{k}e}+\hbar\omega_0}+\frac{1}{\epsilon_{\mathbf{k}o}-\epsilon_{\mathbf{k}e}-\hbar\omega_0}\right\}. \tag{S-11}$$

Here the index o and e denotes the occupied ($\epsilon_{\mathbf{k}o} < \epsilon_F$) and empty bands ($\epsilon_{\mathbf{k}e} > \epsilon_F$), and

$$D_{\mathbf{k}o,\mathbf{k}e} = \langle \mathbf{k}o|\frac{\partial H}{\partial u}|\mathbf{k}e\rangle. \tag{S-12}$$

Now we consider only the π and π^* bands and we substitute $1/N_{\mathbf{k}}\sum_{\mathbf{k}}$ with $A/(2\pi)^2\int d^2k$, where A is the unit-cell area and the integral is restricted on a circle of radius $\bar{k}$, centered on $\mathbf{K}$. Assuming a Dirac dispersion for the π and π^* bands, $\epsilon_{\mathbf{k}e} - \epsilon_{\mathbf{k}o} \geq 2\epsilon_F$. Thus, if the condition of Eq. S-9 holds, $|\epsilon_{\mathbf{k}e} - \epsilon_{\mathbf{k}o}| \gg \hbar\omega_0$ and the $\hbar\omega_0$ in the denominators of Eq. S-11 can be neglected. Eq. S-11 becomes

$$F_{\mathbf{0}}^{\epsilon_F} = \frac{8A}{(2\pi)^2}\int_{\epsilon(\mathbf{k},\pi^*,\mathbf{0})>\epsilon_F, k<\bar{k}} \frac{|D_{\mathbf{k}\pi^*,\mathbf{k}\pi}|^2}{\epsilon(\mathbf{k},\pi,\mathbf{0}) - \epsilon(\mathbf{k},\pi^*,\mathbf{0})}\ d^2k, \tag{S-13}$$

where $\epsilon(\mathbf{k},\pi/\pi^*,\mathbf{0})$ are the bands of the undistorted graphene structure. From Eq. S-10,

$$\hbar\Delta\omega = \frac{\hbar}{2M\omega_0}\left\{-\frac{8A}{(2\pi)^2}\int_{\epsilon(\mathbf{k},\pi^*,\mathbf{0})<\epsilon_F} \frac{|D_{\mathbf{k}\pi^*,\mathbf{k}\pi}|^2}{\epsilon(\mathbf{k},\pi,\mathbf{0}) - \epsilon(\mathbf{k},\pi^*,\mathbf{0})}\ d^2k\right\}. \tag{S-14}$$

From textbook static second order perturbation theory

$$\frac{1}{2}\left.\frac{d^2\epsilon(\mathbf{k},\pi^*,\mathbf{u})}{(du)^2}\right|_{u=0} = \frac{|D_{\mathbf{k}\pi^*,\mathbf{k}\pi}|^2}{\epsilon(\mathbf{k},\pi^*,\mathbf{0}) - \epsilon(\mathbf{k},\pi,\mathbf{0})}. \tag{S-15}$$

Substituting Eq. S-15 in Eq. S-14 we have

$$\hbar\Delta\omega = \frac{\hbar}{2M\omega_0}\left\{\frac{4A}{(2\pi)^2}\int_{\epsilon(\mathbf{k},\pi^*,\mathbf{0})<\epsilon_F}\frac{d^2\epsilon(\mathbf{k},\pi^*,\mathbf{u})}{(du)^2}\,d^2k\right\}. \tag{S-16}$$

Eq. S-8 is, finally, obtained by taking the derivation with respect to u in Eq. S-16 outside the integral.

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[3] M. Lazzeri, F. Mauri, Non-adiabatic Kohn-anomaly in a doped graphene monolayer. Phys. Rev. Lett. **97**, 266407 (2006).