

# Cooperative Charge Ordering Signature of Trimer Molecules in Infinite-Layer $\text{CaCoO}_2$

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The infinite-layer compound  $\text{CaCoO}_2$  provides a compelling platform to explore how local orbital distortions evolve into collective electronic order. Using resonant soft x-ray scattering (RSXS) and its time-resolved counterpart (tr-RSXS), we reveal a cooperative coupling between two intertwined orders at the same in-plane wave vector,  $q \approx (1/4, 1/4, 0)$ , comprising a quasi-two-dimensional orbital order associated with the distorted  $\text{Co}_{(1)}$  sites and a quasi-three-dimensional trimerlike charge order stabilized through Co-O-Ca hybridization. The charge-sensitive component exhibits a uniform relaxation time of  $\sim 400$  fs ( $391 \pm 5$  fs) across multiple Co resonances, evidencing a collective charge response. A comparable timescale observed in the orbital order associated with the highly distorted  $\text{Co}_{(1)}$  sites indicates that this collective behavior naturally originates from the same orbital framework that mediates both charge and orbital degrees of freedom. Together, these findings establish  $\text{CaCoO}_2$  as a model system in which Jahn-Teller distortions, orbital hybridization, and geometric frustration cooperate to form molecular trimer units that dictate the macroscopic electronic behavior.

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## I. INTRODUCTION

Understanding quantum effects in the orbital physics of “molecular crystals” is crucial to determine their profound influence on electronic, magnetic, and structural properties [1–9]. Unlike systems dominated by single-site or isolated

cluster behavior, an emerging class of inorganic materials can be considered as molecular crystals, in which the cooperative interactions among ordered molecular units play a central role in defining material properties. These molecular systems introduce new opportunities to explore how geometrical frustration, the Jahn-Teller effect (JTE), and spin-orbit coupling influence macroscopic properties such as conductivity, magnetism, and potential functionalities for device applications [5–12]. For instance, geometrical frustration can induce significant changes in the electronic states of molecular clusters, such as dimers or trimers, affecting their interactions within the crystal lattice [10–14].

The recently discovered infinite-layer compound  $\text{CaCoO}_2$  exemplifies this landscape of complex interactions [15].

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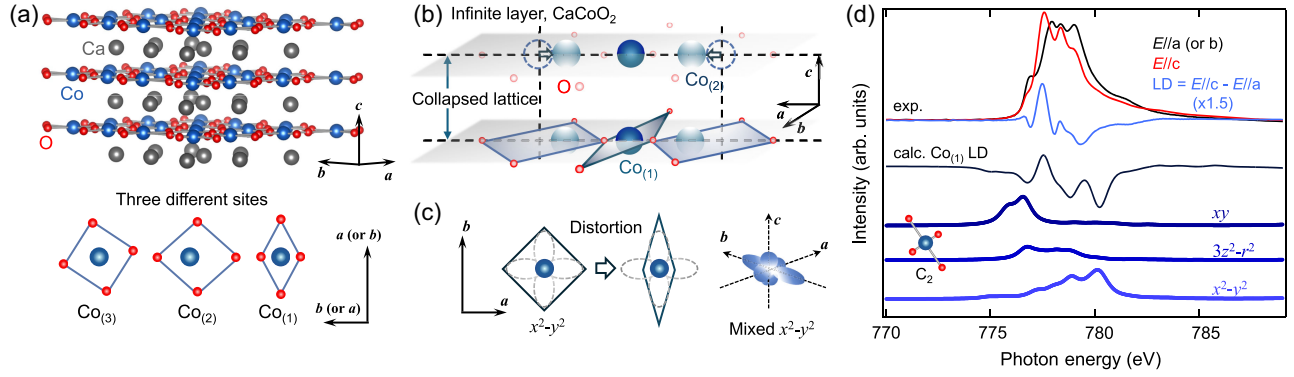


FIG. 1. (a) Schematic of the infinite thin layer of the  $\text{CaCoO}_2$  film, showing three different Co sites in the layer, labeled as  $\text{Co}_{(1)}$ , which is the strongly JT distorted,  $\text{Co}_{(2)}$ , which has a broken inversion symmetry, and  $\text{Co}_{(3)}$ , which forms a square-planar  $\text{CoO}_4$  plaquette. (b) Refined Co atomic sites in the infinite-layer compound  $\text{CaCoO}_2$ , highlighting the herringbone arrangement. The strongly JT distorted  $\text{Co}_{(1)}$  site and the off-centered  $\text{Co}_{(2)}$  site (arrows) break local inversion symmetry, while the absence of apical oxygen in the  $\text{CoO}_4$  plaquettes leads to a collapsed lattice along the  $c$  axis. (c) Schematic Co  $d$ -orbital configurations. In an undistorted ( $C_4$  symmetry) square-planar geometry within the  $ab$  plane, the  $x^2-y^2$  orbital is favored. At the JT-distorted  $\text{Co}_{(1)}$  site ( $C_2$  symmetry), however, orbital mixing leads to a hybridized  $x^2-y^2$  character. (d) Polarization-dependent XAS measurement on  $\text{CaCoO}_2$ . Black and red curves correspond to  $E||a$  (or  $b$ ) and  $E||c$ , respectively. The blue line indicates its linear dichroism, which is compared with the calculated LD on  $\text{Co}_{(1)}$  site. The positive and negative LD signal are compared with the relevant orbital state that is for the highly distorted  $\text{Co}_{(1)}$  site ( $C_2$  symmetry) are extracted by multiplet calculations (see more in Supplemental Material [17]).

As shown in Fig. 1(a), its refined structure features Ångström-scale distortions that give rise to a “herringbone” arrangement of  $\text{CoO}_4$  units, which minimizes electrostatic interactions between electric quadrupole moments [16]. This arrangement originates from the off-centered displacement of the  $\text{Co}_{(2)}$  sites together with the highly distorted  $\text{Co}_{(1)}$  site [see Fig. 1(b)]. Density-functional theory (DFT) calculations further suggest that this arrangement is stabilized when the  $\text{Co}_{(1)}$  orbital state hybridizes and the spin state becomes low-spin [15]. These findings highlight the crucial role of the  $\text{Co}_{(1)}$  site in governing the Jahn-Teller-driven distortions and orbital physics of  $\text{CaCoO}_2$ .

Nevertheless, the orbital configuration of the  $\text{Co}_{(1)}$  site, and its corresponding functionality in  $\text{CaCoO}_2$ , is unlikely to be simple [see Fig. 1(c)]. In a typical square-planar coordination with  $C_4$  local symmetry, the Co  $d$ -orbital configuration favors the  $x^2-y^2$  orbital, consistent with recent spectroscopic studies [15,18]. This description is appropriate for the  $\text{Co}_{(2,3)}$  sites. In contrast, the strong distortion at the  $\text{Co}_{(1)}$  site lowers the local symmetry to  $C_2$ , which enforces mixing between the  $x^2-y^2$  and other  $d$  orbitals, producing an orbital shape incompatible with the ideal square-planar field. Such orbital mixing and local distortions have been proposed to facilitate trimerlike arrangements via electrostatic (quadrupolar or dipolarlike) interactions between  $\text{Co}_{(1)}$  and neighboring  $\text{Co}_{(2)}$  sites [15]. Clarifying whether these distortions merely provide a convenient structural description or instead reflect a genuine collective state requires further experimental verification. In either case, understanding the role of  $\text{Co}_{(1)}$  in

mediating orbital hybridization and possible trimerization is central to unraveling the orbital physics of  $\text{CaCoO}_2$ , with potential implications for functional properties arising from the interplay of local distortions and collective ordering phenomena [19–23].

In this work, we focus on clarifying the orbital character of the distorted  $\text{Co}_{(1)}$  site in  $\text{CaCoO}_2$  and on understanding how it stabilizes collective ordering in this system. Using polarization-dependent resonant soft x-ray scattering (RSXS), we show that the  $\text{Co}_{(1)}$  site hosts a mixed  $x^2-y^2$  orbital character, whose hybridization plays a decisive role in mediating ordering phenomena. Static RSXS reveals two closely coupled orders emerging at the same in-plane wave vector,  $q \approx (1/4, 1/4)$ : a quasi-two-dimensional orbital order tied to the  $\text{Co}_{(1)}$  orbital; and a quasi-three-dimensional trimerlike order stabilized through charge redistribution across the Co sites. Their coexistence at an identical momentum transfer already indicates strong coupling between the orbital and trimer degrees of freedom. Time-resolved RSXS (tr-RSXS) further shows that both orders share nearly identical relaxation dynamics of approximately 400 femtoseconds, thus providing dynamical evidence that complements the static signatures of their coupling. Considering both static and dynamic results, our study reveals how local orbital hybridization and distortions propagate into cooperative electronic states in  $\text{CaCoO}_2$ . More broadly, this study illustrates how orbital-selective RSXS can uncover the microscopic degrees of freedom underlying molecular ordering phenomena in correlated oxides.

## II. RESULTS

### A. Spectroscopic signature of the Co<sub>(1)</sub> site

Considering the central importance of orbital physics in infinite-layer CaCoO<sub>2</sub>, we begin by investigating the Co *d*-orbital configuration, focusing in particular on the distorted Co<sub>(1)</sub> site, using polarization-dependent x-ray absorption spectroscopy (XAS). As shown in Fig. 1(d), a pronounced linear dichroism (LD) is observed between spectra measured with in-plane ( $E\parallel a$  or  $b$ ) and out-of-plane ( $E\parallel c$ ) polarizations. Negative and positive LD values reflect predominantly in-plane and out-of-plane components of the Co *d*-orbital states [24].

In a simple square-planar environment with  $C_4$  symmetry, such dichroism would be expected from the separation between  $x^2-y^2$  and  $3z^2-r^2$  orbitals, as is the case for the nearly undistorted Co<sub>(2,3)</sub> sites. However, the observed LD is significantly stronger and more complex than this undistorted picture can explain, implying that the distorted Co<sub>(1)</sub> site provides the dominant contribution. The lowered local symmetry ( $C_2$ ) at Co<sub>(1)</sub> enforces mixing between  $x^2-y^2$  and  $3z^2-r^2$ , giving rise to a hybrid orbital state.

To test this interpretation, we performed full multiplet cluster calculations for the Co<sub>(1)</sub> site. Using established parameters ( $U_{dd} = 5.0$ ,  $\Delta = 7.0$ ,  $U_{pd} = 6.5$ ,  $pd\sigma = -0.70$ , and  $pd\pi = 0.35$  eV; see Supplemental Material [17,25,26]), the calculation shows that the high-spin  $d^7$  ( ${}^4F_{9/2}$ ) configuration is disfavored and a low-spin ground state is stabilized.

In this distorted  $C_2$  environment, the unoccupied orbital is elongated toward the nearest oxygen atoms, resulting in a mixed orbital with approximately 75%  $x^2-y^2$  and 25%  $3z^2-r^2$  character, consistent with lowered-symmetry  $e_g$  mixing expected for a distorted square-planar field, as well as the mixed orbital character reported in other strongly correlated systems [27]. This hybridization naturally places the  $3z^2-r^2$  component at higher energy and reproduces the observed LD in Fig. 1(d), while the pure  $xy$  orbital remains at relatively lower energy. The overall configuration is consistent with the LD spectrum in Fig. 1(c), supporting the presence of a mixed ( $x^2-y^2 \oplus 3z^2-r^2$ ) orbital at the Co<sub>(1)</sub> site in a low-spin configuration. This analysis indicates that the distorted Co<sub>(1)</sub> site provides a dominant contribution to the linear dichroism response and is closely associated with the cooperative ordering phenomena discussed below. Since CaCoO<sub>2</sub> does not exhibit magnetic ordering, the observed linear dichroism in the XAS reflects orbital and structural anisotropy rather than magnetic contributions.

Here we clarify the scope of the spectroscopic interpretation used in this work. XAS, LD, and ligand-field calculations are employed as qualitative, symmetry-based tools for interpreting the experimental results, rather than for quantitative modeling of the full electronic structure.

In particular,  $L_3$ -edge XAS is not strictly orbital selective or site selective for a  $d^7$  configuration. While the LD signal is most sensitive to the distorted Co<sub>(1)</sub> environment, the measured XAS response remains site averaged and includes contributions from Co<sub>(2,3)</sub>. Accordingly, stronger LD should be interpreted as enhanced sensitivity to local anisotropy associated with symmetry lowering, rather than exclusive site selectivity. The assignment of Co<sub>(1)</sub> as the dominant contributor to the LD signal therefore follows from the combination of prior structural information and multiplet modeling, rather than from direct site-selective experimental isolation. Consistent with this scope, the ligand-field calculations are used in a deliberately limited manner to illustrate polarization-dependent trends and local symmetry effects relevant to the present spectroscopic analysis.

### B. Experimental validation of the mixed Co<sub>(1)</sub> orbital state

Building on the static LD and multiplet analysis in Fig. 1, we used time-resolved x-ray absorption spectroscopy (tr-XAS) to test whether the distorted Co<sub>(1)</sub> site indeed carries a mixed  $x^2-y^2 \oplus 3z^2-r^2$  orbital that governs the spectroscopic response. In a general pump-probe scheme [Fig. 2(a)], an optical pulse excites carriers across the optical gap, and a delayed ( $\Delta t$ ) soft-x-ray probe at the Co  $L_3$ -edge measures how the orbital-resolved unoccupied states evolve in time. Because the absorption at a fixed photon energy depends on both the transient orbital population and the dipole matrix element, tr-XAS provides orbital selectivity when combined with polarization control. To make the orbital contrast explicit, we monitored two representative photon energies chosen from the static dichroism and supported by the multiplet calculation [Fig. 1(c)]. The feature at  $E = 777.0$  eV emphasizes predominantly in-plane states with strong  $xy$  weight (characteristic of the nearly all square-planar environments). For  $E = 778.8$  eV case, it is more sensitive to the mixed  $x^2-y^2 \oplus 3z^2-r^2$  state where is relevant to the distorted Co<sub>(1)</sub> site, revealed most clearly with an out-of-plane probe component. We note that the orbital sensitivity associated with these selected photon energies is qualitative rather than exclusive: both energies contain mixed orbital contributions, and the assignment relies on spectral trends supported by multiplet calculations.

Figure 2(b) shows an expected dynamics for these two differences of orbital characteristic based on the free energy framework. The observed differences in response amplitude and recovery times can be qualitatively discussed in terms of the orbital character emphasized at different probe energies. When the probe is sensitive to states with predominantly in-plane character and higher local symmetry, the photoinduced response tends to be stronger and the recovery faster. In contrast, when the probe emphasizes

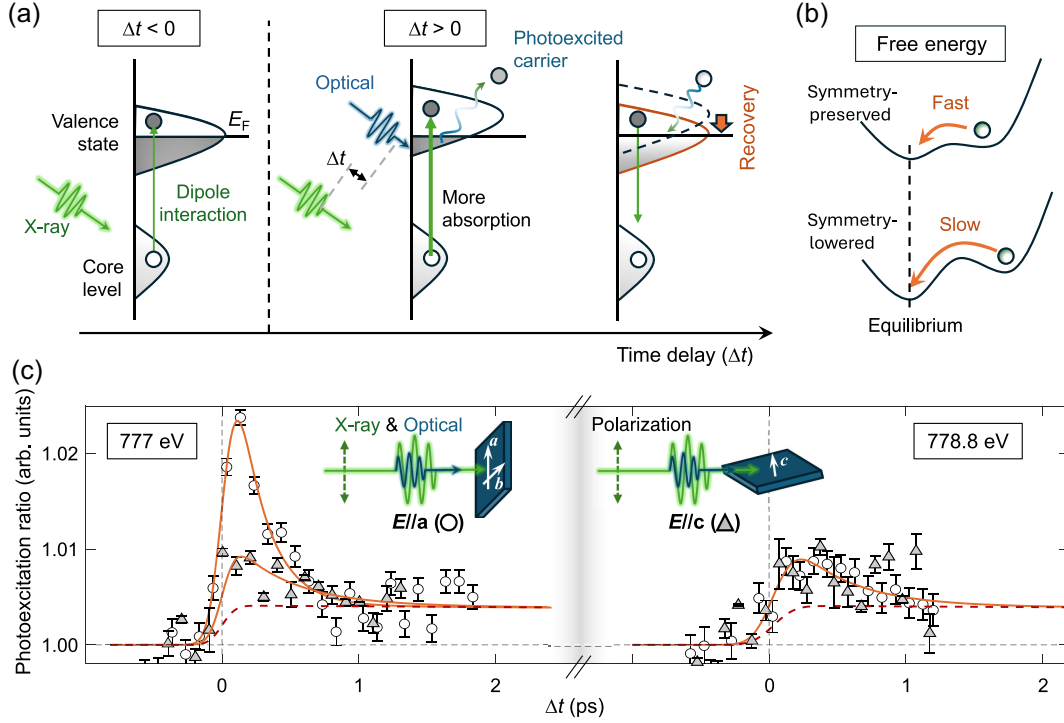


FIG. 2. Time-resolved XAS used to experimentally confirm the mixed  $\text{Co}_{(1)}$  orbital. (a) Schematic of the pump-probe process. For  $\Delta t < 0$ , an x-ray pulse probes the  $\text{Co } 2p \rightarrow 3d$  dipole transition into unoccupied  $3d$  states; the absorption amplitude at a given photon energy reflects the orbital-resolved hole population and the dipole matrix element. For  $\Delta t > 0$ , a 3.1 eV optical pump excites carriers across the gap, transiently modifying the  $3d$  hole distribution and the corresponding x-ray absorption. The schematic depicts a temporary enhancement followed by recovery as carriers relax. (b) Conceptual free-energy landscape illustrating two representative relaxation channels. A symmetry-preserved (single-orbital) channel couples efficiently to decay pathways, yielding a strong, fast response, whereas a symmetry-lowered (hybridized) channel relaxes more slowly through charge and lattice redistribution. This schematic does not imply a thermodynamic transition. (c) Polarization-resolved tr-XAS transients at representative photon energies. Symbols (circles and triangles for  $E||a$  and  $E||c$ ) show the photoexcitation ratio  $I(\Delta t)/I_{\Delta t < 0}$  at 777.0 eV (left) and 778.8 eV (right). Solid curves are fits including the instrumental response; dashed lines indicate thermal contributions. The in-plane ( $E||a$ ) signal shows a stronger and faster recovery, while the out-of-plane ( $E||c$ ) signal, dominated by the mixed  $\text{Co}_{(1)}$  orbital, exhibits a weaker but slower relaxation.

states associated with a symmetry-lowered environment at the  $\text{Co}_{(1)}$  site, where the wave functions have mixed  $x^2-y^2 \oplus 3z^2-r^2$  character, the response is weaker and the recovery slower. We stress that this comparison is phenomenological in nature and is intended to provide a qualitative physical picture linking orbital character and relaxation behavior, rather than to identify specific decay pathways or a uniquely defined energy landscape. This phenomenological use of time-resolved x-ray absorption spectroscopy to correlate spectral sensitivity with relaxation behavior follows the established interpretive framework of tr-XAS studies in correlated materials [28,29].

The resulting transients in two different polarizations are shown in Fig. 2(c). Experimental geometries are depicted in the insets. The optical gap of this material was measured to be approximately 1.6 eV (see Supplemental Material [17]). To probe photoexcited effects, we used a 3.1 eV optical pump energy to ensure efficient above-gap excitation of the  $\text{CaCoO}_2$  film during the time-resolved experiments, with a pump fluence of  $2.1 \text{ mJ/cm}^2$  well below the threshold

fluence ( $\sim 7 \text{ mJ/cm}^2$ ) where thermal effects become significant (see Ref. [17]). Note that transient traces were fit by convolving single-exponential decays within the instrument resolution ( $\sim 100 \text{ fs}$ ). Experiential details are provided in the Appendix. At 777.0 eV, the transient response depends strongly on probe polarization. With  $E||a$ , the signal exhibits a large amplitude and a rapid recovery, with a fitted time constant of  $\tau = 207 \pm 5 \text{ fs}$ . This reflects excitation into a single-orbital-dominated, symmetry-preserved pathway that couples efficiently to decay channels. Note that the initial rise near  $\Delta t \sim 0$  is indistinguishable within our statistical accuracy for all cases, consistent with the  $\sim 100 \text{ fs}$  temporal resolution [30]. In contrast, with  $E||c$  at the same energy, the response is weaker and relaxes more slowly, indicating that the out-of-plane probe emphasizes hybridized orbital contributions and a more complex redistribution pathway. At 778.8 eV, where the distorted  $\text{Co}_{(1)}$  site is expected to be contributed through a mixed  $x^2-y^2 \oplus 3z^2-r^2$  orbital character, both in-plane and out-of-plane polarizations converge to a slower recovery of  $\tau = 405 \pm 5 \text{ fs}$ .

Taken together, the polarization- and energy-selective tr-XAS results experimentally establish the mixed orbital character at the distorted  $\text{Co}_{(1)}$  site, consistent with the static LD and multiplet calculations in Fig. 1. This validates that  $\text{Co}_{(1)}$  does not simply host a conventional square-planar orbital but instead carries a hybridized  $x^2-y^2 \oplus 3z^2-r^2$  state. Such an orbital configuration naturally couples to lattice distortions and charge redistribution, making  $\text{Co}_{(1)}$  the key site that mediates cooperative phenomena. These spectroscopic insights motivate a direct investigation of how the  $\text{Co}_{(1)}$  orbital character stabilizes collective ordering in  $\text{CaCoO}_2$ .

### C. Exploring collective orderings in $\text{CaCoO}_2$

Having established in the discussion surrounding Figs. 1 and 2 that the distorted  $\text{Co}_{(1)}$  site hosts a mixed  $x^2-y^2 \oplus 3z^2-r^2$  orbital, we now explore whether such orbital physics couples to a collective ordering. In addition, considering the reported geometrical frustration of the  $Q_2$ -JTE in this system [15], the orbital character could undergo a zigzag pattern in the  $\text{CoO}_2$  planar layer and could stabilize trimer-like arrangements through dipolar interactions between  $\text{Co}_{(1)}$  and neighboring  $\text{Co}_{(2)}$  sites as shown in Figs. 1(a) and 1(b), expecting a superstructure reflection around  $(h, k) \sim (\pm 1/4, \pm 1/4)$ . Using resonant soft x-ray scattering (RSXS) [31], we investigate such a reflection. For this study, we tuned the incident x-ray photon energy around the Co  $L$ -edge since this corresponds to a symmetry-forbidden reflection [15].

Figure 3(a) shows the scattering geometry (see the Appendix). Since the putative reflection at  $(1/4, 1/4)$  lies within the  $\text{CoO}_2$  planar layer, the scattering plane was aligned nearly parallel to the crystal  $ab$  plane. We measured the diffracted intensity under both  $\pi$  and  $\sigma$  incident polarizations ( $\epsilon$ ). Within the electric-dipole ( $E1$ – $E1$ ) formalism [32–35], the scattered intensity can be expressed as

$$I(Q, E; \epsilon_{\text{in}} \rightarrow \epsilon_{\text{out}}) \propto |\epsilon_{\text{out}}^T \mathbf{F}(Q, E) \epsilon_{\text{in}}|^2, \quad (1)$$

where  $\mathbf{F}$  is the resonant scattering tensor, discussed here at the level of its symmetry properties. Within the standard tensor formalism of resonant elastic x-ray scattering, the polarization dependence is governed by the anisotropic (traceless) components of the resonant scattering tensor under a given experimental geometry [32,34,36,37]. This consideration is qualitative in nature and follows from the general form of the resonant scattering cross section, rather than from a detailed microscopic or numerical calculation. If the ordering were dominated by a single anisotropic  $e_g$  orbital at the distorted  $\text{Co}_{(1)}$  site, the leading contribution would arise from this traceless component, which couples most strongly to cross-polarized geometries. Accordingly, comparable responses in the  $\pi \rightarrow \sigma'$  and  $\sigma \rightarrow \pi'$  channels

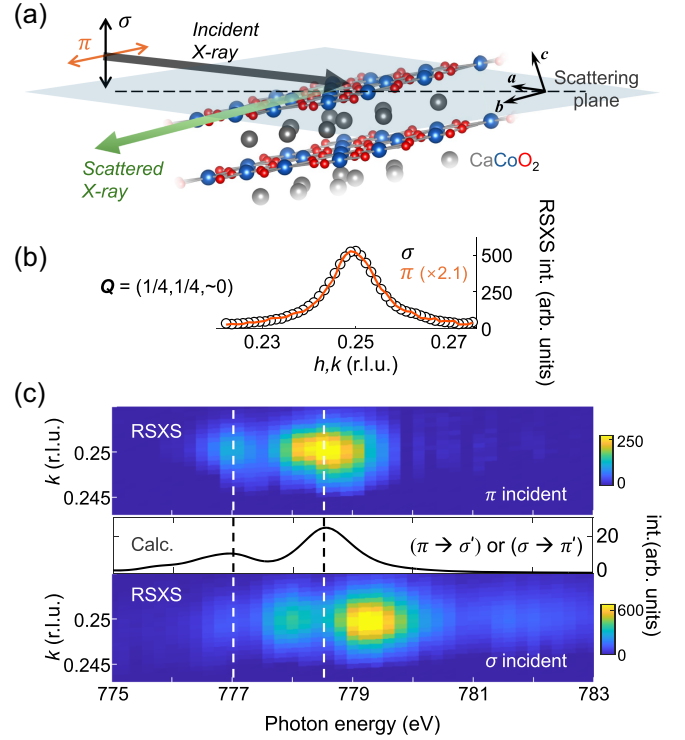


FIG. 3. RSXS measurement for collective ordering in  $\text{CaCoO}_2$ . (a) Experimental scattering geometry. Incident  $\pi$ - or  $\sigma$ -polarized soft x-rays are directed onto the  $\text{CaCoO}_2$  film, and the diffracted intensity is collected in the scattering plane. (b) Momentum scan along  $h$  at  $Q = (1/4, 1/4, \sim 0)$  shows a well-defined superlattice peak. The peak is strongly enhanced under  $\pi$  incident polarization, consistent with an orbital-selective origin. (c) Photon-energy dependence of the RSXS signal around the Co  $L_3$  edge. Color maps display the scattered intensity as a function of photon energy and momentum transfer for  $\pi$  (top) and  $\sigma$  (bottom) incident polarizations. The resonance is maximized near 777.5–778.5 eV, and its polarization dependence agrees well with multiplet calculations (middle), supporting the assignment to a collective order involving the mixed  $\text{Co}_{(1)}$  orbital state. The extended high-energy tail in the  $\sigma$  channel reflects contributions from hybridized Co–O states.

can be qualitatively anticipated for our experimental configuration.

Since the scattered polarization was not analyzed, the measured intensity under each incident polarization represents a sum of both cross- and co-polarized channels, with their relative weights determined by the scattering geometry. As shown in Fig. 3(b), the experiment indeed reveals a reflection at the putative  $(1/4, 1/4, \sim 0)$  position, consistent with the expectation of orbital ordering tied to the mixed  $x^2-y^2 \oplus 3z^2-r^2$  character of the  $\text{Co}_{(1)}$  site, consistent with previous observations at the same in-plane wave vector [18]. The calculated orbital-order profile reproduces well the  $\pi$ -incident spectrum, confirming that this channel predominantly captures the  $\text{Co}_{(1)}$  orbital contribution. However, the data also show a pronounced asymmetry:

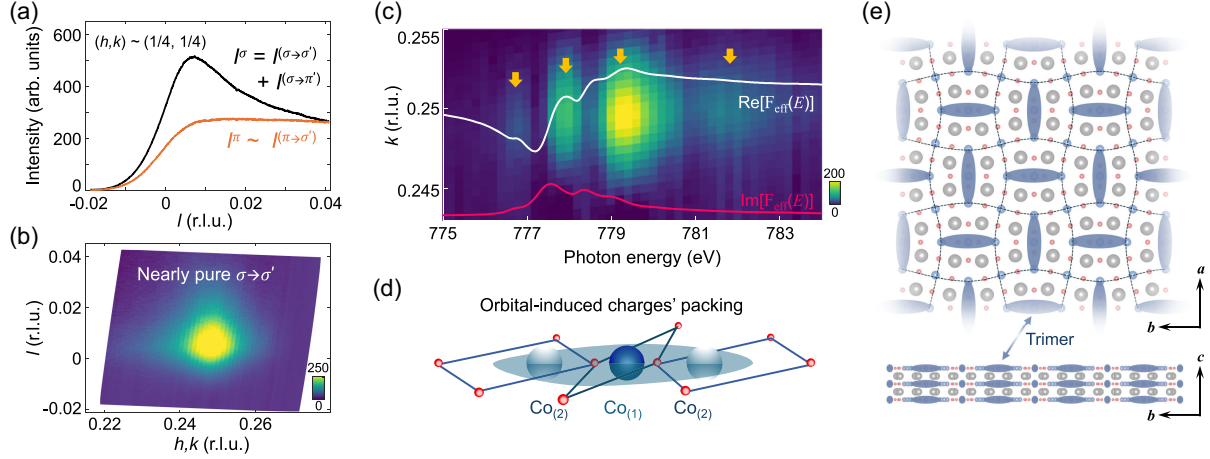


FIG. 4. Signature of trimer ordering in  $\text{CaCoO}_2$ . (a)  $l$  dependence of the  $(1/4, 1/4, l)$  reflection measured with  $\sigma$  (black) and  $\pi$  (orange) incident polarization, revealing distinct dimensional characteristics despite sharing the same in-plane modulation vector  $\sim(1/4, 1/4)$ . (b) Reciprocal-space map of the nearly pure  $\sigma \rightarrow \sigma'$  scattering channel, obtained by subtracting the  $\pi$ -incident  $\sim(\pi \rightarrow \sigma')$  contribution from the  $\sigma$ -incident ( $\sigma \rightarrow \pi' + \sigma \rightarrow \sigma'$ ) signal. The result highlights a well-confined three-dimensional pattern. (c) Extracted a resonant profile of the nearly pure  $\sigma \rightarrow \sigma'$  channel. Arrows mark four pronounced resonant energies (776.8, 778, 779.2, and 781.8 eV). Overlaid curves show the imaginary ( $\text{Im}[F_{\text{eff}}(E)]$ , red) and real ( $\text{Re}[F_{\text{eff}}(E)]$ , white) parts of the scattering factor. (d) Schematic illustration of orbital-induced charge packing. Local dipole arrangements associated with displaced  $\text{Co}_{(2)}$  sites stabilize trimerized molecular units centered at the distorted  $\text{Co}_{(1)}$  site. Elliptical shading denotes the effective trimer packing. (e) Cartoon of the long-range arrangement of trimer molecules within the Co layer: top view in the  $ab$  plane (top panel) and side view in the  $bc$  plane (bottom panel). This schematic illustrates the 3D connectivity of the trimer-based charge order across Ca spacers; the orbital-order dimensionality is inferred from the  $l$  dependence discussed in the text.

the  $\sigma$ -incident channel yields nearly twice the intensity of the  $\pi$ -incident case and, moreover [Fig. 3(c)], exhibits an extended resonance tail at higher energies where Co-O hybridized states dominate the XAS continuum [38–40]. This behavior is difficult to reconcile with a simple Co-multiplet orbital-order picture and points to an additional contribution beyond orbital anisotropy.

These observations indicate that the  $(1/4, 1/4, 0)$  reflection cannot be explained by a single-orbital ordering picture alone, as anticipated from the tensor form above. The  $\pi$ -incident channel is consistent with orbital order tied to the mixed orbital character of  $\text{Co}_{(1)}$ , whereas the anomalously strong and extended  $\sigma$ -incident signal indicates that additional collective degrees of freedom are involved. In particular, the coupling to higher-energy Co-O hybridized states suggests a charge-redistribution component beyond a purely orbital multiplet scenario. These polarization-dependent signatures indicate that the observed ordering cannot be attributed to orbital effects alone, but instead involves additional contributions such as charge redistribution.

#### D. Identifying the scattering feature in $\sigma$ incidence

Considering the previous RIXS measurement on  $\text{CaCoO}_2$  [18], where an ordering feature was observed using  $\pi$  polarization and a large scattering angle ( $2\theta \approx 150^\circ$ ), the  $(1/4, 1/4)$  reflection can be regarded as a quasi-two-dimensional modulation confined to the  $\text{CoO}_2$

planes. This is because, in our RSXS geometry with the detector set close to  $90^\circ$ , the probed  $l$  component differs substantially, which allows us to directly probe correlations along the  $c$  axis under both incident polarizations. Beyond the intensity contrast and resonance profile asymmetry identified in Fig. 3, this dimensional analysis provides additional insight into the origin of the anomalous  $\sigma$ -incident feature.

Figure 4(a) shows the  $l$  dependence of the reflection for both incident polarizations. As expected, the  $\pi$ -incident case displays a broad profile along  $l$ , consistent with a quasi-two-dimensional modulation confined to the  $\text{CoO}_2$  planes. In comparison, the  $\sigma$ -incident reflection exhibits a much narrower  $l$  profile around  $l \approx 0$ , indicating enhanced interlayer coherence at the same in-plane wave vector. This behavior suggests that, while maintaining a quasi-two-dimensional modulation associated with the  $\pi \rightarrow \sigma'$  orbital-order channel, the  $\sigma$  incidence contains an additional contribution that drives enhanced interlayer coherence. Because the trimerlike charge redistribution couples to local dipole moments, the  $\sigma$ -polarized geometry, sensitive to the parallel ( $\sigma \rightarrow \sigma'$ ) component of the scattering tensor, maximizes charge-scattering sensitivity in this configuration [32–35]. This motivates us to decompose the scattering tensor for a more detailed assessment of this possibility.

To assess the additional contribution in the  $\sigma$  channel, we revisit the scattering tensor decomposition introduced in Eq. (1):

$$\mathbf{F}(Q, E) = f_c(E) + \mathbf{f}^Q(E) + i\mathbf{f}^M(E),$$

where  $f_c$  is the isotropic scalar (charge-like) term,  $\mathbf{f}^Q$  the symmetric traceless tensor associated with orbital anisotropy, and  $\mathbf{f}^M$  the antisymmetric magnetic term [32,33]. As discussed above in Fig. 3,  $\mathbf{f}^Q$  primarily contributes to the cross-polarization channels. Although density-functional calculations have suggested that a low-spin configuration of  $\text{Co}_{(1)}$  may suppress long-range magnetism in  $\text{CaCoO}_2$  [15], no experimental evidence for magnetic order has been reported to date. Thus, we treat  $\mathbf{f}^M$  as negligible for the present discussion. Meanwhile,  $f_c$  enhances the parallel channels ( $\pi \rightarrow \pi'$ ,  $\sigma \rightarrow \sigma'$ ), making them the natural fingerprint of charge-redistribution effects. In our scattering geometry, however, the  $\pi \rightarrow \pi'$  contribution is strongly suppressed by polarization selection rules (see Supplemental Material [17]), due to the near-orthogonality between the incident and scattered polarization vectors ( $\epsilon_{\text{in}}$  and  $\epsilon_{\text{out}}$ ). As a result, the  $\sigma$ -incident signal necessarily contains a substantial admixture of the  $\sigma \rightarrow \sigma'$  channel in addition to the  $\sigma \rightarrow \pi'$  contribution. Taking the difference,  $I^{\sigma \rightarrow \sigma'} \approx I_{\text{inc}}^{\sigma} - I_{\text{inc}}^{\pi}$ , provides a practical estimate of a nearly pure  $\sigma \rightarrow \sigma'$  response.

The resulting map, shown in Fig. 4(b), exhibits a well-confined three-dimensional profile in reciprocal space, indicating that the ordering in  $\text{CaCoO}_2$  contains a nearly pure chargelike component, as expected for a dominant  $\sigma \rightarrow \sigma'$  contribution. However, a residual contribution from orbital anisotropy cannot be fully excluded. Because the outgoing polarization is not analyzed, this procedure assumes comparable crossed-channel intensities,  $I^{\sigma \rightarrow \pi'} \sim I^{\pi \rightarrow \sigma'}$ , and should therefore be regarded as an effective, rather than exact, separation of polarization channels.

Figure 4(c) shows the resonant profile of the extracted  $\sigma \rightarrow \sigma'$  channel. As seen in the  $\sigma$ -incident spectrum of Fig. 3(c), this channel exhibits a stronger overall resonance than the  $\pi$ -incident case and extends toward higher energies. Within this broad structure, four pronounced resonances appear at 776.8, 778.0, 779.2, and 781.8 eV (arrows), reflecting the mixed Co-O charge character of this resonance. Consistent with the polarization-extinction geometry discussed above, charge scattering is strongly suppressed in the  $\pi$ -polarization channel. As a result, the  $\sigma$ -polarization channel remains sensitive to charge-related excitations, accounting for the extended high-energy tail observed here. The correspondence with this substantial spectral weight, rather than with the multiplet-dominated envelope emphasized in XAS, indicates that the  $\sigma \rightarrow \sigma'$  channel's contribution is not governed by orbital anisotropy alone. To illustrate this point, we overlay the dispersive (Re: real) and absorptive (Im: imaginary) components of the effective form factor,  $\mathbf{F}_{\text{eff}}(E) \equiv \epsilon_{\text{out}}^T \mathbf{F}(Q, E) \epsilon_{\text{in}}$  [41]. As expected,  $\text{Re}[\mathbf{F}_{\text{eff}}(E)]$  exhibits anomalous dispersive features that align with the four resonant energies and

extend with a broad tail into the hybridized region, while  $\text{Im}[\mathbf{F}_{\text{eff}}(E)]$  closely reproduces the orbital-selective multiplet structure seen in XAS.

Given that the  $\sigma \rightarrow \sigma'$  channel reveals a charge-sensitive component coupled to Co-O hybridization, the additional contribution can be understood as local dipolar-like charge redistributions centered on the distorted  $\text{Co}_{(1)}$  sites (consistent with quadrupolar interactions inferred from structural refinements units [15,16]) can stabilize trimerlike molecular motifs [Fig. 4(d)]. When such charge arrangements propagate through the lattice, they naturally couple across the Ca spacer and develop appreciable three-dimensional coherence [Fig. 4(e)], consistent with RIXS evidence for enhanced Co-Ca interlayer coupling [18]. Meanwhile, the orbital order detected in the  $\pi$  channel remains quasi-two-dimensional, as evidenced by its rodlike  $l$  dependence without a pronounced peak in the scattering signal [Fig. 4(a)], indicating negligible interlayer coherence. This behavior contrasts with the trimer-based charge order, which exhibits a well-defined peak structure along  $l$  direction, signaling finite three-dimensional coherence across the Ca spacer layers, as illustrated schematically in Fig. 4(e).

This misalignment weakens the stacking pathway and prevents long-range correlations, yielding the broad  $l$  profiles observed under  $\pi$  incidence. In this context, while orbital anisotropy produces a primarily two-dimensional modulation (seen in the  $\pi \rightarrow \sigma'$  and  $\sigma \rightarrow \pi'$  channels), the additional  $\sigma \rightarrow \sigma'$  signal reflects a charge-ordering tendency that promotes three-dimensional coherence.

### E. Dynamics of charge vs orbital ordering

The static RSXS results already establish a clear polarization asymmetry. The  $\pi$  channel reflects orbital anisotropy tied to  $\text{Co}_{(1)}$  sites, whereas the  $\sigma$  channel contains an additional charge-sensitive contribution with enhanced interlayer coherence. To complement the static analysis and clarify the nature of the  $\sigma$  component, we turned to time-resolved RSXS (tr-RSXS) measurements. In a collective charge arrangement spanning multiple sites, the relaxation dynamics are expected to remain uniform across different resonant energies [42–47], whereas orbital order should display orbital-selective responses.

Figure 5(a) shows the tr-RSXS results at the  $(1/4, 1/4, \sim 0)$  reflection under  $\sigma$  incidence (see the Appendix). The dynamics were measured at the four distinct resonances identified in Fig. 4: 776.8, 778.0, 779.2, and 781.8 eV. As expected, all four features exhibit nearly identical behavior within experimental resolution, yielding a characteristic relaxation time of  $\sim 400$  fs ( $391 \pm 5$  fs) uniformly across all Co resonances. This relaxation time is obtained from single-exponential fits convolved with the experimental time resolution, as detailed in Figs. S9 and S10 of the Supplemental Material [17]. The resonant profiles measured at  $\Delta t < 0$  and  $\Delta t = 0.5$  ps, and their difference

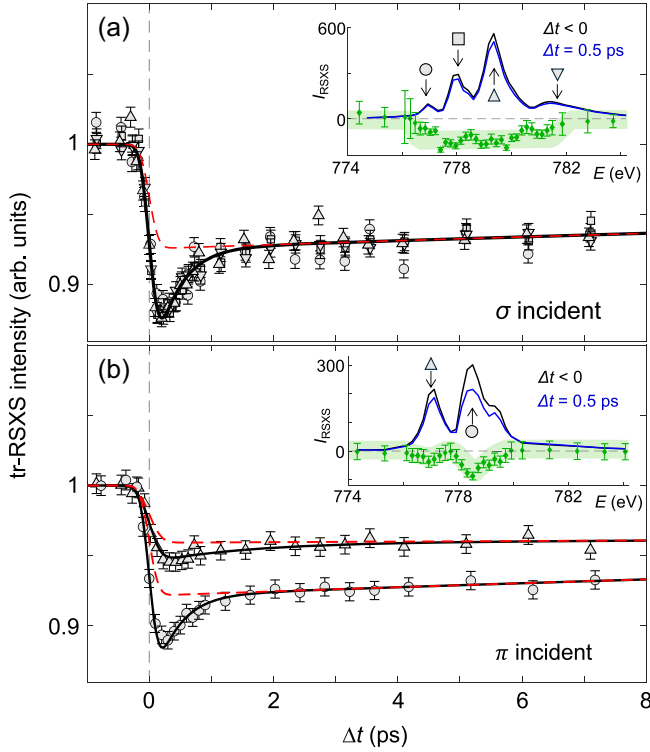


FIG. 5. Dynamics of charge and orbital ordering. (a) Tr-RSXS response under  $\sigma$  incidence. Solid curves are exponential fits (see Supplementary Material [17]); red dashed lines denote estimated thermal effects. Inset: integrated resonant profiles at  $\Delta t < 0$  (black) and  $\Delta t = 0.5$  ps (blue) and their scaled difference (green). Dynamics are uniform across all four resonant energies. Arrows mark four pronounced resonant energies: 776.8 eV (circle), 778.0 eV (square), 779.2 eV (up-triangle), and 781.8 eV (down-triangle). Photoexcited dynamics are uniform across all four energies. (b) Tr-RSXS response of the orbital channel, measured under  $\pi$  incidence at two representative resonant energies: 777 eV (dominated by  $xy$  character of  $\text{Co}_{(1)}$ ) and 778.8 eV (dominated by mixed  $x^2-y^2 \oplus 3z^2-r^2$  character of  $\text{Co}_{(1)}$ ). The inset shows integrated resonant profiles and their difference, highlighting the distinct dynamics at the two energies.

[see the inset of Fig. 5(a)], further support the uniform response across energies. These results indicate that the  $\sigma$  response, dominated by the  $\sigma \rightarrow \sigma'$  channel, originates from a collective charge arrangement spanning multiple sites, consistent with the trimerlike order inferred from the static data.

With  $\pi$  incidence, which probes the orbital-order channel dominated by the distorted  $\text{Co}_{(1)}$  sites, the dynamics depend strongly on photon energy [see Fig. 5(b)]. The inset further illustrates this contrast by comparing integrated resonant profiles at  $\Delta t < 0$  and  $\Delta t = 0.5$  ps. Their difference shows that spectral weight is redistributed in an energy-dependent way, underscoring that the orbital-order response is not uniform but orbital selective. For example, the feature near 777 eV relaxes more slowly ( $\sim 1.6$  ps), whereas the mixed  $x^2-y^2 \oplus 3z^2-r^2$  resonance at 778.8 eV

relaxes on the same timescale of  $391 \pm 5$  fs as the charge-sensitive  $\sigma$  channel. Interestingly, this trend is opposite to what was observed in the local XAS dynamics (Fig. 2), where the 777 eV feature relaxed faster owing to symmetry preservation and efficient coupling to the lattice. In the RSXS ordering case, however, the same  $xy$  states are constrained by intersite correlations and lattice coherence, which slows their recovery. Particularly, the dynamics of the mixed orbitals matches the charge-sensitive  $\sigma$  channel, highlighting that orbital order couples to the lattice in an orbital-selective way, while the mixed  $\text{Co}_{(1)}$  orbitals provide the bridge that ties orbital anisotropy to the collective charge-order dynamics.

While the transient XAS signal in Figs. 5(a) and 5(b) reveals a redistribution of spectral weight after optical excitation, we do not observe the emergence of new peaks or distinct energy shifts within the present time resolution and energy range. This behavior differs from recent tr-XAS studies of NiO, where photoexcitation induces clear spectral transients linked to local energy shifts and new features [48]. A systematic energy-resolved tr-XAS mapping of  $\text{CaCoO}_2$  would be highly valuable to further elucidate the microscopic origin of these dynamics, and represents an important direction for future work.

Viewed collectively, these results further support a coherent picture in which the  $\sigma$  channel captures a collective charge-ordering tendency with three-dimensional coherence, while the  $\pi$  channel reflects orbital anisotropy that remains quasi-two-dimensional and orbital-selective. The convergence of the mixed-orbital dynamics in the  $\pi$  channel with the uniform charge dynamics in the  $\sigma$  channel suggests that the distorted  $\text{Co}_{(1)}$  environment acts as the microscopic bridge that intertwines orbital order with emergent charge correlations. This dynamical link provides a framework for understanding how local orbital distortions evolve into trimerlike collective order, reinforcing the interpretation developed from the static measurements. Such cooperative behavior naturally arises from the shared electronic states across the  $\text{Co}_{(1-3)}$  sites, which are mediated by exchange interactions [49–51], lattice coupling [19,20,52–55], and local symmetry constraints [56–58].

### III. CONCLUSION AND OUTLOOK

Our results demonstrate that trimerized Co units in  $\text{CaCoO}_2$  act as a fundamental structural and electronic building block that governs the macroscopic properties of the material. Orbital hybridization plays a stabilizing role, reinforcing the pre-formed trimer arrangement rather than initiating its formation. The dynamics of the trimer order reflect a collective electronic state that extends across the lattice, supported by strong interactions among the three Co sites.

The coexistence of quasi-three-dimensional trimer order with quasi-two-dimensional orbital order further shows that

the trimer unit mediates between different dimensional interactions in  $\text{CaCoO}_2$ . This dimensional interplay is likely crucial for the robust insulating state of the material, because the trimer structure suppresses charge hopping both within the  $\text{CoO}_2$  planes and across layers, leading to strong localization of carriers [15,42,49]. In this way, the trimer stabilizes the overall structure through cooperative charge redistribution and orbital-lattice coupling.

The emergence of trimerization also highlights the intertwined roles of geometric frustration and the JTE in defining the fundamental unit. The JTE induces strong local distortions in  $\text{CoO}_4$  units, while geometric constraints within the infinite-layer structure prevent these distortions from propagating freely. Instead, they self-organize into a periodic trimer pattern that minimizes strain and electrostatic energy. In this sense, the observed state is better described as a Jahn-Teller order of trimer units rather than a simple atomic JTE frustrated by lattice geometry. This explains why the trimerized molecules behave as a fundamental unit, with both charge and orbital configurations strongly cooperative and synchronized.

In summary, our comprehensive resonant x-ray scattering study reveals how orbital physics, charge order, and lattice geometry intertwine in  $\text{CaCoO}_2$ . The trimer units are stabilized through Co-O-Ca orbital hybridization and form a collective charge-ordered state. More broadly, this work shows how geometric frustration, Jahn-Teller distortions, and orbital hybridization can cooperate to produce localized molecular building blocks that dictate macroscopic properties. These insights suggest new routes for designing complex oxides in which engineered trimer or other molecular units may enable novel quantum functionalities.

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## DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

## APPENDIX: MATERIALS AND METHODS

### 1. Material preparation

High-quality  $\text{CaCoO}_2$  films were obtained by topotactic reduction of brownmillerite  $\text{CaCoO}_{2.5}$  films, which were deposited on  $\text{SrTiO}_3$  (001) substrates via pulsed laser deposition (PLD) as described in Ref. [15]. To prevent degradation during and after the reduction process, the as-deposited  $\text{CaCoO}_{2.5}$  films were capped with a protective layer of five unit cells of  $\text{SrTiO}_3$ . These precursor  $\text{CaCoO}_{2.5}$  films were then reduced to  $\text{CaCoO}_2$ , validated using Co  $L$ -edge XAS measurements (see Supplemental Material [17]). The insulating transport properties of these samples were consistent with previously reported results in Ref. [15].

### 2. RSXS measurements

Static resonant scattering experiments at the Co  $L$ -edge, including the spectroscopic measurements such as XAS and LD, were conducted at beamline 13-3 of the Stanford Synchrotron Radiation Lightsources (SSRL). The sample was mounted on a custom in-vacuum 4-circle diffractometer [31]. To access both the trimer and orbital ordering, the sample surface, which is perpendicular to the  $c$ -axis, was positioned within the near scattering plane. Detailed scattering geometries are described in the Supplemental Material [17]. By controlling the incident x-ray polarization (either vertical or horizontal), both charge and orbital order were selectively explored (see the polarization extinction section in [17]). Note that the thin film structure made the exact  $l = 0$  reciprocal lattice unit (r.l.u.) inaccessible. Instead, by tilting the sample by approximately  $5^\circ$  within the scattering plane, the  $q$  vector at  $(1/4, 1/4, \sim 0)$  was accessed. For XAS measurements, the sample surface was aligned within the scattering plane, and the angle between the  $c$ -axis and the incident x-ray was set to  $60^\circ$  to measure the LD signal (i.e.,  $E\|c$  and  $E\|ab$ ) by varying the incident x-ray polarization.

### 3. tr-XAS and tr-RSXS measurements

The dynamic experiments, i.e., tr-RSXS and tr-XAS measurements, were carried out at the RSXS end station of PAL-XFEL [30]. The sample was mounted on a six-axis manipulator and measured at room temperature. The surface of the sample faced horizontally or down, and measurements were performed in two different scattering geometries: vertical and horizontal scattering planes. These

configurations were achieved using a fixed horizontal incident x-ray polarization, allowing sensitivity to  $\sigma$ - and  $\pi$ -polarized components, respectively. Detailed scattering geometries are described in the Supplemental Material [17]. X-ray pulses with a duration of  $\sim 80$  fs and a 60 Hz repetition rate were used as the probe (ultimate instrumental resolution  $\sim 100$  fs).

Given the estimated band gap of  $\sim 1.6$  eV, a 3.1 eV (400 nm) optical laser pump with 50 fs pulse duration and  $p$  polarization, generated by a Ti:sapphire laser, was employed (see more details in Supplemental Material [17]). Note that 800 nm laser pulses were used to test the photoexcitation. A pump fluence of about  $2.1 \text{ mJ/cm}^2$  was primarily used to minimize a thermal effect (see more details in Supplemental Material [17]). The time delay between the pump and probe pulses was controlled using a mechanical delay stage. X-ray scattering signals, including tr-XAS fluorescence yield (FY) signals, were collected using an avalanche photodiode (APD) and recorded with high-speed digitizers for shot-to-shot analysis.

#### 4. Multiplet calculation

To refine the orbital sensitivity and interpret the LD in XAS spectra, we performed systematic configuration interaction (CI) model calculations [59]. These calculations include full atomic multiplets and crystal field splitting, reproducing the fine structure of the XAS spectrum, including the LD line shape. In highly distorted  $\text{CoO}_4$  square-planar configurations, particularly for the  $\text{Co}_{(1)}$  state with significant orbital anisotropy, the XAS LD exhibits a strong mixture of orbital contributions.

Multiplet calculation for Co 3d orbitals in undistorted ( $C_4$  symmetry) and distorted ( $C_2$  symmetry) environments: In the undistorted square-planar case, the orbital hierarchy follows  $E(x^2-y^2) > E(xy) > E(yz, zx) \approx E(3z^2-r^2)$ , and no orbital mixing occurs. Upon distortion to  $C_2$  symmetry,  $x^2-y^2$  and  $3z^2-r^2$  orbitals hybridize  $[(Y_2^+ + Y_2^-)/\sqrt{2} \leftrightarrow Y_2^0]$ , forming a mixed state of approximately 75%  $x^2-y^2$  and 25%  $3z^2-r^2$  character. Multiplet cluster calculations reproduce this polarization dependence and confirm that  $\text{Co}_{(1)}$  adopts a mixed orbital character in a low-spin configuration (see more in Supplemental Material [17]). Also, the cluster-model calculation [59] using  $U_{dd} = 5.0$ ,  $\Delta = 7.0$ ,  $U_{pd} = 6.5$ ,  $pd_\sigma = -0.70$ , and  $pd_\pi = 0.35$  eV reproduces the low-spin  $\text{Co}^{2+}$  configuration shown in Fig. 1.

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