

Symmetry-based design rules for second-harmonic generation in stacked and twisted MoS₂ bilayers

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Understanding how stacking controls the nonlinear optical response of two-dimensional materials is key to designing van der Waals heterostructures with tailored functionalities. Here, we establish a comprehensive symmetry-based framework mapping the structural configuration of MoS₂ bilayers across four point groups (D_{3h} , D_{3d} , C_{3v} , C_3) to their second-order susceptibility tensor $\chi^{(2)}$. Using group-theory arguments benchmarked against first-principles response-function calculations, we demonstrate how symmetry breaking controls the activation and suppression of individual tensor elements in these systems. We show that the emergence of the in-plane component χ_{xxx} in twisted configurations (C_3 group) induces a rigid azimuthal rotation of the second-harmonic generation polar lobes, which remains frequency-independent across the entire optical spectrum, locking to half of the structural twist angle. Our findings establish a direct, wavelength-independent optical route for twist-angle determination and provide a clear roadmap for engineering nonlinear optical responses in two-dimensional materials.

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I. INTRODUCTION

Two-dimensional transition-metal dichalcogenides (TMDs) have emerged as an appealing platform for nonlinear optics, combining broken inversion symmetry, strong light-matter interaction, and a lattice highly sensitive to specific stacking configurations [1–5]. In their monolayer form, semiconducting TMDs with the chemical formula MX_2 (with $M = \text{Mo, W}$; $X = \text{S, Se, Te}$) preferentially crystallize in the noncentrosymmetric point group D_{3h} [6–8]. This inherent absence of inversion symmetry permits a nonvanishing second-order susceptibility tensor $\chi^{(2)}$ and enables second-harmonic generation (SHG) [1,9–13]. This technique represents a powerful, nondestructive probe for mapping layer counts, stacking order, and crystallographic orientations across a wide variety of layered materials and moiré superlattices [14–18].

A bilayer stack is characterized by an additional, highly tunable structural degree of freedom: relative translation and rotation of the constituent monolayers, which dramatically expand the accessible symmetry landscape. Depending on the specific configuration, the resulting point group can range from highly symmetric D_{3h} and centrosymmetric D_{3d} , to lower-symmetry C_{3v} and C_3 twisted configurations [1,9,14,19]. Since the analytical structure of the $\chi^{(2)}$ tensor is

entirely determined by the crystal point group via Neumann's principle [20], this stacking-controlled symmetry hierarchy translates into a systematic modulation of the nonlinear optical responses, ranging from complete suppression of SHG to the activation of new tensor components that are silent in the freestanding monolayer [1,9,14,21].

First-principles calculations of nonlinear susceptibilities have successfully captured the response of idealized TMDs [22–25]. However, full-fledged *ab initio* evaluations of $\chi^{(2)}$ spectra become exceptionally costly or even unfeasible for realistic low-symmetry configurations and large-scale moiré superlattices [26–28]. This computational bottleneck makes a rigorous symmetry-based analysis vital to map the nonlinear response of these systems across arbitrary structural settings without relying on brute-force calculations. Establishing such a framework on a qualitatively reliable and physically accessible baseline, as offered by the independent-particle approximation, provides the necessary foundation to subsequently understand the role of many-body effects and to develop numerically robust high-throughput screening workflows for SHG in realistic two-dimensional (2D) material architectures.

To bridge this gap, we present a systematic study coupling this predictive symmetry analysis with targeted first-principles validations of the frequency-dependent angular response. Using MoS₂ as a representative member of the TMD family, we map monolayer and bilayer configurations across four distinct point groups (D_{3h} , D_{3d} , C_{3v} , and C_3) to their respective $\chi^{(2)}$ tensors. While polarization-resolved SHG rotation has previously been used to extract twist angles in TMD bilayers [19], typically interpreted via phenomenological interference between independent monolayers, we apply Neumann's principle to derive the complete $\chi^{(2)}$ tensor structure by treating the stacked or twisted bilayer as

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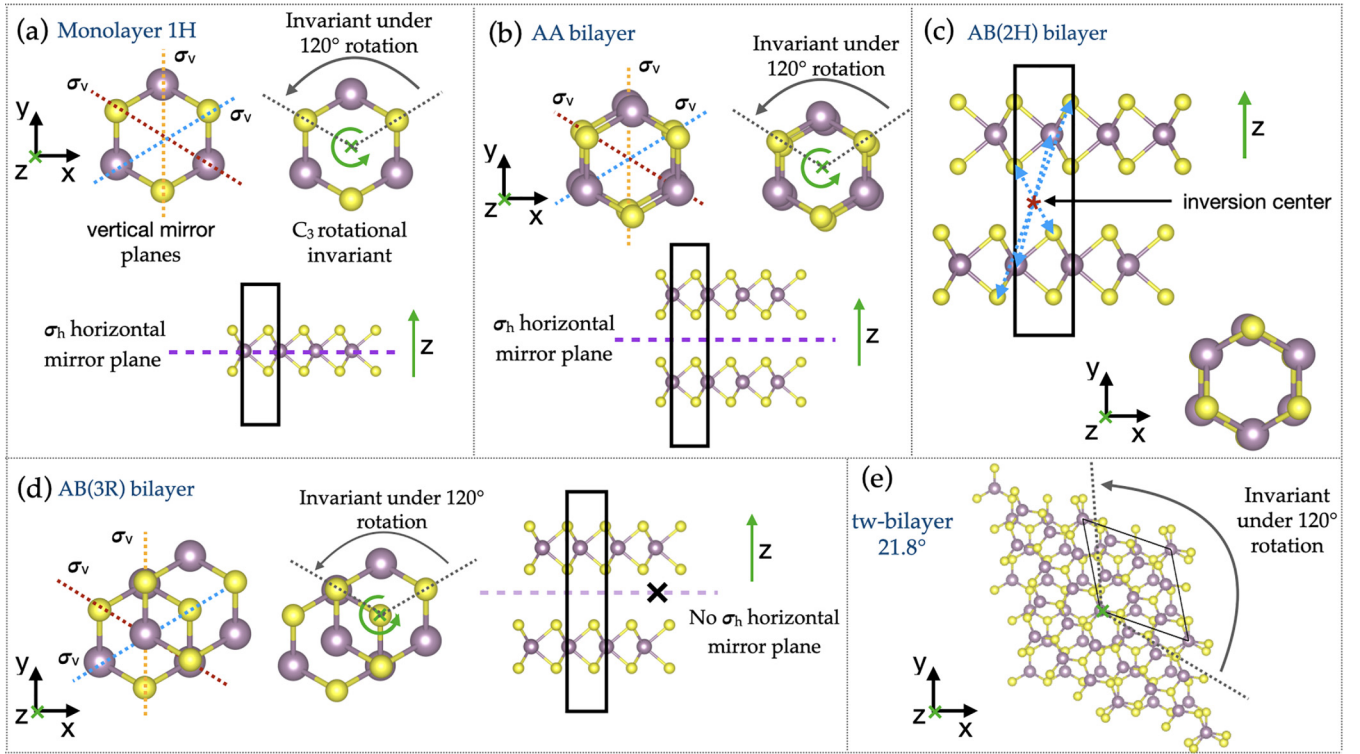


FIG. 1. Overview of the atomic structures and symmetry elements of the five MoS₂ configurations considered in this work. Mo and S atoms are shown in violet and yellow, respectively. (a) Monolayer 1H (D_{3h}): top view displaying the three vertical mirror planes σ_v (colored dashed lines) alongside the C_3 rotational invariance, and side view showing the horizontal mirror plane σ_h (purple dashed line). (b) Bilayer in the AA-stacking (D_{3h}), retaining all symmetry elements of the monolayer, including σ_v , C_3 , and σ_h . (c) AB(2H)-stacked bilayer (D_{3d}), enabling the activation of an inversion center ($\mathcal{I}$, red asterisk). (d) AB(3R) bilayer (C_{3v}): σ_v and C_3 symmetries are retained while the horizontal mirror plane σ_h is broken. (e) Twisted bilayer (C_3): twisted by 21.8° , invariant under 120° rotation.

a single composite crystal. This symmetry-first approach holds independently of interlayer coupling strength and unifies all translational and rotational stacking configurations within a single, self-consistent framework. Starting from pure group-theory arguments, we determine the allowed and forbidden tensor components for each symmetry class and define how these constraints dictate macroscopic SHG angular patterns. Benchmarking these analytical relations against first-principles calculations establishes a clear, transferable set of design rules connecting stacking configurations to nonlinear optical signatures, including complete SHG suppression in centrosymmetric configurations and the emergence of a spectrally invariant and geometrically locked SHG lobe shift in twisted bilayers.

II. SYMMETRY ANALYSIS AND DESIGN RULES

A. Crystal structures and point groups

Monolayer MoS₂ in the 1H structure consists of a Mo atomic plane sandwiched between two S planes in a trigonal prismatic coordination. The resulting crystal belongs to the D_{3h} point group, with symmetry elements including a three-fold rotation axis C_3 , a horizontal mirror plane σ_h , and three vertical mirror planes σ_v . Crucially, the lack of an inversion center permits a nonvanishing $\chi^{(2)}$ [Fig. 1(a)]. Forming a bilayer introduces an additional structural degree of freedom via the relative translation and rotation of the two layers,

giving rise to a family of distinct stackings with qualitatively different symmetries. In the following analysis, we consider a selection of representative configurations Figs. 1(b)–1(e) belonging to different symmetry groups (Table I).

The AA-stacked bilayer, in which the top and bottom sheets are directly eclipsed, retains the same D_{3h} symmetry of the parent monolayer [Fig. 1(b)]. In contrast, the AB(2H) stacking, associated with the thermodynamically stable form of bulk MoS₂ [6,29], places the Mo atom of the top layer directly above the S atom of the bottom layer. This arrangement introduces an inversion center ($\mathcal{I}$) at the interlayer midpoint, elevating the point group to D_{3d} and rendering the structure centrosymmetric [Fig. 1(c)]. Translating the layers into the AB(3R) configuration breaks both the inversion symmetry of the 2H-stacking and the horizontal reflection symmetry

TABLE I. Point groups and key symmetry elements for the targeted monolayer and bilayer MoS₂ configurations.

System	Stacking	Point group	C_3	σ_h	σ_v	$\mathcal{I}$
Monolayer	1H	D_{3h}	✓	✓	✓	×
Bilayer	AA	D_{3h}	✓	✓	✓	×
Bilayer	AB(2H)	D_{3d}	✓	×	✓	✓
Bilayer	AB(3R)	C_{3v}	✓	×	✓	×
Twisted bilayer	$\theta_{tw} = 21.8^\circ$	C_3	✓	×	×	×

of the AA bilayer phase, yielding a noncentrosymmetric C_{3v} point group where only the threefold rotation axis and the three vertical mirrors (σ_v) are preserved [Fig. 1(d)]. Finally, introducing a relative rotation between the layers destroys all mirror symmetries, σ_h and σ_v . For instance, a twisted (tw) bilayer at the commensurate angle $\theta_{tw} = 21.8^\circ$ forms a coincidence site lattice supercell with 42 atoms, which retains only the threefold rotation axis [Fig. 1(e)], reducing the symmetry to the C_3 point group (Table I).

The symmetry reduction from the highest-symmetry parent bilayers to the twisted configuration follows two separate pathways:

$$D_{3h} \xrightarrow{\text{translation}} C_{3v} \xrightarrow{\text{twisting}} C_3, \quad (1)$$

$$D_{3d} \xrightarrow{\text{twisting}} C_3. \quad (2)$$

While relative interlayer translation breaks horizontal symmetries, rotational twisting eliminates all mirror planes and inversion centers, leaving the C_3 subgroup as the lowest common structural denominator for all twisted and moiré configurations.

B. $\chi^{(2)}$ tensor structure from Neumann's principle

The second-order susceptibility $\chi_{ijk}^{(2)}(\omega)$ is a third-rank polar tensor relating the second-harmonic polarization to the external electric field:

$$P_i(2\omega) = \sum_{jk} \chi_{ijk}^{(2)}(\omega) E_j(\omega) E_k(\omega). \quad (3)$$

Neumann's principle imposes the invariance of the tensor under any spatial symmetry operation g belonging to the crystal point group [20]:

$$\chi_{ijk}^{(2)} = R_{il} R_{jm} R_{kn} \chi_{lmn}^{(2)}, \quad (4)$$

where R is the matrix representation of g , and summation over repeated indices is implied. Applying this constraint to the generators of each point group, while invoking the intrinsic permutation symmetry $\chi_{ijk}^{(2)} = \chi_{ikj}^{(2)}$ imposed by the indistinguishability of the two photons in the SHG process, yields independent, nonzero tensor components for each configuration.

Before evaluating individual point groups, we note that the presence of a threefold rotation axis ($C_3 \parallel z$) common to all five systems imposes a strong restriction to the 27 tensor components. Specifically, it forces all elements with in-plane index (x or y) combined with two out-of-plane (z) indices to vanish identically (see details in the Appendix):

$$\chi_{xzz}^{(2)} = \chi_{yzz}^{(2)} = \chi_{zxx}^{(2)} = \chi_{zxy}^{(2)} = \chi_{zyx}^{(2)} = \chi_{zzx}^{(2)} = \chi_{zzy}^{(2)} = \chi_{zyz}^{(2)} = \chi_{yzz}^{(2)} = 0. \quad (5)$$

Furthermore, components featuring mixed in-plane indices combined with a single z index at the primary position, namely $\chi_{zxy}^{(2)}$ and $\chi_{zyx}^{(2)}$, are also strictly forbidden by C_3 symmetry. The remaining nonzero elements are linked via rotational invariants, which are subsequently lifted or constrained by the mirror planes and inversion centers of each point group (Table II).

D_{3h} (monolayer, AA bilayer). The horizontal mirror plane σ_h maps coordinates as $z \rightarrow -z$, forcing all tensor elements

containing an odd number of z indices to vanish identically. The remaining purely in-plane components are simultaneously bounded by the C_3 axis and the vertical mirrors σ_v , reducing to

$$\chi_{yyy}^{(2)} = -\chi_{yxx}^{(2)} = -\chi_{xyx}^{(2)} = -\chi_{xyy}^{(2)}. \quad (6)$$

All out-of-plane elements (e.g., $\chi_{zzz}^{(2)}$, $\chi_{zxx}^{(2)}$, $\chi_{xxz}^{(2)}$, and so on) vanish under σ_h , leaving the nonzero components in Eq. (6) to rule the entire nonlinear optical response of the system.

D_{3d} [AB(2H) bilayer]. The presence of an inversion center $\mathcal{I}$ maps all coordinates as $x_i \rightarrow -x_i$, transforming any third-rank polar tensor component to its negative:

$$\chi_{ijk}^{(2)} \xrightarrow{\mathcal{I}} -\chi_{ijk}^{(2)}. \quad (7)$$

Combined with the invariance requirement, this yields

$$\chi_{ijk}^{(2)} = 0, \quad \forall i, j, k. \quad (8)$$

Hence, SHG is completely forbidden within the electric-dipole approximation for the AB(2H) stacking.

C_{3v} [AB(3R) bilayer]. The absence of a σ_h mirror plane activates tensor components with an odd number of z indices. The three vertical mirrors σ_v are retained, imposing $\chi_{xxx}^{(2)} = 0$ and constraining the remaining in-plane elements to the same form as in the D_{3h} group. Accounting for intrinsic permutation rules, the independent nonzero components are

$$\begin{aligned} \chi_{yyy}^{(2)} &= -\chi_{yxx}^{(2)} = -\chi_{xyx}^{(2)} = -\chi_{xyy}^{(2)}, & \chi_{zzz}^{(2)}, \\ \chi_{zxx}^{(2)} &= \chi_{zyy}^{(2)}, \\ \chi_{xxz}^{(2)} &= \chi_{xzx}^{(2)} = \chi_{yyz}^{(2)} = \chi_{yzy}^{(2)}. \end{aligned} \quad (9)$$

The activation of out-of-plane elements ($\chi_{zzz}^{(2)}$ and $\chi_{zxx}^{(2)}$) makes the nonlinear response accessible via oblique-incidence or cross-polarized experimental setups, while the in-plane component matches the monolayer baseline.

C_3 (twisted bilayers). In twisted configurations, only the threefold rotation axis survives, and the absence of any mirror symmetry operation distinguishes this case from all higher-symmetry stackings. The independent nonzero tensor components are

$$\begin{aligned} \chi_{yyy}^{(2)} &= -\chi_{yxx}^{(2)} = -\chi_{xyx}^{(2)} = -\chi_{xyy}^{(2)}, \\ \chi_{xxx}^{(2)} &= -\chi_{xyy}^{(2)} = -\chi_{yxy}^{(2)} = -\chi_{yyx}^{(2)}, & \chi_{zzz}^{(2)}, \\ \chi_{zxx}^{(2)} &= \chi_{zyy}^{(2)}, \\ \chi_{xxz}^{(2)} &= \chi_{yyz}^{(2)}, \\ \chi_{xyz}^{(2)} &= -\chi_{yxz}^{(2)}. \end{aligned} \quad (10)$$

The defining feature here is the simultaneous activation of $\chi_{xxx}^{(2)}$ alongside $\chi_{yyy}^{(2)}$. Since $\chi_{xxx}^{(2)} = 0$ is no longer enforced by σ_v , its emergence provides a direct optical signature of the structural twist. Additionally, the chiral out-of-plane components ($\chi_{xyz}^{(2)} = -\chi_{yxz}^{(2)}$) become allowed, offering an additional degree of freedom unique to twisted moiré superlattices.

C. Angular SHG patterns and lobe shift

For a normally incident fundamental beam with linear polarization at angle θ measured from the zigzag (x) axis, the

TABLE II. Classification of all 27 components of the $\chi_{ijk}^{(2)}$ tensor for each point group. The checkmark ($\checkmark$) denotes an independent, nonzero component. Formulations explicitly show the relationship dictated by the responsible symmetry element. $\times(C_3)$ indicates components forced to zero by the threefold rotation axis alone across all groups; $\times(\sigma_h)$ marks suppression via the horizontal mirror plane (odd number of z indices); $\times(\sigma_v)$ indicates vertical mirror suppression; $\times(\mathcal{I})$ indicates centrosymmetric elimination via inversion; “perm” denotes relations via intrinsic SHG permutation symmetry $\chi_{ijk}^{(2)} = \chi_{ikj}^{(2)}$.

Component	D_{3h}	D_{3d}	C_{3v}	C_3
<i>In-plane, σ_v-sensitive components</i>				
$\chi_{xxx}^{(2)}$	$\times(\sigma_v)$	$\times(\mathcal{I})$	$\times(\sigma_v)$	$\checkmark$
$\chi_{xyy}^{(2)}$	$\times(\sigma_v)$	$\times(\mathcal{I})$	$\times(\sigma_v)$	$= -\chi_{xxx}^{(2)}(C_3)$
$\chi_{yyx}^{(2)}$	$\times(\sigma_v)$	$\times(\mathcal{I})$	$\times(\sigma_v)$	$= -\chi_{xxx}^{(2)}(C_3)$
$\chi_{yyy}^{(2)}$	$\times(\sigma_v)$	$\times(\mathcal{I})$	$\times(\sigma_v)$	$= -\chi_{xxx}^{(2)}(C_3)$
<i>In-plane, C_3-related components</i>				
$\chi_{yyy}^{(2)}$	$\checkmark$	$\times(\mathcal{I})$	$\checkmark$	$\checkmark$
$\chi_{yxx}^{(2)}$	$= -\chi_{yyy}^{(2)}(C_3)$	$\times(\mathcal{I})$	$= -\chi_{yyy}^{(2)}(C_3)$	$= -\chi_{yyy}^{(2)}(C_3)$
$\chi_{xxy}^{(2)}$	$= -\chi_{yyy}^{(2)}(C_3)$	$\times(\mathcal{I})$	$= -\chi_{yyy}^{(2)}(C_3)$	$= -\chi_{yyy}^{(2)}(C_3)$
$\chi_{yyx}^{(2)}$	$= -\chi_{yyy}^{(2)}(C_3)$	$\times(\mathcal{I})$	$= -\chi_{yyy}^{(2)}(C_3)$	$= -\chi_{yyy}^{(2)}(C_3)$
<i>Out-of-plane, one z index (σ_h-sensitive)</i>				
$\chi_{xxz}^{(2)}$	$\times(\sigma_h)$	$\times(\mathcal{I})$	$\checkmark$	$\checkmark$
$\chi_{xzx}^{(2)}$	$\times(\sigma_h)$	$\times(\mathcal{I})$	$= \chi_{xxz}^{(2)}(\text{perm})$	$= \chi_{xxz}^{(2)}(\text{perm})$
$\chi_{yyz}^{(2)}$	$\times(\sigma_h)$	$\times(\mathcal{I})$	$= \chi_{xxz}^{(2)}(C_3)$	$= \chi_{xxz}^{(2)}(C_3)$
$\chi_{yzx}^{(2)}$	$\times(\sigma_h)$	$\times(\mathcal{I})$	$= \chi_{xxz}^{(2)}(\text{perm}+C_3)$	$= \chi_{xxz}^{(2)}(\text{perm}+C_3)$
$\chi_{zxx}^{(2)}$	$\times(\sigma_h)$	$\times(\mathcal{I})$	$\checkmark$	$\checkmark$
$\chi_{zxy}^{(2)}$	$\times(\sigma_h)$	$\times(\mathcal{I})$	$= \chi_{zxx}^{(2)}(C_3)$	$= \chi_{zxx}^{(2)}(C_3)$
$\chi_{zzx}^{(2)}$	$\times(\sigma_h)$	$\times(\mathcal{I})$	$\checkmark$	$\checkmark$
<i>Mixed, one z index, σ_v-sensitive</i>				
$\chi_{xyz}^{(2)}$	$\times(\sigma_v)$	$\times(\mathcal{I})$	$\times(\sigma_v)$	$\checkmark$
$\chi_{xzy}^{(2)}$	$\times(\sigma_v)$	$\times(\mathcal{I})$	$\times(\sigma_v)$	$= \chi_{xyz}^{(2)}(\text{perm})$
$\chi_{yxz}^{(2)}$	$\times(\sigma_v)$	$\times(\mathcal{I})$	$\times(\sigma_v)$	$= -\chi_{xyz}^{(2)}(C_3)$
$\chi_{yzx}^{(2)}$	$\times(\sigma_v)$	$\times(\mathcal{I})$	$\times(\sigma_v)$	$= -\chi_{xyz}^{(2)}(\text{perm}+C_3)$
<i>Zero by C_3 for all point groups under consideration.</i>				
$\chi_{zzz}^{(2)}, \chi_{yzz}^{(2)}, \chi_{zxx}^{(2)}, \chi_{zxy}^{(2)}, \chi_{zyz}^{(2)}, \chi_{zyx}^{(2)}, \chi_{zyx}^{(2)}$	$\times(C_3)$	$\times(C_3)$	$\times(C_3)$	$\times(C_3)$

copolarized SHG intensity $I_{\parallel}(\theta)$ is determined by contracting the in-plane components of $\chi^{(2)}$ with the polarization vector $\hat{e} = (\cos \theta, \sin \theta, 0)$. The resulting second-harmonic polarization components are given by

$$\begin{aligned} P_x(2\omega) &\propto \chi_{xxx}^{(2)}E_x^2 + \chi_{xyy}^{(2)}E_y^2 + 2\chi_{xxy}^{(2)}E_xE_y, \\ P_y(2\omega) &\propto \chi_{yxx}^{(2)}E_x^2 + \chi_{yyy}^{(2)}E_y^2 + 2\chi_{yyx}^{(2)}E_xE_y. \end{aligned} \quad (11)$$

The copolarized component is defined as $P_{\parallel} = P_x \cos \theta + P_y \sin \theta$, where the intensity scales as $I_{\parallel} \propto |P_{\parallel}|^2$.

D_{3h} (monolayer, AA stacked bilayer). Substituting the single independent component $\chi_{yyy}^{(2)}$ along with the symmetry-enforced relations $\chi_{xxy}^{(2)} = \chi_{xyx}^{(2)} = -\chi_{yyy}^{(2)}$ and $\chi_{yxx}^{(2)} = -\chi_{yyy}^{(2)}$ [Eq. (6)] into the polarization equations yields

$$\begin{aligned} P_x(2\omega) &\propto -2\chi_{yyy}^{(2)}E^2 \cos \theta \sin \theta, \\ P_y(2\omega) &\propto \chi_{yyy}^{(2)}E^2(\sin^2 \theta - \cos^2 \theta). \end{aligned} \quad (12)$$

Projecting these components along the fundamental polarization axis gives

$$P_{\parallel} \propto \chi_{yyy}^{(2)} \sin \theta [\sin^2 \theta - 3 \cos^2 \theta] = -\chi_{yyy}^{(2)} \sin(3\theta), \quad (13)$$

which yields a copolarized SHG intensity profile of

$$I_{\parallel}(\theta) \propto |\chi_{yyy}^{(2)}|^2 \sin^2(3\theta). \quad (14)$$

This expression leads to the well-known six-lobed polar pattern with nodes spaced every 60° [1,9,10]. By aligning the x -axis with the zigzag direction, all intensity nodes fall exactly on the zigzag crystallographic axes ($\theta = 0^\circ, 60^\circ, 120^\circ, \dots$), whereas the maxima align with the armchair directions ($\theta = 30^\circ, 90^\circ, 150^\circ, \dots$). This orientation provides direct crystallographic edge selectivity: a zigzag-terminated edge produces no copolarized SHG signal, while an armchair edge yields the maximum possible emission.

D_{3d} (2H bilayer). Incorporating the condition $\chi_{ijk}^{(2)} = 0$ [Eq. (8)] leads to

$$I_{\parallel}(\theta) = 0 \quad \forall \theta, \quad (15)$$

representing an identically vanishing polar response across all angles due to destructive interlayer interference.

C_{3v} (*3R bilayer*). Since the in-plane tensor structure of the C_{3v} group is formally identical to that of D_{3h} , where vertical mirror reflections σ_v enforce $\chi_{xxx}^{(2)} = 0$, the copolarized in-plane pattern is identical to the monolayer baseline:

$$I_{\parallel}(\theta) \propto |\chi_{yyy}^{(2)}|^2 \sin^2(3\theta). \quad (16)$$

As a consequence, all nodes remain along the zigzag directions. The activated out-of-plane components ($\chi_{zzz}^{(2)}, \chi_{zxx}^{(2)}, \chi_{xxz}^{(2)}$) do not contribute directly to the normal-incidence copolarized profile, although they become accessible in oblique-incidence or cross-polarized measurement settings.

C_3 (*twisted bilayers*). In twisted configurations, both $\chi_{xxx}^{(2)}$ and $\chi_{yyy}^{(2)}$ are simultaneously active and independent [Eq. (10)]. Evaluating the projection equations with the full C_3 constraints ($\chi_{xxy}^{(2)} = -\chi_{yyy}^{(2)}, \chi_{xyy}^{(2)} = -\chi_{xxx}^{(2)}, \chi_{yxx}^{(2)} = -\chi_{yyz}^{(2)}$, and $\chi_{yyx}^{(2)} = -\chi_{xzz}^{(2)}$) yields the following polarization components:

$$P_x \propto \chi_{xxx}^{(2)}(\cos^2 \theta - \sin^2 \theta) - 2\chi_{yyy}^{(2)} \cos \theta \sin \theta, \quad (17)$$

$$P_y \propto \chi_{yyy}^{(2)}(\sin^2 \theta - \cos^2 \theta) - 2\chi_{xxx}^{(2)} \cos \theta \sin \theta. \quad (18)$$

Contracting these expressions into the parallel projection ($P_{\parallel} = P_x \cos \theta + P_y \sin \theta$) simplifies via standard trigonometric identities to

$$P_{\parallel} \propto -\chi_{yyy}^{(2)} \sin(3\theta) + \chi_{xxx}^{(2)} \cos(3\theta), \quad (19)$$

which leads to the macroscopic copolarized SHG intensity:

$$I_{\parallel}(\theta) \propto |\chi_{yyy}^{(2)} \sin(3\theta) - \chi_{xxx}^{(2)} \cos(3\theta)|^2. \quad (20)$$

This relation can be rewritten in a compact, phase-shifted form as

$$I_{\parallel}(\theta) \propto (|\chi_{yyy}^{(2)}|^2 + |\chi_{xxx}^{(2)}|^2) \sin^2[3(\theta - \varphi_0)], \quad (21)$$

where the phase-induced azimuthal lobe shift angle φ_0 is analytically defined by

$$\varphi_0 = \frac{1}{3} \arctan\left(\frac{\chi_{xxx}^{(2)}}{\chi_{yyy}^{(2)}}\right). \quad (22)$$

Crucially, while the characteristic sixfold envelope due to threefold rotational symmetry is preserved, the entire polar lobe structure is subject to a rigid rotation by an angle φ_0 relative to the high-symmetry reference D_{3h} . Since $\chi_{xxx}^{(2)}(\omega)$ and $\chi_{yyy}^{(2)}(\omega)$ are frequency-dependent complex quantities, $\varphi_0(\omega)$ could, in principle, vary dynamically across the optical range. Whether this parameter exhibits substantial spectral variation or remains locked to the structural twist angle θ_{tw} is a key question that we will address from first principles in Sec. IV.

D. Accessing out-of-plane components

The out-of-plane tensor elements $\chi_{zzz}^{(2)}, \chi_{zxx}^{(2)}$, and $\chi_{xxz}^{(2)}$, which are activated in the AB(3R) bilayer (C_{3v}) and twisted configuration (C_3) due to the σ_h symmetry breaking, remain inaccessible in normal-incidence experiments where the fundamental driving field lies entirely within the xy plane ($E_z = 0$). An oblique-incidence experimental setting provides a direct and elegant route to probe these otherwise inaccessible components.

When a p -polarized fundamental beam hits the sample at angle of incidence β relative to the surface normal (z axis), propagating in the xz plane, the electric field vector possesses both in-plane and out-of-plane components:

$$\mathbf{E}(\omega) = E(\omega)(\cos \beta \hat{x} - \sin \beta \hat{z}), \quad (23)$$

with $E_x = E \cos \beta$ and $E_z = -E \sin \beta$. Contracting these field components with the symmetry-allowed elements for the C_{3v} and C_3 point groups, the second-harmonic polarization becomes

$$P_z(2\omega) \propto \chi_{xxx} \cos^2 \beta + \chi_{zzz} \sin^2 \beta, \quad (24)$$

$$P_x(2\omega) \propto \chi_{xxx} \cos^2 \beta - \chi_{xxz} \cos \beta \sin \beta, \quad (25)$$

where the C_3 rotational constraints $\chi_{xzz}^{(2)} = 0$ and $\chi_{zxx}^{(2)} = 0$ have been applied.

As explicitly revealed by Eqs. (25) and (24), the out-of-plane tensor contributions scale as $\sin^2 \beta$ and $\sin \beta \cos \beta$, and vanish identically at normal incidence ($\beta = 0$) while scaling up with increasing tilt angles. An s -polarized beam at oblique incidence maintains $E_z = 0$, failing to activate these out-of-plane signals. Hence, p -polarized light is indispensable for mapping these components.

In high-symmetry D_{3h} systems, such as the isolated monolayer and the AA bilayer, the horizontal reflection plane σ_h enforces $\chi_{zzz} = \chi_{zxx} = \chi_{xxz} = 0$ regardless of β . Consequently, the probed SHG response remains invariant to changes in the incidence tilt angle β , marking normal-incidence angular dependence. By contrast, in C_{3v} and C_3 systems, these elements are active and introduce prominent β -dependent SHG signals. This distinguishing behavior allows oblique-incidence measurements to provide a direct optical fingerprint of broken σ_h symmetry, cleanly separating AB(3R) and twisted bilayers from monolayers and AA-stacks without requiring additional structural characterization.

The above-mentioned procedure can be complemented by cross-polarized detection, positioning the analyzer perpendicular to the fundamental polarization plane (p -in/ s -out or s -in/ p -out). Such a setting filters out the dominant symmetric paths and isolates the y -component of the induced second-harmonic polarization, allowing the cross-polarized response to selectively give access to the $\chi_{xzz}^{(2)} = \chi_{yyz}^{(2)}$ elements in both C_{3v} and C_3 symmetries, directly mapping the pure chiral tensor element $\chi_{xyz}^{(2)}$ in twisted C_3 superlattices. This geometry complements the copolarized oblique-incidence measurements, forming a robust protocol for isolating the complete out-of-plane crystal response.

III. COMPUTATIONAL METHODS

First-principles calculations were performed using the Vienna *ab initio* simulation package (VASP) [30,31] within the Perdew-Burke-Ernzerhof (PBE) [32,33] generalized gradient approximation, using the projector augmented wave method [34] to describe core-valence interactions. Long-range van der Waals (vdW) forces were treated via the density functional theory (DFT)-D3 correction [35], and spin-orbit coupling was included self-consistently throughout. All considered MoS₂ bilayers were fully relaxed until residual interatomic forces fell below 0.01 eV/Å. A vacuum layer of 20 Å was inserted

along the out-of-plane direction to prevent spurious interactions between periodic images. Brillouin-zone sampling was performed using a Γ -centered $12 \times 12 \times 1$ k -mesh for all self-consistent calculations in the primitive cells, and a $6 \times 6 \times 1$ k -mesh for the twisted bilayer supercell.

To compute the nonlinear optical response, maximally localized Wannier functions were constructed using WANNIER90 [36] interfaced with VASP. The initial projections were chosen on the Mo d_{z^2} , $d_{x^2-y^2}$, d_{xy} , d_{xz} , d_{yz} and S p_x , p_y , p_z atomic orbitals. The Wannier fitting was performed on the $24 \times 24 \times 1$ DFT k -mesh for primitive cells and a $6 \times 6 \times 1$ grid for twisted supercell. The accuracy of the resulting Wannier interpolation was validated by checking that the interpolated band structures match those explicitly computed with DFT (see the Supplemental Material [37]). These DFT calculations deliver the relaxed structure and underlying ground-state band structure.

The frequency-dependent susceptibility $\chi_{ijk}^{(2)}(\omega)$ is subsequently evaluated from a separate first-principles response-function calculation, built on Wannier-interpolated momentum matrix elements within the independent-particle approximation. Specifically, the frequency-dependent second-order susceptibility tensor $\chi_{ijk}^{(2)}(\omega)$ was computed using the POSTW90 utility [28,38], which evaluates the SHG response in the velocity gauge using Wannier-interpolated momentum matrix elements. The total macroscopic response is decomposed into interband and intraband contributions:

$$\chi_{ijk}^{(2)} = \chi_{ijk}^{(2),\text{inter}} + \chi_{ijk}^{(2),\text{intra}}, \quad (26)$$

where the interband term involves three-band transitions:

$$\chi_{ijk}^{(2),\text{inter}} = \frac{e^3}{\hbar^2 \omega^2} \sum_{\mathbf{k}} \sum_{n \neq m \neq l} \left[\frac{v_{nm}^i v_{ml}^j v_{ln}^k f_{ln}}{(\omega_{mn} - 2\omega - i\eta)(\omega_{ln} - \omega - i\eta)} + \frac{v_{nm}^i v_{ml}^j v_{ln}^k f_{ml}}{(\omega_{mn} - 2\omega - i\eta)(\omega_{lm} + \omega + i\eta)} \right], \quad (27)$$

and the intraband term captures Fermi-surface contributions:

$$\chi_{ijk}^{(2),\text{intra}} = \frac{e^3}{\hbar^2 \omega^3} \sum_{\mathbf{k}} \sum_{n \neq m} \left[\frac{v_{nm}^i (v_{mm}^j - v_{nn}^j) v_{mn}^k}{\omega_{mn} - 2\omega - i\eta} + \frac{(v_{nm}^i v_{mn}^j)_{,k}}{\omega_{mn} - \omega - i\eta} \right] f_{nm}. \quad (28)$$

Here, the k -covariant derivative of the velocity matrix product along the Cartesian direction l is

$$(v_{nm}^i v_{mn}^j)_{,k} = \partial_{k_k} (v_{nm}^i v_{mn}^j) - i(A_{nn}^k - A_{mm}^k) v_{nm}^i v_{mn}^j, \quad (29)$$

where $A_{nm}^k = i \langle n\mathbf{k} | \partial_{k_k} | n\mathbf{k} \rangle$ is the intraband Berry connection of state n . Here, the notation $(\cdot)_{,k}$ denotes the k -covariant derivative introduced by Sipe and Shkrebtii [38], in which the ordinary partial derivative ∂_{k_k} of the velocity-matrix-element product is corrected by the difference of the intraband Berry connections of the two bands involved [Eq. (29)]. The quantities $v_{nm}^i = \langle n\mathbf{k} | \hat{v}_i | m\mathbf{k} \rangle$ represent velocity matrix elements, $\omega_{mn} = (E_{m\mathbf{k}} - E_{n\mathbf{k}})/\hbar$ denote interband transition frequencies, and $f_{nm} = f_n - f_m$ indicates the corresponding Fermi occupation differences.

As formulated, the interband term in Eq. (27) captures coherent virtual loops among three distinct bands ($n \rightarrow m \rightarrow l \rightarrow n$), which undergo resonant enhancements whenever the fundamental ($\hbar\omega$) or second-harmonic ($2\hbar\omega$) energies match an electronic energy gap. Concurrently, the Berry connection in Eq. (29) encodes the nontrivial quantum geometric phase contribution to the nonlinear polarization [28]. The point-group selection rules derived via Neumann's principle are embedded within these products of matrix elements: for any symmetry-forbidden tensor element, individual contributions across the full Brillouin zone sum undergo pairwise cancellation.

To ensure high spectral resolution and numerical convergence of these resonant profiles, Brillouin zone integration was performed on an ultradense $108 \times 108 \times 1$ k -mesh (additional details are reported in the Supplemental Material [37]). A Lorentzian broadening parameter $\eta = 0.01$ eV was applied across all spectra. We note that these calculations are conducted within the independent-particle approximation, in which many-body corrections are omitted. This approach aligns with the main scope of this work, aimed at establishing universal tensor structures, spatial selection rules, and geometric phase invariants, rather than reproducing experimental peak energies and intensities.

IV. RESULTS AND ANALYSIS

A. Validation of tensor structure: High-symmetry stackings and twisted bilayers

To systematically test the symmetry-derived design rules discussed in Sec. II, we investigate from first principles one representative MoS₂ configuration for each considered point group: the freestanding 1H monolayer (D_{3h}), the centrosymmetric AB(2H) bilayer (D_{3d}), the noncentrosymmetric and AB(3R) bilayers (C_{3v}), and a twisted bilayer (C_3) with angle $\theta_{\text{tw}} = 21.8^\circ$. This analysis allows us to track how the spectral weight of the frequency-dependent macroscopic $\chi^{(2)}(\omega)$ tensor shifts suppresses, or splits as the spatial symmetry elements of the parent monolayer are sequentially eliminated by stacking modifications and interlayer twisting.

The spectrum of the 1H monolayer exhibits only a single non-vanishing component, $|\chi_{yyy}^{(2)}|$, while all other tensor elements vanish within numerical precision [Fig. 2(a)]. This SHG profile matches the single-component landscape imposed by D_{3h} symmetry, with the specific permutation relations $\chi_{yxx}^{(2)} = \chi_{xxy}^{(2)} = \chi_{xyx}^{(2)} = -\chi_{yyy}^{(2)}$ satisfied across the entire frequency range explored.

The inclusion of a second layer completely alters the nonlinear response of MoS₂. In the AB(2H) bilayer stacking [Fig. 2(b)], all computed $\chi^{(2)}$ components vanish. This provides direct numerical verification of our structural design framework: the activation of an inversion center within the D_{3d} point group completely erases the electric-dipole SHG contribution, causing destructive interlayer interference that overrides the strong nonlinear responses of the individual constituent monolayers. A detailed inspection of Fig. 2(b), reveals an exceptionally weak residual signal near 0.9 eV, where the monolayer hosts the B-resonance. We note that this feature does not stem from a physical violation of the crystal point

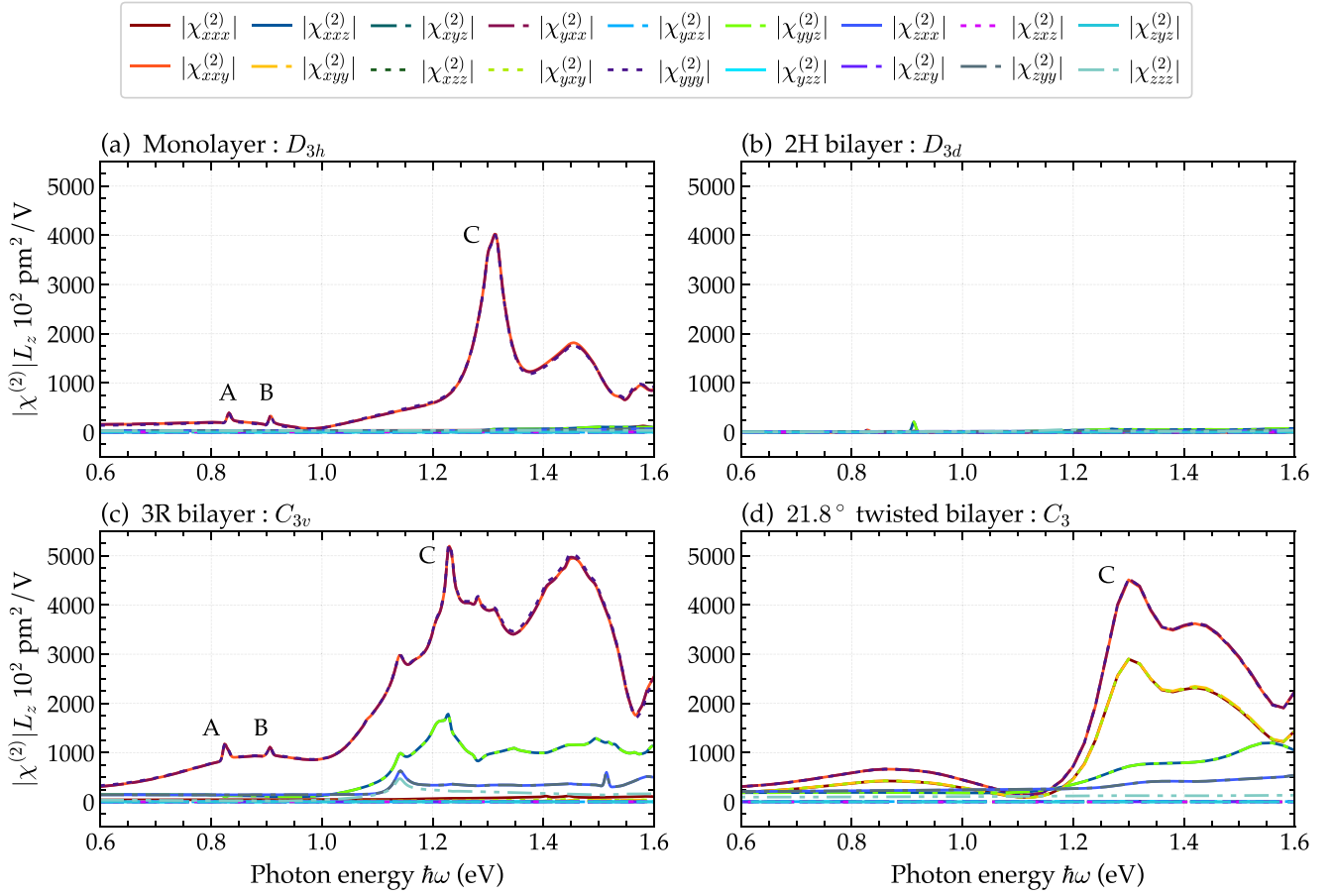


FIG. 2. Frequency-dependent susceptibility spectra $|\chi_{ijk}^{(2)}(\omega)|L_z$ computed for a representative set of MoS₂ structures spanning different point groups with progressively reduced symmetry: $D_{3h} \rightarrow D_{3d} \rightarrow C_{3v} \rightarrow C_3$. Spectral features labeled A, B, and C correspond to key two-photon resonances. (a) In the monolayer (D_{3h}), only $|\chi_{yyy}^{(2)}| \neq 0$, while all other components vanish identically by symmetry. (b) In the AB(2H) bilayer (D_{3d}), all SHG components are suppressed by the inversion center. (c) In the AB(3R) bilayer (C_{3v}), the in-plane $|\chi_{yyy}^{(2)}|$ element is retained, and the out-of-plane components $|\chi_{zzz}^{(2)}|$, $|\chi_{xxz}^{(2)}|$, and $|\chi_{xzz}^{(2)}|$ are activated by the broken horizontal reflection σ_h ; the in-plane element $\chi_{xxx}^{(2)}$ remains zero under σ_v . (d) In the $\theta_{tw} = 21.8^\circ$ twisted bilayer (C_3), both $|\chi_{yyy}^{(2)}|$ and $|\chi_{xxx}^{(2)}|$ emerge as independent, nonzero tensor components along with the out-of-plane contributions, confirming the unconstrained C_3 tensor structure. Here, L_z is the supercell length along the out-of-plane direction.

group during structural relaxation, but likely originates from the Wannier function interpolation scheme, where tiny residual errors in the momentum matrix element cancellations can become visible in the vicinity of intense, localized electronic resonances.

By rigidly translating the upper layer into the non-centrosymmetric AB(3R) stacking sequence [Fig. 2(c)], the inversion center is broken, and the nonlinear response is reactivated. While the in-plane component $|\chi_{yyy}^{(2)}|$ mirrors the behavior of the monolayer, the absence of the horizontal mirror plane (σ_h) activates a manifold of out-of-plane components: $|\chi_{zzz}^{(2)}|$, $|\chi_{xxz}^{(2)}|$, and $|\chi_{xzz}^{(2)}|$. Concomitantly, the retained vertical mirror planes σ_v maintain the other in-plane component $|\chi_{xxx}^{(2)}| = 0$. These internal C_{3v} symmetry constraints ($\chi_{zzx}^{(2)} = \chi_{zyy}^{(2)}$ and $\chi_{xxz}^{(2)} = \chi_{yyz}^{(2)}$) are numerically validated by our DFT results. Notably, these allowed out-of-plane elements are comparable in magnitude to the in-plane baseline $|\chi_{yyy}^{(2)}|$, indicating that breaking the horizontal reflection operation has a massive quantitative impact on the macroscopic nonlinear polarization.

Finally, eliminating all remaining mirror symmetries via relative layer twist (C_3 symmetry) unlocks the most complex tensor landscape, as shown in Fig. 2(d) for the $\theta_{tw} = 21.8^\circ$ twisted bilayer. The optical fingerprint of the structural twist is manifested by the simultaneous activation of both $|\chi_{yyy}^{(2)}|$ and $|\chi_{xxx}^{(2)}|$ as independent, nonzero components. Since $\chi_{xxx}^{(2)} = 0$ is no longer enforced by vertical reflection planes, its prominent spectral signature represents a direct indicator of the low-symmetry C_3 phase. Our numerical results faithfully reproduce the expected C_3 rotational invariants, confirming the equivalence $\chi_{xyy}^{(2)} = \chi_{yxy}^{(2)} = \chi_{yyx}^{(2)} = -\chi_{xxx}^{(2)}$ and $\chi_{yxx}^{(2)} = \chi_{xxy}^{(2)} = \chi_{xyx}^{(2)} = -\chi_{yyy}^{(2)}$, while verifying the activation of the out-of-plane components $|\chi_{zzz}^{(2)}|$, $|\chi_{zyy}^{(2)}|$, and $|\chi_{xxz}^{(2)}|$.

Notably, our first-principles calculations reveal that its magnitude remains exceptionally small across the entire frequency range, even though group-theory arguments predict that the chiral out-of-plane component $\chi_{xyz}^{(2)}$ is symmetrically allowed under the C_3 point group. This suppression stems directly from the weak nature of the interlayer interactions.

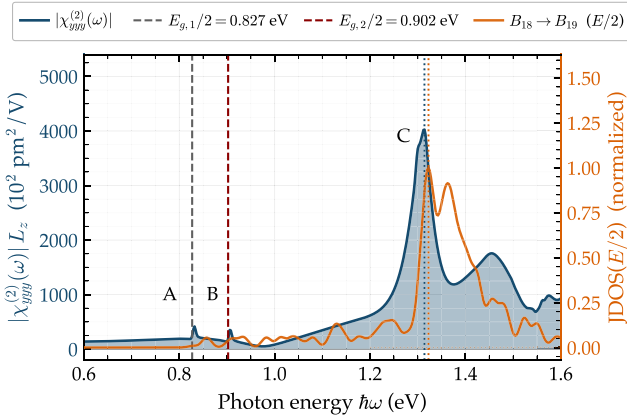


FIG. 3. Computed $|\chi_{yyy}^{(2)}(\omega)|L_z$ spectrum (blue shaded area) and partial $\text{JDOS}_{\text{VBM} \rightarrow \text{CBM}}(E/2)$ (orange curve) of monolayer MoS_2 , evaluated between the frontier valence and conduction bands ($B_{18} \rightarrow B_{19}$). Vertical dotted lines mark the A and B direct-gap transition thresholds at the K point, split by spin-orbit coupling: $E_{g,1}/2 = 0.827$ eV (A transition, $\text{VBM} \rightarrow \text{CBM}$) and $E_{g,2}/2 = 0.902$ eV (B transition, $\text{VBM} - 1 \rightarrow \text{CBM}$). Two additional vertical dotted lines mark the C peak in the SHG spectrum (blue) and the aligned JDOS peak (orange), offset by $\Delta\omega = 8$ meV, confirming two-photon resonances between the VBM and CBM as the primary origin of the SHG spectral structure at the independent-particle level. Here, L_z is the supercell length along the out-of-plane direction.

Since the electronic states remain predominantly localized within the individual monolayers, where the horizontal mirror symmetry operation is locally preserved, the global breaking of σ_h and the resulting chiral coupling between orbitals with out-of-plane (z) and in-plane (x, y) distribution contribute only marginally to the macroscopic nonlinear susceptibility. Consequently, the in-plane elements $\chi_{yyy}^{(2)}$ and $\chi_{xxx}^{(2)}$ remain the dominant observables for detecting and characterizing twisted phases.

Finally, we note that the monolayer and the AA-stacked bilayer (D_{3h} point group) possess twofold C'_2 rotation axes, i.e., in-plane axes oriented perpendicular to the principal C_3 axis [39]. Although these C'_2 operations have an impact on the nonlinear optical response, all out-of-plane $\chi^{(2)}$ components are already forced to zero by the horizontal mirror σ_h . In an idealized macroscopic twisted homobilayer, the presence of these twofold C'_2 axes would similarly enforce $\chi_{zzz}^{(2)} = \chi_{zxx}^{(2)} = \chi_{xxz}^{(2)} = 0$. In our DFT calculations, however, the minimal periodic supercell chosen to represent the twisted bilayer explicitly lacks this C'_2 axis, projecting the system strictly into the C_3 point group. As a consequence, the out-of-plane elements $\chi_{zzz}^{(2)}$ and $\chi_{xxz}^{(2)}$ are symmetry-allowed and yield non-zero values in our calculations.

B. Two-photon resonances in monolayer MoS_2

To connect the spectral features of $\chi^{(2)}$ computed from first principles to the underlying electronic structure, we contrast the dominant $|\chi_{yyy}^{(2)}(\omega)|$ spectrum of monolayer MoS_2 against the partial joint density of states evaluated at half the photon energy, $\text{JDOS}(E/2)$, tracking the frontier electronic manifolds (Fig. 3). Within the independent-particle

approximation, SHG satisfies a two-photon resonance condition whenever the second-harmonic energy $2\hbar\omega$ coincides with a real, single-particle interband electronic transition. Hence, peaks appearing in the $|\chi_{yyy}^{(2)}(\omega)|$ spectrum at the fundamental photon energy $\hbar\omega$ correspond directly to features in the $\text{JDOS}(E/2)$ plotted on the same energy axis.

Monolayer MoS_2 is characterized by direct band-gap transitions at the K/K' valleys of its hexagonal Brillouin zone [29,40,41]. The valence-band maximum (VBM) is split into two distinct subbands by the strong spin-orbit coupling inherent to the Mo 4d valence manifold. Within our single-particle band structure, the lowest-energy transition (labeled A) originates from the upper VBM to the conduction band minimum (CBM), corresponding to a single-particle two-photon threshold of $2\hbar\omega_A = 1.654$ eV ($E_{g,1}/2 = 0.827$ eV). The higher-energy feature (labeled B) stems from transitions originating at the spin-orbit-split lower valence band ($\text{VBM} - 1$) targeting the CBM at $2\hbar\omega_B = 1.804$ eV ($E_{g,2}/2 = 0.902$ eV). These single-particle valley resonances are marked by vertical dashed indicators in Fig. 3. The close correspondence between the onset of $|\chi_{yyy}^{(2)}(\omega)|$ and these key JDOS threshold features confirms that the low-energy non-linear response is dominated by two-photon K-valley band-edge transitions.

At higher excitation energies, the $|\chi_{yyy}^{(2)}(\omega)|$ spectrum exhibits another prominent feature, labeled C, that aligns remarkably well (within 8 meV) with the dominant global maximum of the JDOS. This correspondence confirms that the C peak originates from strong two-photon, band-nesting transitions linking parallel valence and conduction bands along the Γ -K or K-M paths within the Brillouin zone. The residual offset of 8 meV between the $\chi^{(2)}$ maximum and the JDOS peak is consistent with the finite Lorentzian broadening ($\eta = 0.01$ eV) applied to visualize the spectra. We emphasize that within the independent-particle approximation, A, B, and C label the noninteracting single-particle transitions. While electron-hole (excitonic) binding effects will renormalize absolute peak positions downward in experimental spectra, these single-particle resonances dictate the fundamental orbital selection rules and underlying band symmetries governing the SHG response.

C. SHG polar patterns

To monitor how the stacking-controlled tensor modifications manifest in experiments, we map the angular dependence of the co-polarized SHG intensity as a function of the incident polarization angle. To connect this analysis with the electronic structure of each phase, the angular profiles are evaluated at their respective C-peak resonance energies: $\hbar\omega = 1.31$ eV for the monolayer, $\hbar\omega = 1.28$ eV for the AA-stacked bilayer, and $\hbar\omega = 1.30$ eV for the $\theta_{\text{tw}} = 21.8^\circ$ twisted bilayer (Fig. 4).

As shown in Figs. 4(a) and 4(b), both the 1H monolayer and the AA-stacked bilayer display the characteristic six-lobed $\sin^2(3\theta)$ pattern predicted for the D_{3h} point group [Eq. (14)]. The nodes fall precisely along the zigzag directions ($\theta = 0^\circ, 60^\circ, 120^\circ, \dots$), whereas the intensity maxima align with the armchair directions ($\theta = 30^\circ, 90^\circ, 150^\circ, \dots$). The fact that the nodal structure and lobe orientation are identical for both configurations confirms that the macroscopic SHG polar pattern is determined entirely by the point group

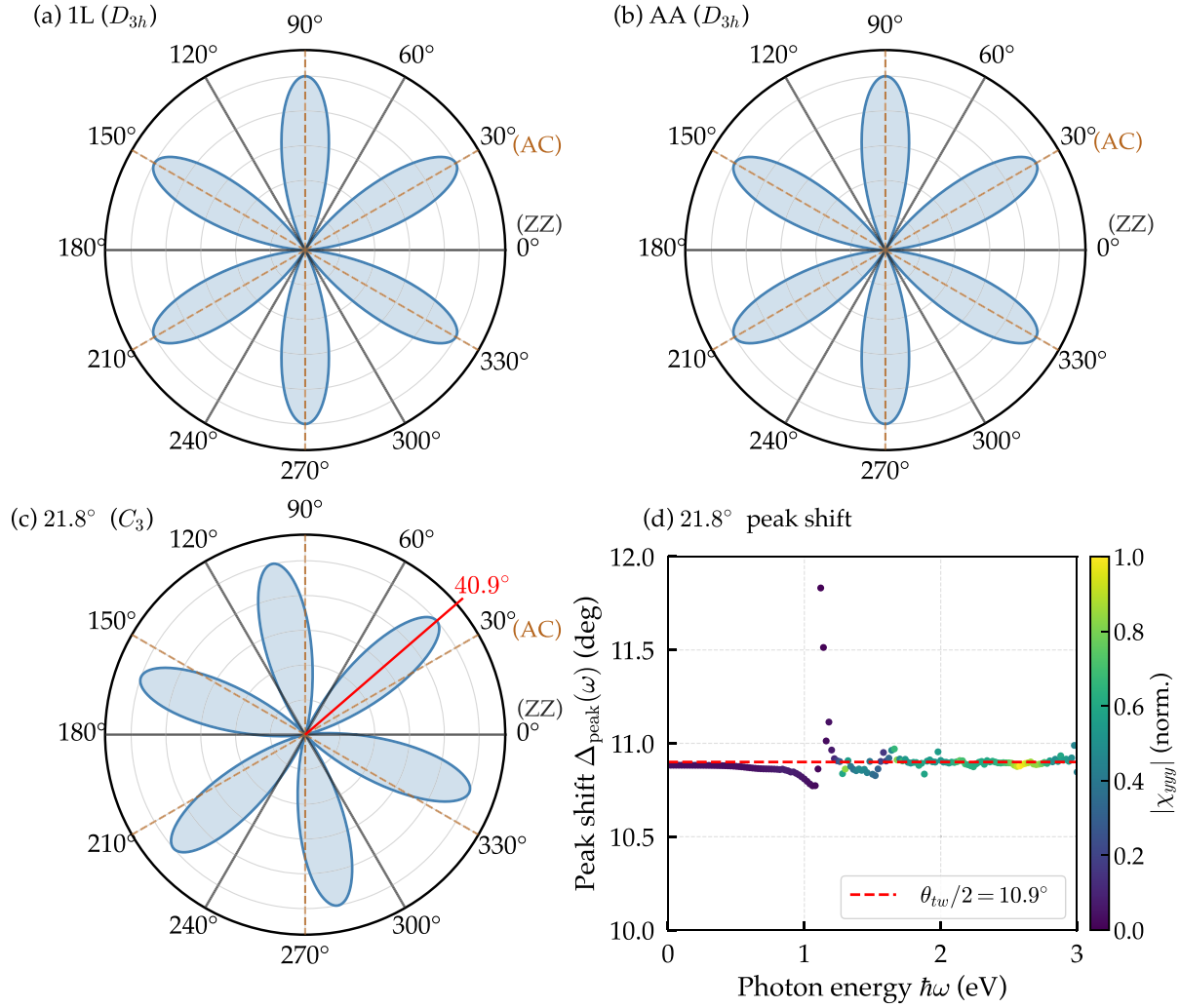


FIG. 4. Copolarized SHG polar patterns $I_{\parallel}(\theta)$ computed for (a) monolayer MoS₂ at $\hbar\omega = 1.31$ eV, (b) AA bilayer at $\hbar\omega = 1.28$ eV, and (c) 21.8° twisted bilayer at $\hbar\omega = 1.30$ eV, each at their respective C-peak energy. The graphs in each panel are normalized independently to their maximum value. Orange dotted lines mark the armchair (AC) directions. Gray solid lines mark the zigzag (ZZ) directions with the AC axis offset by 30°. The red line in (c) marks the rotated lobe maximum at $\theta_{\text{lobe}} = 40.9^\circ$, shifted by $\varphi_0 = 10.9^\circ$ due to the activation of the $\chi_{xxx}^{(2)}$ element in the C_3 phase. (d) Computed SHG lobe shift angle $\varphi_0(\omega)$ as a function of photon energy $\hbar\omega$ for the $\theta_{\text{tw}} = 21.8^\circ$ twisted bilayer (C_3). Each data point is color-coded according to the normalized amplitude $|\chi_{yyy}^{(2)}(\omega)|$. The red horizontal dashed line marks the analytical prediction $\varphi_0 = \theta_{\text{tw}}/2 = 10.9^\circ$.

symmetry and remains insensitive to the number of layers as long as the spatial operations of the parent layer are preserved by the stacking arrangement.

In contrast, the $\theta_{\text{tw}} = 21.8^\circ$ twisted bilayer displays a qualitatively different angular profile [Fig. 4(c)]. While the six-lobed pattern is preserved, consistent with the retained threefold rotational symmetry (C_3), the entire lobe structure is rigidly rotated relative to the D_{3h} -symmetric reference. The principal intensity maximum, which falls at $\theta = 30^\circ$ (armchair direction) in the D_{3h} phase, rotates to $\theta_{\text{lobe}} = 40.86^\circ \approx 40.9^\circ$ under a $\theta_{\text{tw}} = 21.8^\circ$, corresponding to a net azimuthal lobe shift of $\varphi_0 = 10.9^\circ$, in agreement with our analytical prediction [Eq. (22)] when evaluated from the first-principles complex tensor components $\chi_{xxx}^{(2)}$ and $\chi_{yyy}^{(2)}$ at this specific excitation energy.

To clarify whether the C_3 tensor structure permits a dynamically evolving SHG angular response, we evaluate the energy

dependence of the phase-induced lobe shift angle $\varphi_0(\omega)$ [Fig. 4(d)]. Since the independent tensor components $\chi_{xxx}^{(2)}(\omega)$ and $\chi_{yyy}^{(2)}(\omega)$ stem from distinct electronic transitions and exhibit different dynamical profiles, their trigonometric ratio could, in principle, undergo severe fluctuations near sharp valley resonances. Activated by the broken mirror symmetries of the C_3 twisted stacking (Sec. II A), the calculated lobe shift remains remarkably constant around 10.9° across the entire computed spectral range, exhibiting only minor deviations. Notably, $\varphi_0 = 10.9^\circ$ corresponds precisely to half of the macroscopic twist angle $\theta_{\text{tw}} = 21.8^\circ$, demonstrating that the relative phase and amplitude ratio of the in-plane $\chi^{(2)}$ components are locked to the geometry of the twisted lattice. Within the adopted independent-particle approximation, where dynamical correlations are neglected, the relative ratio $\chi_{xxx}^{(2)}/\chi_{yyy}^{(2)}$ is solely dictated by the spatial projection of the atomic coordinates rather than evolving independently with the individual

interband transitions. An analytical proof demonstrating how coherent field superposition between rigidly rotated monolayers locks the tensor ratio to $\tan(3\theta_{\text{tw}}/2)$, and consequently forces $\varphi_0 = \theta_{\text{tw}}/2$ across arbitrary twist angles, is provided in Appendix B.

This geometric interpretation is further substantiated by the color-coded spectral weight mapping in Fig. 4(d). In energy windows where the nonlinear signal is robust, matching the A, B, and C two-photon resonances, the data points converge onto the ideal $\theta_{\text{tw}}/2 = 10.90^\circ$ baseline. Minor fluctuations occur exclusively where the magnitude of the tensor components approaches zero, rendering the trigonometric ratio in the definition of φ_0 [Eq. (22)] highly sensitive to numerical background noise.

V. CONCLUSIONS

In summary, we have presented a unified analytical and first-principles investigation of SHG in TMD subjected to different bilayer stackings, taking MoS_2 as the reference material and the freestanding monolayer as the structural baseline. Using Neumann's principle, we derived the complete $\chi^{(2)}$ tensor structure for each considered point group (D_{3h} , D_{3d} , C_{3v} , and C_3) and established a set of design rules connecting stacking configuration to nonlinear optical response.

Our structural framework resolves into the following key physical principles:

(1) *Inversion symmetry and SHG elimination.* The activation of a macroscopic inversion center within the AB(2H) configuration (D_{3d} point group) enforces a strict $\chi^{(2)} = 0$ identity, overriding the strong nonlinear response of the constituent layers via destructive interlayer interference.

(2) *Horizontal mirror plane and out-of-plane paths.* The horizontal mirror plane σ_h inherent to the monolayer and the AA bilayer (D_{3h}) strictly forbids all out-of-plane $\chi^{(2)}$ tensor elements. Conversely, removing σ_h in AB(3R) stackings (C_{3v}) and twisted bilayers (C_3) activates the $\chi_{zzz}^{(2)}$, $\chi_{zxz}^{(2)}$, and $\chi_{xxz}^{(2)}$ elements, creating an experimental path to probe hidden vertical polarization vectors via oblique-incidence p -polarized geometries.

(3) *Vertical mirror plane and lobe rotation.* The vertical mirror plane σ_v acts as the defining operation that forces $\chi_{xxx}^{(2)} = 0$ in all nontwisted bilayers. Releasing this constraint through artificial twisting (C_3) unlocks $\chi_{xxx}^{(2)}$ as a fully independent, active tensor component, driving a rigid spatial rotation of the macroscopic copolarized SHG polar lobes.

Finally, our first-principles calculations reveal that this phase-induced azimuthal lobe shift angle φ_0 is extraordinarily stable across the explored optical window. It remains locked to the clear geometric limit dictated by the spatial projection of the atomic coordinates:

$$\theta_{\text{tw}} = 2\varphi_0. \quad (30)$$

This relation follows directly from the coherent superposition of two rigidly rotated, identical monolayer responses (Appendix B), and holds for arbitrary twist angle in this weak-coupling regime, not being specific to $\theta_{\text{tw}} = 21.8^\circ$. As such, it provides an elegant, material-agnostic, and nondestructive optical protocol for mapping localized twist profiles and

structural moiré domains, at twist angles for which the twisted bilayer retains its rigid, uniformly rotated character.

The design principles formulated in this work are universal, being dictated by global crystal symmetries rather than material-specific details. As such, their application is straightforward to all 2H-TMD bilayers and other vdW crystals with analogous structural symmetries. Most importantly, the proposed analytical framework provides a symmetry-based roadmap for engineering the nonlinear optical response of layered materials solely through stacking control. This complements parallel advances in symmetry reduction via Janus engineering and in-plane heterostructuring aimed at extreme directional SHG anisotropy [42], together forming a comprehensive paradigm for tailoring 2D nonlinear optics. Concurrently, the relation $\theta_{\text{tw}} = 2\varphi_0$ provides a simple and experimentally accessible optical probe of twist angle that warrants further investigation across a broader range of commensurate and incommensurate twisted TMD bilayers, paving the way for high-throughput screening of this novel material class with a noninvasive optical tool.

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DATA AVAILABILITY

The data that support the findings of this study are available on Zenodo [43]. The archive contains VASP and WANNIER90 input/output files, together with the computed second-order susceptibility tensor $\chi_{ijk}^{(2)}(\omega)$ for all 27 tensor components, for the MoS_2 monolayer and all four bilayer stacking configurations (AA, 2H, 3R, and 21.8° twisted bilayer) studied in this work.

APPENDIX A: SYMMETRY OPERATIONS ON $\chi^{(2)}$

The second-order susceptibility $\chi_{ijk}^{(2)}$ is a third-rank polar tensor with $3^3 = 27$ elements. In this appendix, we provide the explicit algebraic reduction of these components under intrinsic permutation symmetry and relevant point group operations based on Neumann's principle.

1. Intrinsic permutation symmetry

In the SHG experimental setting, two incoming photons oscillate at the identical frequency ω , making the last two indices of $\chi_{ijk}^{(2)}$ completely interchangeable:

$$\chi_{ijk}^{(2)} = \chi_{ikj}^{(2)}. \quad (\text{A1})$$

For any fixed index $i \in \{x, y, z\}$, the remaining jk pair possesses $3 \times 3 = 9$ permutations, only six of which are linearly independent under $j \leftrightarrow k$ exchange:

$$\{jk\} \in \{xx, yy, zz, xy(=yx), xz(=zx), yz(=zy)\}. \quad (\text{A2})$$

This constraint reduces the 27 initial components to $3 \times 6 = 18$ independent elements.

2. Reduction by C_3 rotation

The threefold rotation operation C_3 around the out-of-plane z -axis represents a counterclockwise rotation by 120° about the z -axis, defined by the standard transformation matrix:

$$R(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (\text{A3})$$

Neumann's principle requires that the tensor must remain invariant under any valid symmetry operations of the crystal point group:

$$\chi_{ijk}^{(2)} = R_{il}R_{jm}R_{kn}\chi_{lmn}^{(2)}. \quad (\text{A4})$$

Since $R_{zz} = 1$ and $R_{xz} = R_{yz} = R_{zx} = R_{zy} = 0$, the z axis is invariant under C_3 . This has two main consequences:

(i) *Elements mixing one in-plane index with two out-of-plane indices.* Taking $\chi_{xzz}^{(2)}$ as a representative baseline and noting that $R_{zm} = \delta_{zm}$ isolates the out-of-plane projection, the transformation simplifies to $\chi_{xzz}^{(2)} = R_{xl}\chi_{lzz}^{(2)}$. Expanding over $l \in \{x, y, z\}$ yields

$$\begin{aligned} \chi_{xzz}^{(2)} &= R_{xx}\chi_{xzz}^{(2)} + R_{xy}\chi_{yzz}^{(2)} + R_{xz}\chi_{zzz}^{(2)} \\ &= -\frac{1}{2}\chi_{xzz}^{(2)} - \frac{\sqrt{3}}{2}\chi_{yzz}^{(2)} + 0, \end{aligned} \quad (\text{A5})$$

which reduces to $\frac{3}{2}\chi_{xzz}^{(2)} = -\frac{\sqrt{3}}{2}\chi_{yzz}^{(2)}$. Performing the identical operation for the complementary component $\chi_{yzz}^{(2)}$ results in

$$\begin{aligned} \chi_{yzz}^{(2)} &= R_{yx}\chi_{xzz}^{(2)} + R_{yy}\chi_{yzz}^{(2)} + R_{yz}\chi_{zzz}^{(2)} \\ &= \frac{\sqrt{3}}{2}\chi_{xzz}^{(2)} - \frac{1}{2}\chi_{yzz}^{(2)} + 0, \end{aligned} \quad (\text{A6})$$

which simplifies to $\frac{3}{2}\chi_{yzz}^{(2)} = \frac{\sqrt{3}}{2}\chi_{xzz}^{(2)}$. Solving this paired system of linear equations simultaneously forces both components to vanish:

$$\chi_{xzz}^{(2)} = \chi_{yzz}^{(2)} = 0. \quad (\text{A7})$$

The same algebra applied to $\chi_{zxx}^{(2)}, \chi_{zxy}^{(2)}, \chi_{zyx}^{(2)}, \chi_{zyy}^{(2)}$ gives

$$\chi_{zxx}^{(2)} = \chi_{zxy}^{(2)} = \chi_{zyx}^{(2)} = \chi_{zyy}^{(2)} = 0. \quad (\text{A8})$$

(ii) *Elimination of mixed in-plane elements $\chi_{zxy}^{(2)}$.* Applying Eq. (A4) to $\chi_{zxy}^{(2)}$ requires expanding across the entire in-plane manifold ($m, n \in \{x, y\}$):

$$\begin{aligned} \chi_{zxy}^{(2)} &= R_{xm}R_{yn}\chi_{zmn}^{(2)} \\ &= -\frac{\sqrt{3}}{4}\chi_{zxx}^{(2)} + \frac{1}{4}\chi_{zxy}^{(2)} - \frac{3}{4}\chi_{zyx}^{(2)} + \frac{\sqrt{3}}{4}\chi_{zyy}^{(2)}. \end{aligned} \quad (\text{A9})$$

Enforcing permutation symmetry $\chi_{zxy}^{(2)} = \chi_{zyx}^{(2)}$ alongside the structural constraint $\chi_{zxx}^{(2)} = \chi_{zyy}^{(2)}$, which can be verified independently by passing $\chi_{zxx}^{(2)}$ through the identical C_3

transformation matrix:

$$\begin{aligned} \chi_{zxx}^{(2)} &= R_{xm}R_{xn}\chi_{zmn}^{(2)} \\ &= \frac{1}{4}\chi_{zxx}^{(2)} - \frac{\sqrt{3}}{4}\chi_{zxy}^{(2)} - \frac{\sqrt{3}}{4}\chi_{zyx}^{(2)} + \frac{3}{4}\chi_{zyy}^{(2)}, \end{aligned} \quad (\text{A10})$$

the structural equation reduces neatly to $\frac{3}{2}\chi_{zxy}^{(2)} = 0$. Hence, $\chi_{zxy}^{(2)} = \chi_{zyx}^{(2)} = 0$.

Overall, the C_3 rotation symmetry nullifies eight tensor components:

$$\chi_{xzz}^{(2)} = \chi_{yzz}^{(2)} = \chi_{zxx}^{(2)} = \chi_{zxy}^{(2)} = \chi_{zyx}^{(2)} = \chi_{zyy}^{(2)} = \chi_{zxx}^{(2)} = \chi_{zyy}^{(2)} = 0. \quad (\text{A11})$$

Taking into account permutation rules, this condition leaves 13 unique independent tensor components within the C_3 point group.

3. Horizontal mirror plane σ_h

The horizontal mirror plane σ_h reflects spatial coordinates across the basal plane, mapping $x \rightarrow x, y \rightarrow y, z \rightarrow -z$, with matrix $R(\sigma_h) = \text{diag}(1, 1, -1)$. Under this transformation, each z index (n_z) contributes a factor of -1 :

$$\chi_{ijk}^{(2)} \xrightarrow{\sigma_h} (-1)^{n_z}\chi_{ijk}^{(2)}. \quad (\text{A12})$$

Applying Neumann's principle then forces $\chi_{ijk}^{(2)} = 0$ for any combination where n_z is an odd integer. Taking $\chi_{xzz}^{(2)}$ ($n_z = 1$) as an explicit example, we obtain

$$\begin{aligned} \chi_{xzz}^{(2)} &= R_{xx}R_{xx}R_{zz}\chi_{xzz}^{(2)} \\ &= (1)(1)(-1)\chi_{xzz}^{(2)} = -\chi_{xzz}^{(2)} \Rightarrow \chi_{xzz}^{(2)} = 0. \end{aligned} \quad (\text{A13})$$

Consequently, all tensor components with an odd number of out-of-plane coordinates vanish completely:

$$\chi_{xzz}^{(2)}, \chi_{yyz}^{(2)}, \chi_{zxx}^{(2)}, \chi_{zyy}^{(2)}, \chi_{xyx}^{(2)}, \chi_{xzy}^{(2)}, \chi_{yxz}^{(2)}, \chi_{yzx}^{(2)}, \chi_{zzz}^{(2)} = 0. \quad (\text{A14})$$

Components containing purely in-plane or an even number of out-of-plane coordinates are unaffected.

4. Vertical mirror plane σ_v

The vertical mirror plane σ_v reflects coordinates across a vertical plane perpendicular to the layer, mapping $x \rightarrow x, y \rightarrow -y, z \rightarrow z$, expressed as $R(\sigma_v) = \text{diag}(1, -1, 1)$. Here, each y index (n_y) contributes a factor of -1 :

$$\chi_{ijk}^{(2)} \xrightarrow{\sigma_v} (-1)^{n_y}\chi_{ijk}^{(2)}. \quad (\text{A15})$$

Components with an odd value of n_y vanish. Taking as an example the in-plane component $\chi_{xxx}^{(2)}$, the C_3 rotation symmetry enforces the relation $\chi_{xxx}^{(2)} = -\chi_{xyy}^{(2)}$. Subjecting these elements to σ_v yields

$$\chi_{xxx}^{(2)} \xrightarrow{\sigma_v} \chi_{xxx}^{(2)}, \quad \chi_{xyy}^{(2)} \xrightarrow{\sigma_v} -\chi_{xyy}^{(2)}. \quad (\text{A16})$$

Since Neumann's principle requires $\chi_{xyy}^{(2)} = -\chi_{xyy}^{(2)} = 0$, the constraint reflects back through the rotational relation, ensuring $\chi_{xxx}^{(2)} = 0$. Similarly, any component containing a y -index, such as $\chi_{xyz}^{(2)}$ ($n_y = 1$), is systematically canceled:

$$\chi_{xyz}^{(2)} \xrightarrow{\sigma_v} -\chi_{xyz}^{(2)} \Rightarrow \chi_{xyz}^{(2)} = 0. \quad (\text{A17})$$

This structural constraint applies to both D_{3h} and C_{3v} point groups. The absence of a vertical mirror plane σ_v in the C_3 point group is the exclusive mechanism unlocking $\chi_{xxx}^{(2)}$ and $\chi_{xyz}^{(2)}$ as active, independent tensor elements in twisted bilayers.

5. Inversion symmetry $\mathcal{I}$

A macroscopic spatial inversion operation maps all coordinates through the origin, $\mathbf{r} \rightarrow -\mathbf{r}$, yielding a transformation matrix $R(\mathcal{I}) = \text{diag}(-1, -1, -1)$. For a third-rank polar tensor, this operation introduces an odd transformation parity across all indices simultaneously:

$$\chi_{ijk}^{(2)} = 0 \quad \forall i, j, k. \quad (\text{A18})$$

Enforcing Neumann's principle requires $\chi_{ijk}^{(2)} = -\chi_{ijk}^{(2)}$, which in turn implies

$$\chi_{ijk}^{(2)} = 0 \quad \forall i, j, k. \quad (\text{A19})$$

This complete elimination of tensor elements explains why all electric-dipole SHG paths are completely prohibited within the centrosymmetric 2H bilayer structure (D_{3d} point group).

APPENDIX B: ANALYTICAL DERIVATION OF THE TWIST-ANGLE LOCKING $\varphi_0 = \theta_{tw}/2$

We analytically establish that the relation $\varphi_0 = \theta_{tw}/2$ represents a universal geometric property of weakly coupled C_3 -symmetric twisted bilayers. In the weak-interlayer-coupling limit, a twisted bilayer behaves as two D_{3h} -symmetric monolayers with identical intrinsic in-plane susceptibility $\chi_0(\omega) \equiv \chi_{yyy}^{(2)}(\omega)$, rotated by a relative twist angle θ_{tw} , whose generated SHG fields superpose coherently. As established in Eq. (13), the copolarized nonlinear polarization of the bottom layer ($\theta_{tw} = 0^\circ$) is

$$P_{\parallel}^{(1)}(\theta) \propto -\chi_{yyy} \sin(3\theta). \quad (\text{B1})$$

For the top layer, rotated by θ_{tw} , the armchair direction shifts by θ_{tw} , yielding

$$P_{\parallel}^{(2)}(\theta) \propto -\chi_{yyy} \sin[3(\theta - \theta_{tw})]. \quad (\text{B2})$$

The total macroscopic copolarized response is given by the linear superposition:

$$P_{\parallel}^{\text{tot}}(\theta) \propto -\chi_{yyy} [\sin 3\theta + \sin(3\theta - 3\theta_{tw})]. \quad (\text{B3})$$

Applying the sum-to-product trigonometric identity $\sin A + \sin B = 2 \sin(\frac{A+B}{2}) \cos(\frac{A-B}{2})$, Eq. (B3) reduces to

$$P_{\parallel}^{\text{tot}}(\theta) \propto -2\chi_{yyy} \cos\left(\frac{3\theta_{tw}}{2}\right) \sin\left[3\left(\theta - \frac{\theta_{tw}}{2}\right)\right]. \quad (\text{B4})$$

Comparing Eq. (B4) with the general C_3 polar pattern expression, $P_{\parallel}(\theta) \propto -C \sin[3(\theta - \varphi_0)]$, delivers the geometric identity

$$\varphi_0 = \frac{\theta_{tw}}{2}, \quad C = 2\chi_{yyy} \cos\left(\frac{3\theta_{tw}}{2}\right). \quad (\text{B5})$$

Equivalently, this coherent field superposition locks the ratio of the effective C_3 tensor components to $\chi_{xxx}^{(2)}/\chi_{yyy}^{(2)} = \tan(3\theta_{tw}/2)$, enforcing $\varphi_0 = \theta_{tw}/2$ strictly independently of photon energy $\hbar\omega$ or the absolute magnitude of $\chi_0(\omega)$.

The general relation $\varphi_0 = \frac{1}{3} \arctan(\chi_{xxx}^{(2)}/\chi_{yyy}^{(2)})$ [Eq. (21)] is exact and depends solely on C_3 point-group symmetry. However, the geometric lock $\chi_{xxx}^{(2)}/\chi_{yyy}^{(2)} = \tan(3\theta_{tw}/2)$ assumes a rigid, uniform rotational superposition of intact monolayers. In the small-angle regime ($\theta_{tw} \lesssim 2^\circ$), atomic reconstruction induces local domain-wall formation (e.g., periodic 3R-like and AA-like domains [44]). In this strongly reconstructed limit, local interlayer sliding overrides the uniform rotational mapping, modifying the tensor component ratio from its weak-coupling geometric limit.

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