

Graphene lattice recoil in hard x-ray photoemission: Experiment and theory

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Hard-x-ray C 1s photoemission from monolayer graphene probes a regime in which nuclear recoil and intrinsic electronic asymmetry contribute on comparable energy scales to the observed spectral line shape. Here we combine experiment and modeling over the photon-energy range 0.8–8 keV to resolve this interplay quantitatively. A graphene-specific implementation of the Fujikawa-Takata cumulant formalism, based on an anisotropic vibrational density of states constrained by first-principles phonon calculations, captures the expected recoil scaling with photon energy and emission geometry but fails to reproduce the pronounced asymmetric tails of the measured spectra. To overcome this limitation, we introduce an explicit electronic convolution model in which a photon-energy-independent reference response, dominated by the electronic line shape and extracted from the low-recoil 0.8 keV data through a recoil-inclusive fit, is convolved with a phonon recoil kernel carrying the full dependence on photon energy and emission angle. This approach reproduces both the measured line-shape evolution and the observed peak shifts across the explored energy range without refitting the spectra at higher photon energies. The results show that recoil in graphene cannot be described by a baseline treatment in which the phonon recoil kernel is combined only with symmetric lifetime broadening, but must be treated together with the intrinsic many-body electronic response of the C 1s line.

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I. INTRODUCTION

At hard-x-ray photon energies [1,2], core-level photoemission enters a regime in which the momentum carried by the photoelectron is large enough for nuclear recoil to become an intrinsic part of the excitation process, especially for light elements. In this regime, the emitting atom cannot be regarded as an infinitely massive scatterer: the sudden creation and emission process transfers momentum to the lattice, producing measurable modifications of the spectral profile, including energy shifts, recoil broadening, and geometry-dependent line-shape changes.

A quantitative framework for this problem was developed by Fujikawa and Takata, who formulated the recoil contribution in terms of a cumulant description of the lattice response [3,4]. In their application to graphite, Takata *et al.* showed that the C 1s hard-x-ray photoemission line is reshaped by

the coupling between the photoelectron momentum and the anisotropic vibrational motion of carbon atoms, thereby establishing graphite as a prototypical solid-state system for recoil spectroscopy [4]. Direct experimental evidence of recoil in condensed-matter photoemission was also obtained from the Fermi edge of simple metals, where the displacement and broadening of the Al edge relative to Au demonstrated that nuclear recoil is directly observable at hard-x-ray energies [5]. Consistent recoil signatures in highly oriented pyrolytic graphite were also connected to electron scattering and neutron Compton scattering measurements within the same general physical picture [6]. Related effects have been identified in molecular core-level spectra, where the discrete vibrational structure of light molecules makes the transferred momentum traceable mode by mode [7]. Recent hard x-ray photoelectron spectroscopy (HAXPES) measurements by Roth *et al.* show conventional recoil shifts in elemental Si but enhanced, material-specific shifts in 4H-SiC, where optical phonons and stronger electron-phonon coupling modify the vibrational envelope [8]. Fujikawa and Niki have furthermore formulated recoil, Franck-Condon excitation, and their interference within a unified many-body treatment [9]. Taken together, these studies show that recoil is not merely an instrumental or kinematic correction to hard-x-ray photoemission spectra. Rather, for light-element systems, it is part of the many-body line-shape problem and must be treated together

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with intrinsic electronic structure, vibrational dynamics, and experimental resolution.

Graphene provides a particularly clean setting for this problem. Its lattice dynamics is strongly anisotropic, with distinct in-plane and flexural phonon branches [10–16]. At the same time, the C 1s line shape in sp^2 carbon systems is intrinsically asymmetric: the sudden creation of a core hole couples to low-energy electron-hole excitations, producing the characteristic high-binding-energy tail described by the Doniach-Šunjić (DS) form [17,18]. This asymmetry was established in graphite by Sette *et al.* [19], who showed that lifetime and screening effects are inseparable in the measured line shape and must be modeled explicitly. More recently, soft-x-ray photoemission on graphene membranes confirmed that the asymmetric tail survives in suspended graphene and is therefore an intrinsic feature of the graphene C 1s spectrum [20].

In the hard-x-ray regime, recoil and intrinsic asymmetry act on comparable energy scales. As the photoelectron kinetic energy increases, the free-atom recoil energy

$$E_R = \frac{\hbar^2 k^2}{2M_C} = \frac{m_e}{M_C} E_{\text{kin}} \quad (1)$$

grows linearly with E_{kin} . For carbon, E_R reaches approximately 172 meV at 4 keV and 356 meV at 8 keV, values large enough to compete with the intrinsic linewidth of the C 1s line and to reshape the observed spectrum in a geometry-dependent manner. The resulting problem is therefore not simply one of recoil broadening, but of disentangling phonon-driven spectral redistribution from an already asymmetric intrinsic electronic response.

In this work we address this problem through a combined experimental and theoretical study of angle- and photon-energy-dependent C 1s photoemission from clean monolayer graphene extending into the hard-x-ray regime. We first adapt the Fujikawa-Takata cumulant formalism [3–5,7,21], originally developed for graphite, to a graphene-specific anisotropic vibrational density of states. We then show that a baseline recoil treatment in which nonphononic effects are represented only by a symmetric Lorentzian lifetime term is insufficient to account for the measured spectra and introduce an explicit convolution scheme in which the intrinsic electronic line shape is determined independently from low-recoil data. Section II presents the experiment. Section III summarizes the cumulant framework and its graphene-specific anisotropic vibrational DOS. Section IV introduces the explicit electronic convolution model and compares it with experiment.

II. EXPERIMENT

A photoemission spectroscopy investigation of the C 1s core level was conducted on monolayer graphene in the soft-to-hard x-ray regimes. The experiment was performed at the I09 beamline of Diamond Light Source [22], with photon energies of 801.02, 4053.4, and 8079.2 eV (respectively called 0.8, 4, and 8 keV from here on). The I09 experimental chamber is equipped with a VG Scienta EW400 HAXPES analyzer and the spectral resolution at each photon energy is 0.14 eV (0.8 keV), 0.24 eV (4 keV), and 0.30 eV (8 keV)—as de-

termined by fitting the Fermi edge of a polycrystalline Au reference, mounted in electrical and thermal contact with the graphene sample, with a Fermi-Dirac function convolved with a Gaussian instrumental response. The energy calibration was repeated systematically whenever the photon energy was changed, together with additional checks before or after selected C 1s scans. The standard error of the fitted Fermi-level position was 12 meV at 4 keV and 14 meV at 8 keV; a conservative absolute uncertainty of 20 meV is assigned to the measured energy shifts.

The investigation was conducted on a sample of polycrystalline monolayer graphene grown on electropolished copper via chemical vapor deposition [23,24] then transferred onto a commercial polycrystalline nickel grid (G2000HAN, Ted Pella Inc.) with the standard wet etching technique [23,25,26]—further details on the sample preparation can be found in [20]. Note that the grids employed for transfer are metallic only with no additional lacey carbon film or mesh, in order to avoid superimposition of spurious C 1s signals. Following preparation, the graphene sample underwent high-temperature annealing (650 °C) in ultrahigh vacuum ($\sim 10^{-10}$ mbar) at the LASEC laboratory of Università Roma Tre, in order to remove contaminants and polymeric residuals of the transfer procedure [20]. The sample was then transported in low vacuum ($\sim 10^2$ mbar) to the I09 beamline, where a further annealing in ultrahigh vacuum was performed at 250 °C to remove adventitious contaminants eventually adsorbed during the in-air mounting of the sample in the I09 apparatus.

The C 1s core level was measured at room temperature ($T = 300$ K) from the clean monolayer graphene on grid sample with increasing photon energies while keeping the experimental geometry fixed. In particular, the experiment was conducted at grazing incidence—24° with respect to the surface—enhancing the sensitivity to the single graphene layer. By exploiting the angular acquisition characteristic of the electron analyzer, the spectra were recorded at both 90° and 45° emission angles measured with respect to the sample surface, with 90° corresponding to normal emission, to reveal differences in the phononic excitations driven by recoil mechanisms. At the investigated energies, the photon spot size on the surface is on the order of a few hundred μm^2 . Given the 8 μm diameter of the grid holes, the measured C 1s signal includes contribution from graphene both suspended over the holes and supported by the nickel grid. Prior to the spectral analysis, an iterative Shirley-type background [27] was subtracted from all measured spectra to remove the inelastic scattering contribution. As a robustness test, the complete reference extraction, fit, and high-energy propagation were repeated using a straight-line background over the same interval. The joint-fit residual sum of squares increases from 0.0240 to 0.0344, while the high-binding-energy asymmetry and the principal line-shape conclusion remain unchanged. The measured C 1s spectra at increasing photon energy (0.8, 4, and 8 keV) are reported in Fig. 1, for emission angles of 45° and 90°. The spectra exhibit an asymmetric line shape at all photon energies, indicating the intrinsic electronic contribution associated with the metallic character of graphene. Furthermore, with increasing photon energy the recoil effects induce two distinct signatures: a shift of the peak and a broadening

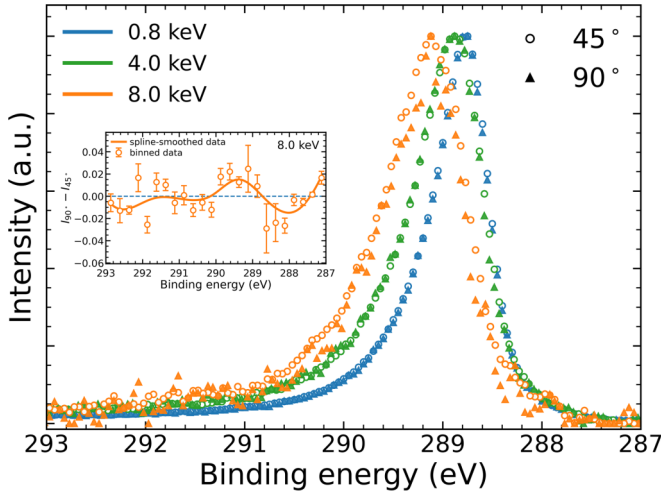


FIG. 1. Experimental graphene C 1s spectra at $T = 300$ K for increasing photon energy, as labeled, and for two emission angles, 45° (open circles) and 90° (triangles), measured with respect to the sample surface; 90° is normal emission. The inset shows the direct angular difference $I_{90^\circ} - I_{45^\circ}$ between the 8 keV spectra. The difference is shown after averaging in 0.25 eV bins, with error bars representing the standard error within each bin; the lightly smoothed spline is included only as a visual guide.

of the spectrum toward higher binding energies. The recoil-driven modifications of the line shape show also an anisotropic behavior at 45° and 90° , enhanced at higher photon energy. The anisotropy reflects the different relative weight of in-plane and flexural phononic excitations depending on the electron emission angle, as will be thoroughly discussed in Sec. III.

III. FUJIKAWA-TAKATA FRAMEWORK APPLIED TO MONOLAYER GRAPHENE

The lattice contribution to recoil in core-level photoemission is described using the cumulant formalism introduced by Fujikawa [3] and extended to anisotropic phonon baths by Takata [4]; related cumulant approaches for phonon contributions to electron spectral functions have also been developed in other contexts [28] and a broader overview is given in Ref. [21]. In the following we summarize the expressions needed for the present analysis and emphasize how the momentum transfer couples to lattice displacements and determines the recoil response of the measured spectrum.

The formal starting point is the Born-Oppenheimer approximation, which separates electronic and nuclear degrees of freedom on the basis of their widely different timescales. Within this approximation, the core orbital remains centered on the instantaneous nuclear position of the emitting atom, and the photoemission matrix element factorizes into an electronic contribution, which encodes the intrinsic line shape, and a lattice contribution, which depends only on the nuclear coordinates. This separation underlies the convolution structure of the full spectrum developed below.

The nuclear coordinate operator is written as $\mathbf{R} = \mathbf{R}_0 + \mathbf{u}$, where $\mathbf{R}_0$ is the equilibrium lattice site and $\mathbf{u}$ is the fluctuating part of the atomic position. Thermal and zero-point lattice

vibrations correspond to fluctuations of $\mathbf{u}$, such that $\langle \mathbf{u} \rangle_\beta = 0$ while $\langle \mathbf{u}^2 \rangle_\beta \neq 0$, where $\langle \cdots \rangle_\beta$ denotes a quantum and canonical thermal average at inverse temperature $\beta = (k_B T)^{-1}$. The time dependence relevant to recoil is governed by the vibrational Hamiltonian H_{vib} and is written in the Heisenberg picture as

$$\mathbf{u}(t) = e^{iH_{\text{vib}}t/\hbar} \mathbf{u} e^{-iH_{\text{vib}}t/\hbar}. \quad (2)$$

Recoil is controlled by the transferred momentum $\hbar \mathbf{Q} = \hbar(\mathbf{k} - \mathbf{K})$. To leading order, $\mathbf{k}$ is fixed by the photoelectron kinetic energy and emission geometry. Here $\mathbf{K}$ is the photon wave vector. Corrections arising from multiple scattering (photoelectron diffraction) have been shown to amount to only a few meV for graphitelike carbon at multi-keV kinetic energies [29] and are therefore not included explicitly. The present graphene was transferred onto a commercial polycrystalline Ni grid rather than grown epitaxially on a single-crystal substrate. Substrate-diffraction contributions affect only the supported fraction and are reduced by orientational and spatial averaging. Within the adiabatic approximation, the C 1s core orbital is assumed to follow the instantaneous position of the emitting carbon atom. Thus, if $\mathbf{R} = \mathbf{R}_0 + \mathbf{u}$, the core-electron wave function is taken as $\langle \mathbf{r} | \psi_c \rangle = \psi_c(\mathbf{r} - \mathbf{R})$. After projection onto the outgoing photoelectron state, this rigid translation of the core orbital produces the recoil phase factor associated with the nuclear displacement. The phonon part of the spectrum is then governed by the correlation function

$$F(t) = \langle e^{i\mathbf{Q} \cdot \mathbf{u}(t)} e^{-i\mathbf{Q} \cdot \mathbf{u}(0)} \rangle,$$

which encodes the lattice response to the impulsive momentum transfer, defined as a canonical average at inverse temperature $\beta = (k_B T)^{-1}$. Its structure is closely related to the time-dependent pair correlation function introduced by van Hove [30] in the context of neutron scattering. The corresponding phonon recoil kernel in the energy domain is obtained from the Fourier transform of $F(t)$, up to an overall prefactor,

$$I_{\text{ph}}(E) \propto \int_{-\infty}^{+\infty} dt \exp\left(-\frac{i}{\hbar}Et\right) F(t). \quad (3)$$

Here E is the binding-energy coordinate measured relative to a fixed low-recoil reference,

$$E \equiv E_B - E_B^{(0)}, \quad (4)$$

where $E_B^{(0)}$ is determined from the low-recoil 0.8 keV spectrum.

In the original Fujikawa-Takata implementation [4], homogeneous broadening associated with the core-hole lifetime is modeled by an additional exponential factor in the time domain, with $\Gamma = 0.16$ eV:

$$I_{\text{FT}}(E) \propto \int_{-\infty}^{+\infty} dt \exp\left(-\frac{i}{\hbar}Et\right) \exp\left(-\frac{\Gamma}{\hbar}|t|\right) F(t). \quad (5)$$

Equivalently, multiplication by $\exp[-(\Gamma/\hbar)|t|]$ corresponds in the energy domain to a convolution with a Lorentzian kernel L_Γ ,

$$I_{\text{FT}}(E) \propto [L_\Gamma * I_{\text{ph}}](E), \quad (6)$$

where $*$ denotes convolution. In what follows, the formulation of Eqs. (5) and (6) is referred to as the *baseline recoil model*: a recoil cumulant treatment in which nonphononic effects are represented by a symmetric homogeneous lifetime broadening. This terminology does not imply that the phonon recoil kernel itself is strictly symmetric; rather, it emphasizes that the baseline model contains no explicit asymmetric electronic line shape. As shown for graphite in Ref. [4], this baseline approach reproduces the characteristic recoil scaling of spectral displacement and overall width with photoelectron energy and emission geometry.

The Fujikawa-Takata formalism is adapted here to monolayer graphene by introducing a graphene-specific anisotropic vibrational DOS. In the harmonic approximation, lattice displacements are Gaussian and the linked-cluster expansion of the generating function terminates exactly at second order. Accordingly, $F(t) = \exp[G(t)]$, with

$$G(t) = -\frac{1}{2} \langle (\mathbf{Q} \cdot [\mathbf{u}(t) - \mathbf{u}(0)])^2 \rangle_\beta. \quad (7)$$

Graphene exhibits strongly anisotropic lattice dynamics, with qualitatively different in-plane and flexural excitations. In the cumulant formulation, the emission-angle dependence becomes explicit in a mode-resolved representation: decomposing the lattice response into in-plane and out-of-plane channels yields the geometric weights $(Q_\parallel(\theta)/k)^2$ and $(Q_\perp(\theta)/k)^2$, where θ denotes the photoelectron emission angle with respect to the sample surface. For the coplanar experimental geometry, with photon incidence $\alpha = 24^\circ$ relative to the sample surface and the 45° emission channel on the forward side of the photon-beam projection, $Q_\parallel = k \cos \theta - K \cos \alpha$ and $Q_\perp = k \sin \theta + K \sin \alpha$. The mode decomposition is written as

$$G(t) = \int_{-\infty}^{+\infty} d\omega (e^{i\omega t} - 1) \left[J_s(\omega) \left(\frac{Q_\parallel(\theta)}{k} \right)^2 + J_b(\omega) \left(\frac{Q_\perp(\theta)}{k} \right)^2 \right]. \quad (8)$$

Stretching ($\lambda = s$) and bending ($\lambda = b$) excitations are treated as two bosonic channels, respectively in-plane and out-of-plane channels, and the cumulant is expressed in terms of channel-resolved spectral densities $J_\lambda(\omega)$ constructed from a normalized vibrational DOS $D_\lambda(\omega)$. Introducing the Bose occupation $n(\omega) = (e^{\beta\hbar\omega} - 1)^{-1}$ for $\omega > 0$ and the step function $\Theta(\omega)$, one obtains, in direct analogy with Ref. [4],

$$J_\lambda(\omega) = \frac{E_R}{\hbar |\omega|} D_\lambda(|\omega|) \{ [n(|\omega|) + 1] \Theta(\omega) + n(|\omega|) \Theta(-\omega) \}. \quad (9)$$

The two terms in braces correspond to phonon emission ($\omega > 0$) and phonon absorption ($\omega < 0$), respectively. Because these contributions are weighted by $n(|\omega|) + 1$ and $n(|\omega|)$, the phonon recoil kernel is not constrained to be strictly symmetric. For the present room-temperature spectra, however, the asymmetry generated by the phonon kernel, after lifetime and instrumental broadening, is not sufficient to account for the pronounced high-binding-energy tail observed experimentally. The temperature dependence follows from the Bose factors in Eq. (9). At 8 keV, cooling from 300 to 10 K

reduces the full width at half maximum (FWHM) of the recoil kernel by 9.2% at 45° and 25.4% at 90° , while the corresponding full-spectrum FWHM decreases by only 2.8% and 5.6%, respectively; the thermally activated negative-energy branch is suppressed. The full temperature series is reported in the Supplemental Material [31].

The free-atom recoil scale in Eq. (1) provides an immediate kinematic estimate of the recoil energy and implies a linear increase of recoil distortions with E_{kin} . Within the cumulant construction, this is reflected by the proportionality $J_\lambda(\omega) \propto E_R$, with the full laboratory kinematics entering through the $Q_\parallel/k$ and $Q_\perp/k$ factors in Eq. (8), so that the strength of the phonon recoil response grows systematically with photoelectron kinetic energy. All quantities defined so far depend parametrically on $(\hbar\nu, E_{\text{kin}}, \theta, T)$; for brevity these arguments are left implicit below, although this dependence is central to the predictive content of the model.

To construct an anisotropic vibrational DOS for graphene, we use the long-wavelength behavior of the acoustic phonons. The in-plane acoustic branches are approximately linear, $\omega \simeq vq$, whereas the flexural (out-of-plane acoustic, ZA) branch is quadratic, $\omega \propto q^2$, as expected for an elastic two-dimensional sheet and confirmed by density functional perturbation theory (DFPT) phonon dispersions [16,32–34]. In two dimensions, these dispersions imply $D(\omega) \propto \omega$ for linear branches and an approximately constant DOS for a quadratic branch. Accordingly, we adopt the analytic form

$$D_\lambda(\omega) = \begin{cases} \frac{2\omega}{\omega_s^2}, & \lambda = s, \quad 0 < \omega < \omega_s, \\ \frac{1}{\omega_b}, & \lambda = b, \quad 0 < \omega < \omega_b, \\ 0, & \text{otherwise,} \end{cases} \quad (10)$$

with cutoff energies fixed from DFPT by the upper edge of the relevant phonon branches: $\hbar\omega_b \simeq 66$ meV and $\hbar\omega_s \simeq 160$ meV [16,33,35,36].

Figure 2 illustrates the *baseline recoil model* applied to monolayer graphene. As E_{kin} increases, the recoil scale $E_R \propto E_{\text{kin}}$ grows, producing both a systematic displacement of the spectrum and a progressive increase in its overall width. A second key feature is the dependence on emission geometry: changing θ modifies the relative weight of in-plane and out-of-plane excitations through Eq. (8), leading to distinct spectral evolutions that directly reflect the anisotropic lattice dynamics of graphene. Overall, the *baseline recoil model* captures the basic recoil trends expected for monolayer graphene. However, as seen in Fig. 1, the experimental spectra display a pronounced asymmetric tail on the high-binding-energy side that cannot be accounted for by a recoil treatment in which the intrinsic electronic contribution is reduced to a symmetric Lorentzian lifetime broadening. This asymmetry originates from the many-body electronic response of the sp^2 carbon lattice and therefore requires an explicit electronic line shape beyond the single-Lorentzian representation used in the baseline model.

IV. EXPLICIT ELECTRONIC SPECTRUM: CONVOLUTION STRATEGY

The intrinsic C 1s line shape of graphene is asymmetric: metallic screening by the π electrons generates a continuum

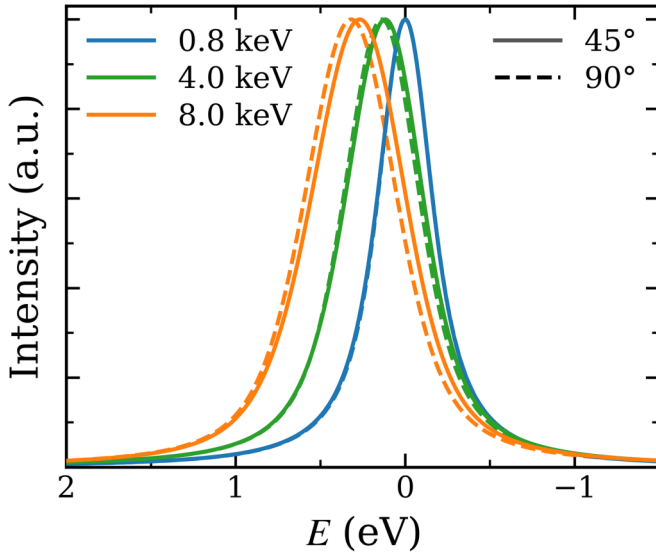


FIG. 2. Theoretical graphene C 1s spectra at $T = 300$ K computed within the *baseline recoil model* [Eq. (5)] using the full transferred momentum $\mathbf{Q} = \mathbf{k} - \mathbf{K}$, for the photon energies indicated in the figure and for emission angles of 45° (solid lines) and 90° (dashed lines).

of low-energy electron-hole excitations, giving rise to the high-binding-energy tail captured analytically by the DS form [17,18]. The interplay between such many-body electronic excitations and nuclear recoil was first discussed by Hedin [37] in the context of shake-up spectra in metals. In graphene at hard-x-ray energies, phonon-driven recoil superimposes additional spectral displacements and broadenings on top of this asymmetric electronic profile. A realistic description therefore requires the electronic and phononic responses to be treated as distinct contributions.

The adiabatic (Born-Oppenheimer) approximation introduced in Sec. III provides the formal basis for this separation. Because electronic excitations occur on timescales of order 10^{-16} s, much shorter than the 10^{-13} s scale of nuclear motion, the electronic and phononic responses decouple in time and their contributions to the photoemission cross section factorize. In the energy domain, this temporal factorization becomes a convolution:

$$I_{\text{model}}(E) = [I_{\text{el}}(E) * I_{\text{ph}}(E)] * R(E), \quad (11)$$

where $I_{\text{el}}(E)$ is the photon-energy-independent reference response, dominated by the asymmetric electronic line shape and determined from the low-recoil 0.8 keV data, $I_{\text{ph}}(E)$ is the phonon recoil kernel of Eq. (3), carrying the full dependence on $(h\nu, E_{\text{kin}}, \theta, T)$, and $R(E)$ is a Gaussian instrumental resolution function with FWHM fixed to 0.14 eV at 0.8 keV, 0.24 eV at 4 keV, and 0.30 eV at 8 keV. The separation into I_{el} and I_{ph} is therefore not merely phenomenological, but follows directly from the separation of electronic and nuclear timescales within the Born-Oppenheimer framework. At fixed temperature, $I_{\text{el}}(E)$ may also contain a momentum-independent Franck-Condon envelope that cannot be separated from the measured reference response. The recoil-Franck-Condon interference term [9] is neglected here

as an expected subleading correction, rather than assumed to vanish identically. A sizable interference contribution would generate an additional momentum-dependent spectral evolution beyond that produced by the pure-recoil kernel; no such extra contribution is required to account for the dominant photon-energy and angular trends reproduced by the fixed-reference model. Its quantitative evaluation would also require microscopic core-hole-phonon coupling parameters that are not independently constrained by the present spectra. A smaller unresolved contribution cannot, however, be excluded.

The photon-energy-independent reference response $I_{\text{el}}(E)$ entering Eq. (11) is determined from the low-recoil reference shown in Fig. 3. We parametrize it as the weighted sum of four DS components plus a broad Gaussian plasmon-loss feature (note that this plasmon loss feature is outside the energy range shown in Fig. 3, being at 6 eV higher binding energy than the main peak). The DS form captures asymmetric core-level line shapes arising from many-body screening and low-energy electron-hole excitations [17], while the Gaussian term accounts for additional incoherent loss weight at larger energy, as expected for plasmon-assisted photoemission [38–41]. Guided by the coexistence, within the probed area, of regions that are effectively freestanding and regions weakly coupled to the substrate, we include two components for each environment. These are labeled sp^2 and sp^3 -like for clarity: sp^2 denotes the graphitic-like contribution characteristic of trigonal carbon in graphene, whereas sp^3 -like is used more broadly as a convenient spectroscopic label for locally perturbed or rehybridized carbon environments associated with a more symmetric line shape and does not imply a measured macroscopic fraction of ideally tetrahedral carbon. This yields a minimal yet flexible representation of the reference spectrum. Although four DS functions are included in the fit, two of them converge to $\alpha = 0$ and therefore reduce to purely Lorentzian line shapes; these are identified with the sp^3 -like contributions, while the remaining two retain finite asymmetry and describe the sp^2 -like components. The best-fit parameters are summarized in Table I. Importantly, they remain essentially unchanged between $\theta = 45^\circ$ and $\theta = 90^\circ$, supporting the use of a single angle-independent $I_{\text{el}}(E)$ determined at 0.8 keV and reused unchanged at higher photon energies. A common-parameter joint fit increases the residual sum of squares by only about 3% relative to the two separate fits while reducing the number of parameters from 38 to 19. Only the summed composite profile is propagated; the individual components are not tracked or refitted at higher photon energy. Bootstrap intervals, the joint-fit parameters, and reduced-component comparisons are reported in the Supplemental Material [31].

Once determined from the 0.8 keV reference, $I_{\text{el}}(E)$ is kept strictly fixed at all higher photon energies and emission geometries: no refitting of electronic parameters is performed at 4 keV or 8 keV. This strategy uses the calculated 0.8 keV recoil kernel explicitly in a forward fit: the recoil scale is small on the total linewidth scale but is not set to zero. Omitting it changes the propagated profiles by approximately 5–7%, so the recoil-inclusive reference extraction is retained. With $I_{\text{el}}(E)$ held fixed, the full energy- and angle-dependent evolution of $I_{\text{model}}(E)$ is predicted entirely by the phonon recoil

TABLE I. Best-fit parameters for the low-recoil, recoil-inclusive reference spectrum at $h\nu = 0.8$ keV. The w_j are relative weights (normalized within each fit), s_j are component positions, and α_j is the Doniach-Šunjić asymmetry parameter ($\alpha_j = 0$ corresponds to the Lorentzian limit). The reduced chi-square χ^2_ν is reported for each emission angle.

θ	Component	w_j	s_j (eV)	Γ_j/FWHM (eV)	α_j
45°	Supported, sp^2	0.547	−0.15	0.14	0.09
	Supported, sp^3 -like	0.096	0.36	0.27	0.00
	Freestanding, sp^2	0.309	0.06	0.13	0.09
	Freestanding, sp^3 -like	0.045	0.57	0.29	0.00
	Plasmon	0.004	6.01	2.49	
$\chi^2_\nu = 1.33$					
90°	Supported, sp^2	0.550	−0.15	0.15	0.09
	Supported, sp^3 -like	0.098	0.36	0.28	0.00
	Freestanding, sp^2	0.304	0.06	0.13	0.09
	Freestanding, sp^3 -like	0.044	0.56	0.29	0.00
	Plasmon	0.004	6.02	2.65	
$\chi^2_\nu = 1.13$					

kernel $I_{\text{ph}}(E)$, while the instrumental resolution $R(E)$ is fixed independently by the measured FWHM at each photon energy. The sensitivity to a possible photon-energy dependence of the supported/freestanding weighting was estimated by varying the complete family ratio by $\pm 10\%$ and $\pm 20\%$; the extreme variation changes the calculated peak displacement by at most 20.6 meV.

The quality of the model predictions across all energies and emission geometries is illustrated in Fig. 4, while the corresponding peak displacements are summarized in Table II. When expressed relative to the low-recoil 0.8 keV reference, the free-atom kinematic estimate yields recoil shifts of approximately 149 meV at 4 keV and 333 meV at 8 keV. Both the *baseline recoil model* and the *explicit electronic convolution model* reproduce the systematic increase of the spectral displacement with photon energy as well as its angular dependence, with larger peak shifts at $\theta = 90^\circ$ than at $\theta = 45^\circ$. This trend is consistent with the anisotropic lattice response encoded in Eq. (8), which changes the relative weight of in-plane and flexural phonon channels with emission geometry.

Quantitatively, however, the two models differ substantially. At 4 keV, the experimental peak shifts, about 137 meV and 139 meV at 45° and 90° , lie slightly below the kinematic estimate. The baseline model gives 118 and 138 meV, whereas

the convolution model gives 154 and 172 meV and therefore predicts somewhat larger absolute shifts than observed. At 8 keV, the experimental peak shifts reach approximately 321–323 meV. Here the baseline values are 269 and 319 meV and the convolution values are 321 and 370 meV. The absolute differences between the measured and convolution-model peak displacements range from 0.4 to 46.8 meV over the four photon-energy and emission-angle combinations. These deviations range from well below to larger than the separately estimated experimental uncertainty and model-sensitivity envelopes, depending on emission geometry. The experimental uncertainty is 20 meV, while the conservative convolution-model systematic-sensitivity envelopes are 19, 16, 21, and 18 meV for 4 keV/ 45° , 4 keV/ 90° , 8 keV/ 45° , and 8 keV/ 90° , respectively. The measured shifts remain close to the free-atom recoil scale, in line with the elemental-Si results of Roth *et al.* [8]; the enhanced response reported for compound 4H-SiC is material specific. These results show that the peak displacement alone does not discriminate fully between the two models; the decisive improvement provided by the convolution model is the reproduction of the complete asymmetric line shape. The effect of retaining the photon momentum, compared with the $\mathbf{Q} = \mathbf{k}$ approximation, is shown in Fig. S4 of the Supplemental Material [31]; the resulting changes in the individual calculated profiles are modest

TABLE II. Peak displacements (meV) relative to the corresponding low-recoil 0.8 keV value at the same angle. Both theoretical models use the full transferred momentum $\mathbf{Q} = \mathbf{k} - \mathbf{K}$. Experimental values in parentheses give the 20 meV uncertainty in the last digits. For the convolution model, the quoted sys values are conservative systematic-sensitivity envelopes, defined point by point as the larger of the background and supported/freestanding family-ratio variations.

Energy	Kinematic estimation	Baseline		Conv.		Data	
		45°	90°	45°	90°	45°	90°
4 keV	149	118	138	$154 \pm 19_{\text{sys}}$	$172 \pm 16_{\text{sys}}$	137(20)	139(20)
8 keV	333	269	319	$321 \pm 21_{\text{sys}}$	$370 \pm 18_{\text{sys}}$	321(20)	323(20)

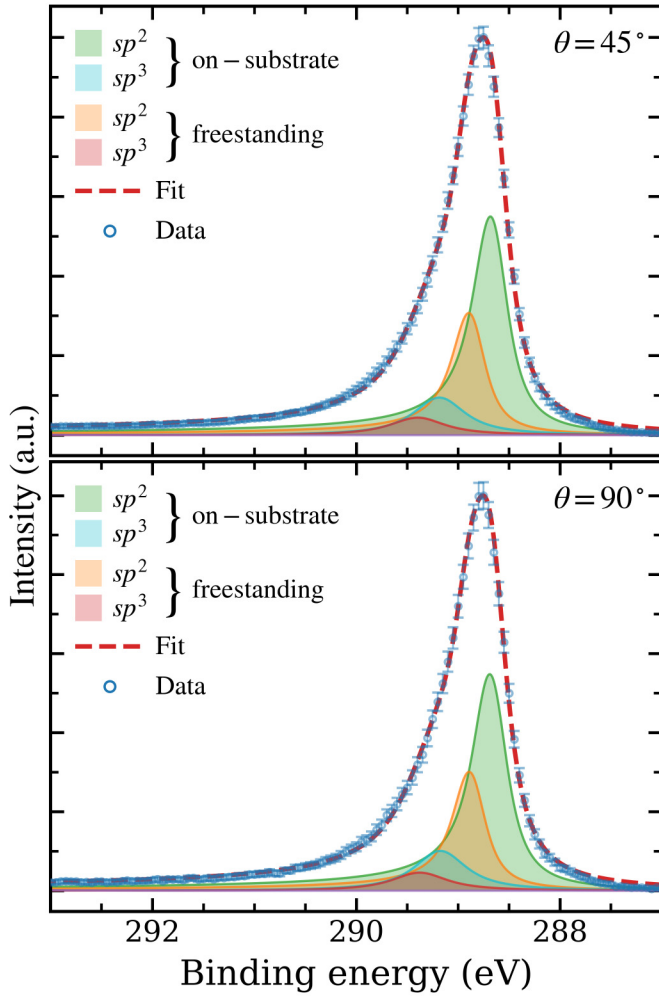


FIG. 3. Low-recoil reference spectrum at 0.8 keV and $T = 300$ K shown on the binding-energy scale for emission angles $\theta = 45^\circ$ (top) and $\theta = 90^\circ$ (bottom). Open circles are the experimental data; the dashed red curve is the best fit obtained by representing the photon-energy-independent reference response as the weighted sum of four Doniach-Šunjić components (sp^2 -like and sp^3 -like, in both supported and freestanding regions) plus a Gaussian plasmon contribution. Shaded areas indicate the individual components visible within the displayed energy window; the plasmon contribution is included in the fit but lies outside the plotted range. Best-fit parameters are reported in Table I.

and leave the overall physical picture and the conclusions of the analysis unchanged.

Beyond the peak displacements, the *explicit electronic convolution model* also provides a compelling account of the full line shapes shown in Fig. 4. Whereas the *baseline recoil model* yields profiles with insufficient high-binding-energy asymmetry, the convolution strategy naturally transfers the intrinsic DS asymmetry of $I_{el}(E)$ into the full spectrum at every photon energy. The model thus captures simultaneously the overall spectral displacement, the progressive broadening with increasing E_{kin} , and the persistent asymmetric tail, all without introducing any additional free parameters beyond those determined from the 0.8 keV reference.

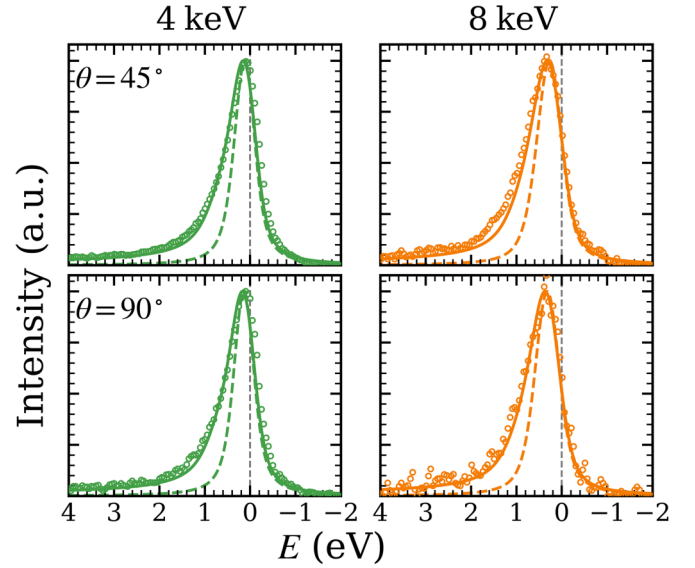


FIG. 4. Comparison between experimental C 1s spectra (open circles) and theoretical predictions at $T = 300$ K for emission angles $\theta = 45^\circ$ (top row) and $\theta = 90^\circ$ (bottom row), at 4 keV (left column) and 8 keV (right column). The solid curves show the *explicit electronic convolution model* [Eq. (11)] and the dashed curves show the *baseline recoil model* [Eq. (5)], both evaluated with $\mathbf{Q} = \mathbf{k} - \mathbf{K}$. All spectra are displayed on the recoil-energy scale relative to the low-recoil 0.8 keV reference. The *explicit electronic convolution model* reproduces the overall recoil-induced spectral evolution, including the peak displacements reported in Table II, the progressive broadening with increasing kinetic energy, and the asymmetric tail on the high-binding-energy side. By contrast, the *baseline recoil model* captures the gross recoil trends but, lacking an explicit asymmetric electronic component, underestimates the high-binding-energy asymmetry at all energies. No free parameters are adjusted at 4 keV or 8 keV; the only fitted quantities are the DS parameters of Table I, determined exclusively from the 0.8 keV reference.

V. CONCLUSIONS

We have investigated hard-x-ray C 1s photoemission from clean monolayer graphene over the photon-energy range 0.8–8 keV, combining experiment with a recoil framework that explicitly retains the intrinsic electronic asymmetry of the graphene line shape.

From a theoretical point of view, the central result is that the spectral evolution of graphene in the multi-keV regime cannot be accounted for by a baseline recoil treatment in which nonphononic effects are represented only by symmetric lifetime broadening. A quantitative description requires two distinct ingredients: an anisotropic phonon recoil kernel, which controls the energy- and angle-dependent redistribution of spectral weight, and an intrinsic electronic line shape, which fixes the asymmetric character of the spectrum. Within the adiabatic framework, these two contributions remain separable and combine naturally through convolution in the energy domain.

Based on this separation, we introduced an *explicit electronic convolution model* in which the photon-energy-independent reference response $I_{el}(E)$ is determined once from the low-recoil 0.8 keV data with the residual recoil

retained in the forward fit and then kept fixed at higher photon energies, while the phonon recoil kernel $I_{\text{ph}}(E)$ carries the full dependence on photon energy, emission geometry, and temperature through a graphene-specific anisotropic vibrational DOS. The reference response is dominated by the explicit electronic asymmetry and may also contain a momentum-independent Franck-Condon envelope. In the framework of Fujikawa and Niki [9], any momentum-independent Franck-Condon envelope is consequently absorbed empirically into $I_{\text{el}}(E)$. The recoil-Franck-Condon interference term is neglected here as a subleading correction, rather than assumed to vanish identically. A sizable interference contribution would generate an additional momentum-dependent spectral evolution beyond the pure-recoil kernel, whereas the fixed-reference model already captures the dominant photon-energy and angular trends without such a term. Its explicit evaluation would furthermore require microscopic core-hole-phonon couplings that are not independently constrained by the present data. Without refitting at 4 keV and 8 keV, this approach reproduces the overall scale of the measured peak displacements and the full line-shape evolution across the explored energy and angular range, whereas the *baseline recoil model* fails to reproduce the pronounced asymmetric tail. Across the four photon-energy and angular conditions, the calculated peak displacements differ from experiment by 0.4–46.8 meV, with the largest difference at 8 keV/90°. Together with the reproduction of the asymmetric line shapes, this provides a stringent quantitative test of the fixed-reference convolution approach.

More broadly, these results show that recoil in graphene is not a simple rigid shift of the C 1s line, but a redistribution of spectral weight governed by the interplay between lattice dynamics and many-body electronic response. The convolution strategy developed here therefore provides a physically grounded route to the analysis of recoil effects in other two-dimensional sp^2 systems and, more generally, in materials where electronic and phononic timescales remain well separated and a low-recoil reference spectrum can be identified. The same framework may also be extended to more complex

lattices with inequivalent sublattices, where mass-dependent recoil decompositions of the spectral line shape have been predicted [42].

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S.R.: Methodology, data curation, software, formal analysis, visualization, writing original draft, writing–review, and editing. A.A.: Conceptualization, investigation, data curation, formal analysis, writing original draft, writing–review, and editing. O.C.: Investigation, data curation, formal analysis, writing–review and editing. J.L.: Supervision, writing–review, and editing. D.C.: Resources writing–review, and editing. C.C.: Resources, funding acquisition, writing–review, and editing. F.O.: Investigation, data curation, supervision, writing–review, and editing. T.-L.L.: Resources writing–review, and editing. A.R.: Conceptualization, investigation, supervision, funding acquisition, writing–review, and editing.

DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

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