
Quantum coherence tomography of light-controlled superconductivity

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Supplementary Information for Quantum Coherence Tomography of Light–Controlled Superconductivity

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Supplementary Note 1: Gauge-Invariant Theory of THz-MDCS Coherent Nonlinear Spectra in Multi-band Superconductors

In thin film superconductors, electromagnetic propagation effects combined with strong SC nonlinearity modify the effective driving electric field from that of the THz laser pulse. This effective driving field accelerates the condensate, which results in a finite Cooper pair center-of-mass momentum that persists well beyond the duration of the laser pulse. To model these time-dependent effects in a gauge-invariant way, we use the Bogoliubov-de Gennes Hamiltonian [1, 2]

$$H = \sum_{\nu, \alpha} \int d^3\mathbf{x} \psi_{\alpha, \nu}^\dagger(\mathbf{x}) [\xi_\nu(\mathbf{p} + e\mathbf{A}(\mathbf{x}, t)) - \mu - e\phi(\mathbf{x}, t) + \mu_H^\nu(\mathbf{x}) + \mu_F^{\alpha, \nu}(\mathbf{x})] \psi_{\alpha, \nu}(\mathbf{x}) - \sum_{\nu} \int d^3\mathbf{x} [\Delta_\nu(\mathbf{x}) \psi_{\uparrow, \nu}^\dagger(\mathbf{x}) \psi_{\downarrow, \nu}^\dagger(\mathbf{x}) + \text{h.c.}] , \quad (1)$$

where the fermionic field operators $\psi_{\alpha, \nu}^\dagger(\mathbf{x})$ and $\psi_{\alpha, \nu}(\mathbf{x})$ create and annihilate an electron characterized by the spin index α and the band index ν ; $\xi_\nu(\mathbf{p} + e\mathbf{A}(\mathbf{x}, t))$ is the band dispersion, with momentum operator $\mathbf{p} = -i\nabla_{\mathbf{x}}$, vector potential $\mathbf{A}(\mathbf{x}, t)$, and electron charge $-e$; μ denotes the chemical potential, while $\phi(\mathbf{x}, t)$ is the scalar potential. The complex SC order parameter component in band ν is given by

$$\Delta_\nu(\mathbf{x}) = -2 \sum_{\lambda} g_{\nu, \lambda} \langle \psi_{\downarrow, \lambda}(\mathbf{x}) \psi_{\uparrow, \lambda}(\mathbf{x}) \rangle = |\Delta_\nu(\mathbf{x})| e^{i\theta_\nu(\mathbf{x})} . \quad (2)$$

The Hartree and Fock energy contributions are

$$\mu_H^\nu(\mathbf{x}) = 2 \sum_{\sigma} \int d^3\mathbf{x}' V(\mathbf{x} - \mathbf{x}') n_{\sigma, \nu}(\mathbf{x}') \quad (3)$$

and

$$\mu_F^{\alpha, \nu}(\mathbf{x}) = -g_{\nu, \nu} n_{\alpha, \nu}(\mathbf{x}) , \quad (4)$$

respectively, where $n_{\sigma, \nu}(\mathbf{x}) = \langle \psi_{\sigma, \nu}^\dagger(\mathbf{x}) \psi_{\sigma, \nu}(\mathbf{x}) \rangle$. $V(\mathbf{x} - \mathbf{x}')$ is the long-ranged Coulomb potential, with Fourier transform $V_{\mathbf{q}} = e^2/(\epsilon_0 q^2)$, which pushes the in-gap Nambu-Goldstone mode up to the plasma frequency located within the quasi-particle continuum, according to the Anderson-Higgs mechanism [3]. The Fock energy $\mu_F^{\alpha, \nu}(\mathbf{x})$ ensures charge conservation. $g_{\lambda, \nu}$ describes the effective inter- ($\lambda \neq \nu$) and intra-band ($\lambda = \nu$) pairing interactions. The numerical results presented below were obtained for a three-band electron and hole bandstructure characteristic of the FeSC systems studied experimentally here, which has been discussed in the literature [4-6].

The multi-band Hamiltonian (1) is gauge invariant under the general gauge transformation [7]

$$\Psi_\nu(\mathbf{x}) \rightarrow e^{i\sigma_3 \Lambda(\mathbf{x})/2} \Psi_\nu(\mathbf{x}) , \quad (5)$$

when the vector potential, scalar potential, and SC order parameter phases transform as

$$\mathbf{A}(\mathbf{x}) \rightarrow \mathbf{A}(\mathbf{x}) + \frac{1}{2e} \nabla \Lambda(\mathbf{x}) , \quad \phi(\mathbf{x}) \rightarrow \phi(\mathbf{x}) - \frac{1}{2e} \frac{\partial}{\partial t} \Lambda(\mathbf{x}) , \quad \theta_\nu(\mathbf{x}) \rightarrow \theta_\nu(\mathbf{x}) + \Lambda(\mathbf{x}) . \quad (6)$$

Here, we introduced the field operator in Nambu space, $\Psi_\nu(\mathbf{x}) = (\psi_{\uparrow, \nu}^\dagger(\mathbf{x}), \psi_{\downarrow, \nu}(\mathbf{x}))^T$, and the Pauli spin matrix $\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$. However, the density matrix $\rho^{(\nu)}(\mathbf{x}, \mathbf{x}') = \langle \hat{\rho}^{(\nu)}(\mathbf{x}, \mathbf{x}') \rangle = \langle \Psi_\nu(\mathbf{x}) \Psi_\nu^\dagger(\mathbf{x}') \rangle$ depends on the specific choice of the gauge. To obtain gauge-invariant SC equations of motion, we introduce center-of-mass and relative coordinates $\mathbf{R} = (\mathbf{x} + \mathbf{x}')/2$ and $\mathbf{r} = \mathbf{x} - \mathbf{x}'$ and define the transformed density matrix [8]

$$\tilde{\rho}^{(\nu)}(\mathbf{r}, \mathbf{R}) = \exp \left[-i e \int_0^{\frac{1}{2}} d\lambda \mathbf{A}(\mathbf{R} + \lambda \mathbf{r}, t) \cdot \mathbf{r} \sigma_3 \right] \rho^{(\nu)}(\mathbf{r}, \mathbf{R}) \exp \left[-i e \int_{-\frac{1}{2}}^0 d\lambda \mathbf{A}(\mathbf{R} + \lambda \mathbf{r}, t) \cdot \mathbf{r} \sigma_3 \right] , \quad (7)$$

where $\rho^{(\nu)}(\mathbf{r}, \mathbf{R}) = \langle \Psi_\nu(\mathbf{R} + \frac{\mathbf{r}}{2}) \Psi_\nu^\dagger(\mathbf{R} - \frac{\mathbf{r}}{2}) \rangle$. By applying the gauge transformation (5), the density matrix $\tilde{\rho}^{(\nu)}(\mathbf{r}, \mathbf{R})$ transforms as [8]

$$\tilde{\rho}^{(\nu)}(\mathbf{r}, \mathbf{R}) \rightarrow \exp [i\sigma_3 \Lambda(\mathbf{R})/2] \tilde{\rho}^{(\nu)}(\mathbf{r}, \mathbf{R}) \exp [-i\sigma_3 \Lambda(\mathbf{R})/2] . \quad (8)$$

In contrast to the transformed phase of $\rho^{(\nu)}(\mathbf{r}, \mathbf{R})$, which depends on both coordinates $\mathbf{R}$ and $\mathbf{r}$, the phase $\Lambda(\mathbf{R})$ of $\tilde{\rho}^{(\nu)}(\mathbf{r}, \mathbf{R})$ only depends on the center-of-mass coordinate. This simplifies the gauge-invariant description of the non-equilibrium dynamics of superconductors. After applying a Fourier transformation with respect to the relative coordinate $\mathbf{r}$, we perform an additional gauge transformation,

$$\tilde{\rho}^{(\nu)}(\mathbf{k}, \mathbf{R}) = e^{-i\sigma_3\theta_{\nu_0}(\mathbf{R})/2} \tilde{\rho}^{(\nu)}(\mathbf{k}, \mathbf{R}) e^{i\sigma_3\theta_{\nu_0}(\mathbf{R})/2}, \quad (9)$$

which eliminates the phase θ_{ν_0} of the SC order parameter for band ν_0 . For a multi-band SC, the equations of motion then depend on the phase difference, $\delta\theta_\nu = \theta_{\nu_0} - \theta_\nu$, of the order parameter components between different bands $\nu \neq \nu_0$. The latter relative phases not only determine the equilibrium symmetry of the multi-band SC order parameter (e.g., s_{++} or s_{+-} [9]), but lead to additional nonlinear dynamics driven by the light-induced relative phase fluctuations $\delta\theta_\nu(t)$. This phase-driven dynamics is of main interest for interpreting the experiment.

In our simulations, we assumed that the multi-band SC system is only weakly spatially-dependent. As a result, we can neglect all orders of $\mathcal{O}(\nabla_{\mathbf{k}} \cdot \nabla_{\mathbf{R}})$ in the gradient expansion of the full spatially-dependent SC Bloch equations presented in Ref. [8]. This is a reasonable approximation for the $s_{\pm}$ -wave superconductor state studied here. We also consider homogeneous excitation conditions, such that we can ignore the $\mathbf{R}$ -dependence of the $\mathbf{E}$ - and $\mathbf{B}$ -fields. In addition, the effect of the Hartree potential on the nonlinear response is small in the limit of weak spatial dependence, so we set for simplicity $\mu_H = 0$.

Supplementary Note 2: Gauge-Invariant Pseudo-Spin Equations of Motion

A SC state is characterized by the spin texture and relative orientations of Anderson pseudo-spins introduced at each momentum point in the different bands. Since the non-equilibrium dynamics of superconductors is traditionally described by using such pseudo-spin formalism introduced by Anderson in Ref. [3], we express here the gauge-invariant density matrix obtained in the previous section in terms of Anderson pseudo-spin components at each wavevector $\mathbf{k}$:

$$\tilde{\rho}^{(\nu)}(\mathbf{k}) = \sum_{n=0}^3 \tilde{\rho}_n^{(\nu)}(\mathbf{k}) \sigma_n. \quad (10)$$

Here, σ_n , $n = 1 \cdots 3$, are the Pauli spin matrices, σ_0 is the unit matrix, and $\tilde{\rho}_n^{(\nu)}(\mathbf{k})$ are the pseudo-spin components of band ν . We then straightforwardly derive gauge-invariant SC Bloch equations of pseudo-spins, thus generalizing Ref. [8] to the multi-band case:

$$\begin{aligned} \frac{\partial}{\partial t} \tilde{\rho}_0^{(\nu)}(\mathbf{k}) &= -e \mathbf{E}(t) \cdot \nabla_{\mathbf{k}} \tilde{\rho}_3^{(\nu)}(\mathbf{k}) - |\Delta_\nu| \left[\sin \delta\theta_\nu (\tilde{\rho}_1^{(\nu)}(\mathbf{k}_-) - \tilde{\rho}_1^{(\nu)}(\mathbf{k}_+)) + \cos \delta\theta_\nu (\tilde{\rho}_2^{(\nu)}(\mathbf{k}_-) - \tilde{\rho}_2^{(\nu)}(\mathbf{k}_+)) \right], \\ \frac{\partial}{\partial t} \tilde{\rho}_1^{(\nu)}(\mathbf{k}) &= -E_\nu(\mathbf{k}) \tilde{\rho}_2^{(\nu)}(\mathbf{k}) - |\Delta_\nu| \sin \delta\theta_\nu N_\nu(\mathbf{k}), \\ \frac{\partial}{\partial t} \tilde{\rho}_2^{(\nu)}(\mathbf{k}) &= E_\nu(\mathbf{k}) \tilde{\rho}_1^{(\nu)}(\mathbf{k}) - |\Delta_\nu| \cos \delta\theta_\nu N_\nu(\mathbf{k}), \\ \frac{\partial}{\partial t} \tilde{\rho}_3^{(\nu)}(\mathbf{k}) &= -e \mathbf{E}(t) \cdot \nabla_{\mathbf{k}} \tilde{\rho}_0^{(\nu)}(\mathbf{k}) - |\Delta_\nu| \left[\sin \delta\theta_\nu (\tilde{\rho}_1^{(\nu)}(\mathbf{k}_-) + \tilde{\rho}_1^{(\nu)}(\mathbf{k}_+)) + \cos \delta\theta_\nu (\tilde{\rho}_2^{(\nu)}(\mathbf{k}_+) + \tilde{\rho}_2^{(\nu)}(\mathbf{k}_-)) \right], \end{aligned} \quad (11)$$

where $\mathbf{k}_\pm = \mathbf{k} \pm \mathbf{p}_S/2$. Three different sources drive light-induced pseudo-spin motion in the above equations:

1. Condensate center-of-mass momentum, which in a homogeneous system is given by $\mathbf{p}_S \equiv \mathbf{p}_S^\nu = -2e \mathbf{A}(t)$
2. Effective chemical potential $\mu_{\text{eff}} = e\phi - \frac{1}{2} \frac{\partial}{\partial t} \theta_{\nu_0} - \mu$
3. Order parameter phase difference between different bands ν , $\delta\theta_\nu = \theta_{\nu_0} - \theta_\nu$, where ν_0 is the reference band

The order parameter amplitude is given by

$$|\Delta_\nu| = -2e^{i\delta\theta_\nu} \sum_{\lambda, \mathbf{k}} g_{\nu, \lambda} \left[\tilde{\rho}_1^{(\lambda)}(\mathbf{k}) + i\tilde{\rho}_2^{(\lambda)}(\mathbf{k}) \right] = -2 \sum_{\lambda, \mathbf{k}} g_{\nu, \lambda} \left[\cos \delta\theta_\nu \tilde{\rho}_1^{(\lambda)}(\mathbf{k}) - \sin \delta\theta_\nu \tilde{\rho}_2^{(\lambda)}(\mathbf{k}) \right], \quad (12)$$

where

$$\sum_{\lambda, \mathbf{k}} g_{\nu, \lambda} \left[\sin \delta\theta_\nu \tilde{\rho}_1^{(\lambda)}(\mathbf{k}) + \cos \delta\theta_\nu \tilde{\rho}_2^{(\lambda)}(\mathbf{k}) \right] = 0 \quad (13)$$

restricts the relative phase dynamics $\delta\theta_\nu(t)$. The above condition is satisfied exactly at all times by our gauge-invariant numerical simulations.

As in previous Anderson pseudo-spin models, the coupling of the laser field leads to the time-dependent band energy

$$E_\nu(\mathbf{k}) = \xi_\nu(\mathbf{k}_-) + \xi_\nu(\mathbf{k}_+) + 2(\mu_{\text{eff}} + \mu_F^\nu). \quad (14)$$

This energy time-dependence comes from the light-induced condensate momentum $\mathbf{p}_S(t)$, the effective chemical potential μ_{eff} , and the Fock energy

$$\mu_F^\nu \equiv \frac{1}{2} (\mu_F^{\downarrow,\nu} + \mu_F^{\uparrow,\nu}) = -g_{\nu,\nu} \sum_{\mathbf{k}} [1 + \tilde{\rho}_3^{(\nu)}(\mathbf{k})]. \quad (15)$$

The spin- $\uparrow$ and spin- $\downarrow$ electron populations determine the phase-space filling contributions:

$$N_\nu(\mathbf{k}) = \tilde{\rho}_0^{(\nu)}(\mathbf{k}_-) - \tilde{\rho}_3^{(\nu)}(\mathbf{k}_-) - \tilde{\rho}_0^{(\nu)}(\mathbf{k}_+) - \tilde{\rho}_3^{(\nu)}(\mathbf{k}_+). \quad (16)$$

Compared to the conventional pseudo-spin models used in the literature before, the gauge-invariant SC Bloch equations (11) include quantum transport terms proportional to the laser electric field, such as $e \mathbf{E} \cdot \nabla_{\mathbf{k}} \tilde{\rho}_3^{(\nu)}(\mathbf{k})$. The latter quantum transport terms also lead to $\pm \mathbf{p}_S(t)/2$ $\mathbf{k}$ -space displacements of the coherences and populations in the finite-momentum-pairing SC state. Inversion symmetry breaking induced by condensate acceleration by the laser field $\mathbf{E}(t)$ leads to the coupling between $\tilde{\rho}_0(\mathbf{k})$ and $\tilde{\rho}_3(\mathbf{k})$ described by Eq. (11), which is absent in conventional pseudo-spin models. As already discussed in Refs. [8, 10–12], by also including the lightwave electromagnetic propagation effects inside the SC system, described by Maxwell's equations, the above inversion symmetry breaking persists after the driving pulse. This light-induced symmetry breaking manifests as inversion-symmetry-forbidden high harmonic generation, gapless superconductivity, and quasi-particle quantum phases controlled by strong THz field pulses [8, 10–12].

The nonlinear differential transmission measured in the experiment is obtained by calculating the transmitted E -field after solving Maxwell's equations. For a SC thin film geometry, we thus obtain the effective driving electric field [8]

$$\mathbf{E}(t) = \mathbf{E}_{\text{THz}}(t) - \frac{\mu_0 c}{2n} \mathbf{J}(t), \quad (17)$$

where $\mathbf{E}_{\text{THz}}(t)$ is the applied THz electric field and n is the refractive index of the SC system. We obtain the experimentally-measured signals by calculating the gauge-invariant supercurrent [8]

$$\mathbf{J}(t) = e \sum_{\mathbf{k}, \lambda} \nabla_{\mathbf{k}} \xi_\lambda(\mathbf{k}) \tilde{\rho}_0^{(\lambda)}(\mathbf{k}) \quad (18)$$

determined by the gauge-invariant pseudo-spin component $\tilde{\rho}_0^{(\lambda)}(\mathbf{k})$. $\mathbf{J}(t)$ is driven by the effective field $\mathbf{E}(t)$. THz lightwave propagation inside the SC thin film is included in our calculation by self-consistently solving Eq. (17) and the gauge-invariant SC Bloch equations (11) [8]. Using the above results, we calculated the nonlinear differential transmission correlated signal measured in the THz-MDCS experiment, which is given by

$$E_{\text{NL}} = E_{\text{AB}}(t, \tau) - E_{\text{A}}(t) - E_{\text{B}}(t, \tau) \quad (19)$$

for the collinear 2-pulse geometry used in the experiment (Fig. 1(a) in the main text). $E_{\text{AB}}(t, \tau)$ is the transmitted E -field induced by both pulses A and B, which depends on both the gate time t and the delay time between the two pulses, τ . $E_{\text{A}}(t)$ and $E_{\text{B}}(t, \tau)$ are the transmitted electric fields resulting from pulse A and pulse B separate driving. The THz-MDCS spectra are obtained by Fourier transform of $E_{\text{NL}}(t, \tau)$ with respect to both t (frequency ω_t) and τ (frequency ω_τ). To analyze the THz-MDCS spectra, we introduce “time vectors” $t' = (t, \tau)$ and “frequency vectors” (ω_t, ω_τ) , such that the electric fields used in the calculations can be written as $\mathbf{E}_{\text{A}}(t') \sin(\omega_{\text{A}} t')$ and $\mathbf{E}_{\text{B}}(t') \sin(\omega_{\text{B}} t')$. In the calculations here, we assume Gaussian envelope functions $\mathbf{E}_{\text{A,B}}(t')$. The corresponding frequency vectors of the two pulses A and B are $\omega_{\text{A}} = (\omega_0, 0)$ and $\omega_{\text{B}} = (\omega_0, -\omega_0)$ where ω_0 is the central frequency of the pulses.

Supplementary Note 3: Non-adiabatic Pseudo-Spin Canting Driven Parametrically by Order Parameter Relative Phase Oscillations

The numerical results presented in the main text were obtained by solving self-consistently the gauge-invariant SC Bloch equations together with Maxwell's equations, as discussed in Supplementary Note 2. These coupled equations

were solved numerically without applying any perturbative susceptibility expansions or other approximations. In this section, we identify the physical origin of the field-induced transition in the quantum state leading to the drastic change in the THz-MDCS spectral profile with increased THz driving in Figs. 2 and 3 in the main text. For this we derive nonlinear oscillator equations of motion from the full gauge-invariant equations of motion (11). First, we express the density matrix $\tilde{\rho}^{(\nu)}(\mathbf{k})$ describing the non-equilibrium SC state as

$$\tilde{\rho}^{(\nu)}(\mathbf{k}) = \tilde{\rho}^{(\nu),0}(\mathbf{k}) + \Delta\tilde{\rho}^{(\nu)}(\mathbf{k}), \quad (20)$$

where $\tilde{\rho}^{(\nu),0}(\mathbf{k})$ is the density matrix of the equilibrium (stationary) state and $\Delta\tilde{\rho}^{(\nu)}(\mathbf{k})$ is the non-equilibrium change induced by the strong driving fields.

We express the order parameters in terms of the x and y pseudo-spin components as follows

$$\begin{aligned} \Delta'_\nu &= |\Delta_\nu| \cos \delta\theta_\nu = -2 \sum_{\lambda, \mathbf{k}} g_{\nu, \lambda} \tilde{\rho}_1^{(\lambda)}(\mathbf{k}), \\ \Delta''_\nu &= |\Delta_\nu| \sin \delta\theta_\nu = 2 \sum_{\lambda, \mathbf{k}} g_{\nu, \lambda} \tilde{\rho}_2^{(\lambda)}(\mathbf{k}). \end{aligned} \quad (21)$$

The order parameter amplitude and relative phase are expressed in terms of the above defined real and imaginary parts as

$$|\Delta_\nu|^2 = (\Delta'_\nu)^2 + (\Delta''_\nu)^2, \quad \tan \delta\theta_\nu = \frac{\Delta''_\nu}{\Delta'_\nu}. \quad (22)$$

We thus introduced two different parametrizations of the order parameter.

We consider $s_\pm$ -symmetry in the SC ground state, as in the studied iron pnictide system. For this equilibrium SC state, $\delta\theta_\nu^0 = 0, \pi$ and $\tilde{\rho}_2^{(\nu),0}(\mathbf{k}) = 0, \tilde{\rho}_1^{(\nu),0}(\mathbf{k}) \neq 0$, i. e., the pseudo-spins point along the x -axis in equilibrium and are anti-parallel between electron and hole bands. By taking the second time derivative of Eq. (11), we obtain the deviations of the x and y pseudo-spin components from equilibrium, $\Delta\tilde{\rho}_1^{(\nu)}(\mathbf{k})$ and $\Delta\tilde{\rho}_2^{(\nu)}(\mathbf{k})$, in terms of equations of motion for two non-linearly coupled oscillators:

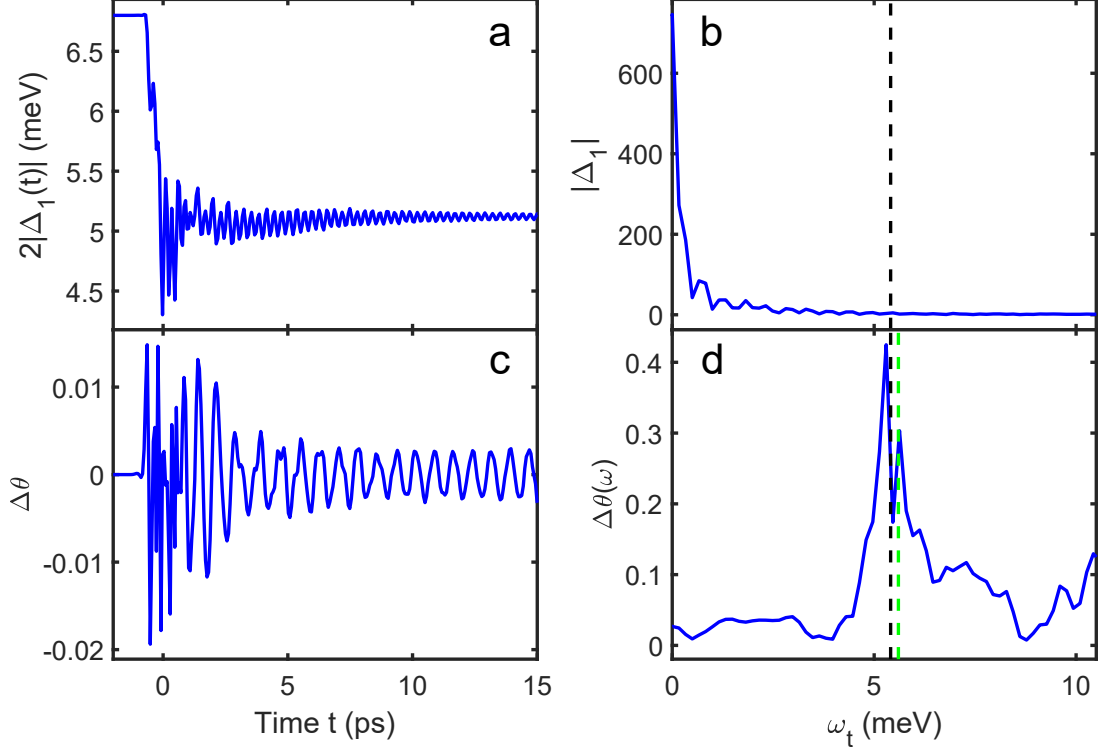
$$\begin{aligned} \partial_t^2 \Delta\tilde{\rho}_1^{(\nu)}(\mathbf{k}) + [E_\nu^2(\mathbf{k}) + 4|\Delta_\nu|^2 \sin^2 \Delta\theta_\nu] \Delta\tilde{\rho}_1^{(\nu)}(\mathbf{k}) + [\partial_t E_\nu(\mathbf{k}) + 2|\Delta_\nu|^2 \sin 2\Delta\theta_\nu] \Delta\tilde{\rho}_2^{(\nu)}(\mathbf{k}) \\ = S_\nu^{(1)}(\mathbf{k}) - [\partial_t \delta\Delta''_\nu - \delta\Delta'_\nu E_\nu(\mathbf{k})] N_\nu(\mathbf{k}), \\ \partial_t^2 \Delta\tilde{\rho}_2^{(\nu)}(\mathbf{k}) + [E_\nu^2(\mathbf{k}) + 4|\Delta_\nu|^2 \cos^2 \Delta\theta_\nu] \Delta\tilde{\rho}_2^{(\nu)}(\mathbf{k}) + [-\partial_t E_\nu(\mathbf{k}) + 2|\Delta_\nu|^2 \sin 2\Delta\theta_\nu] \Delta\tilde{\rho}_1^{(\nu)}(\mathbf{k}) \\ = S_\nu^{(2)}(\mathbf{k}) - [\partial_t \delta\Delta'_\nu + \delta\Delta''_\nu E_\nu(\mathbf{k})] N_\nu(\mathbf{k}), \end{aligned} \quad (23)$$

where the time-dependent fluctuations from the equilibrium state values $\Delta\theta_\nu = \delta\theta_\nu - \delta\theta_\nu^0$, $\delta\Delta'_\nu = \Delta'_\nu - \Delta'_{\nu,0}$, and $\delta\Delta''_\nu = \Delta''_\nu$ describe the light-induced order parameter collective dynamics, with equilibrium values $\delta\theta_\nu^0 = 0, \pi$ in the hole and electron bands respectively and $\Delta'_{\nu,0} \neq 0$, $\Delta''_{\nu,0} = 0$. The nonlinear coupling between the x - and y -components of the pseudo-spins in each band ν in the above equations describes a time-dependent pseudo-spin canting between different bands.

The first terms on the right-hand side (rhs) of Eqs. (23) describe pseudo-spin driving by sum- and difference-frequency Raman and quantum transport processes, which were previously discussed in Ref. [13]. These Raman processes are modified here by the phase fluctuations $\Delta\theta_\nu \neq 0$:

$$\begin{aligned} S_\nu^{(1)}(\mathbf{k}) &= -[\Delta E_\nu^2(\mathbf{k}) + 4|\Delta_\nu|^2 \sin^2 \Delta\theta_\nu] \tilde{\rho}_1^{(\nu),0}(\mathbf{k}) + \Delta [N_\nu(\mathbf{k}) E_\nu(\mathbf{k})] |\Delta_\nu^0| \\ &\quad - |\Delta_\nu| \sin \Delta\theta_\nu \left[e \mathbf{E} \cdot \nabla_{\mathbf{k}_+} (\tilde{\rho}_0^{(\nu)}(\mathbf{k}_+) + \tilde{\rho}_3^{(\nu)}(\mathbf{k}_+)) + e \mathbf{E} \cdot \nabla_{\mathbf{k}_-} (\tilde{\rho}_0^{(\nu)}(\mathbf{k}_-) - \tilde{\rho}_3^{(\nu)}(\mathbf{k}_-)) \right], \\ S_\nu^{(2)}(\mathbf{k}) &= [\partial_t E_\nu(\mathbf{k}) - 2|\Delta_\nu|^2 \sin 2\Delta\theta_\nu] \tilde{\rho}_1^{(\nu),0}(\mathbf{k}) \\ &\quad - |\Delta_\nu| \cos \Delta\theta_\nu \left[e \mathbf{E} \cdot \nabla_{\mathbf{k}_+} (\tilde{\rho}_0^{(\nu)}(\mathbf{k}_+) + \tilde{\rho}_3^{(\nu)}(\mathbf{k}_+)) + e \mathbf{E} \cdot \nabla_{\mathbf{k}_-} (\tilde{\rho}_0^{(\nu)}(\mathbf{k}_-) - \tilde{\rho}_3^{(\nu)}(\mathbf{k}_-)) \right]. \end{aligned} \quad (24)$$

The second terms on the rhs of Eqs. (23) are proportional to the light-induced deviations $\delta\Delta'_\nu$ and $\delta\Delta''_\nu$ of the order parameters from their equilibrium values and describe the collective modes arising from the non-perturbative coupling of the different $\mathbf{k}$ pseudo-spins. The Leggett phase mode and Higgs amplitude mode collective excitations of the ground state are obtained by linearizing Eqs. (23) [14]. The collective modes of the non-equilibrium state are obtained non-perturbatively.



Supplementary Figure 1. Dynamics of (a) the SC order parameter $2|\Delta_1|$ and (c) the interband phase difference $\Delta\theta$. The corresponding spectra are shown in (b) and (d). The Higgs mode energy is indicated by a vertical dashed black line, while the Leggett mode is marked by a vertical dashed green line.

The main effect proposed here comes from parametric driving of the nonlinear oscillator equations of motion (23) by the time-dependent order parameter relative phase $\Delta\theta_\nu(t)$. This parametric driving results in time-dependent canting of the pseudo-spins from their equilibrium directions in different bands, defined by $\delta\theta_\nu^0 = 0, \pi$, as they adjust non-adiabatically to the new time-dependent order parameter phase values. This parametric excitation of the nonlinear oscillators originates from the dependence of the left-hand side (lhs) of Eqs. (23) on $\Delta\theta_\nu(t)$, which determines the non-equilibrium "normal modes". It is enhanced by the coupled phase-amplitude collective mode of the driven non-equilibrium SC state discussed below, which leads to long-lived and pronounced relative phase oscillations at the Higgs mode frequency, following a transient phase increase during the coherent quench of the order parameter amplitude.

In the ground state, the pseudo-spins point along the x -direction and $\tilde{\rho}_2^{(\nu),0}(\mathbf{k}) = 0, \tilde{\rho}_1^{(\nu),0}(\mathbf{k}) \neq 0$. The source term $S_\nu^{(2)}(\mathbf{k})$ drives $\Delta\tilde{\rho}_2^{(\nu)}(\mathbf{k}) \neq 0$, which, assuming that the phase retains its equilibrium values $\delta\theta_\nu^0 = 0, \pi$, oscillates at frequencies given by the quasi-particle excitation energies $\sqrt{E_\nu^2(\mathbf{k}) + 4|\Delta_\nu|^2}$. As already discussed in Ref. [13], these oscillator frequencies are modulated by coherent nonlinear processes leading to time-dependent order parameter amplitudes $|\Delta_\nu|$. Additional to quantum quench, in the case of two-pulse coherent excitation, the time-dependent modulation of the order parameter determined by the pump-probe time delay τ parametrically drives the pseudo-spin oscillators [13]. This parametric driving does not contribute to the low-order nonlinear responses calculated before and manifests as distinct high-order nonlinear peaks displaced from the conventional pump-probe peaks along the vertical ω_τ -axis measuring the pump-probe coherence [13]. In Ref. [13] we showed that such distinct THz-MDCS spectral peaks are expected in the case of narrowband strong pump and weak broadband probe.

For the high intensity broadband pump and probe pulses used here, the main THz-MDCS features of interest come from the $\Delta\theta_\nu(t)$ dependence of Eqs. (23). This phase dynamics leads to the coupling of the pseudo-spin x component $\Delta\rho_1^{(\nu)}$ to $4\sin\Delta\theta_\nu\Delta P_2^{(\nu)}(\mathbf{k})$ and the pseudo-spin y -component $\Delta\rho_2^{(\nu)}$ to $4\cos\Delta\theta_\nu\Delta P_2^{(\nu)}(\mathbf{k})$, where

$$\Delta P_2^{(\nu)}(\mathbf{k}) = \Delta\tilde{\rho}_1^{(\nu)}(\mathbf{k})\sin\Delta\theta_\nu + \Delta\tilde{\rho}_2^{(\nu)}(\mathbf{k})\cos\Delta\theta_\nu \quad (25)$$

is the pseudo-spin y -component in a time-dependent frame of reference rotated by $\Delta\theta_\nu(t)$ with respect to the equi-

librium x - y coordinate frame. Such nonlinear coupling is introduced by the time-dependent deviations of the order parameter relative phase from its equilibrium values and results in pseudo-spin canting parametrically driven by the phase component of the collective mode. Such non-adiabatic response of the pseudo-spins to the light-induced phase changes differs in each band and is pronounced in iron pnictide superconductors, where the order parameter phase is known to dictate the pseudo-spin anti-parallel directions between electron and hole bands in the equilibrium $s_{\pm}$ SC state.

By expanding the nonlinear oscillator equations of motion (23) to lowest order in $\Delta\theta_{\nu}(t)$ and $\mathbf{p}_S(t)$, the pseudo-spin canting from the equilibrium direction that determines the non-equilibrium normal modes of the two coupled oscillators is driven by the time-dependent coupling term

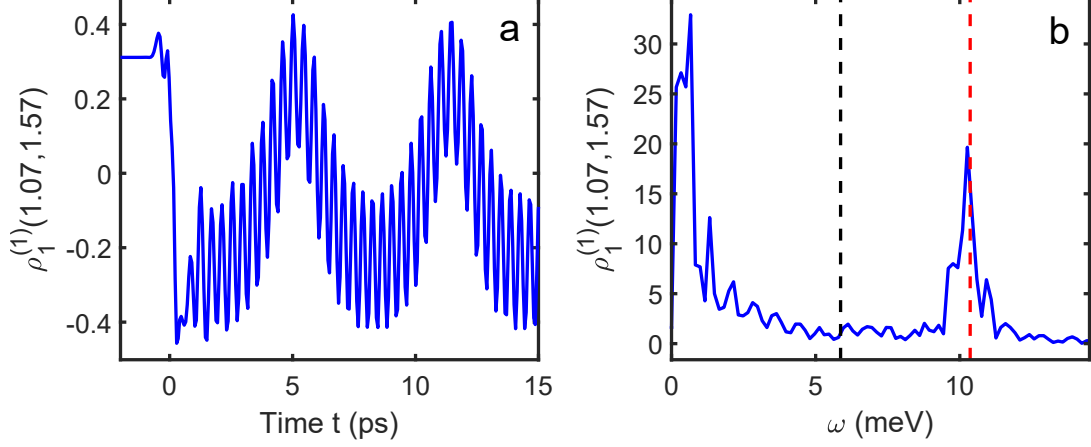
$$[\partial_t E_{\nu}(\mathbf{k}) - 4|\Delta_{\nu}|^2 \Delta\theta_{\nu}(t)] \Delta\rho_1^{(\nu)}, \quad (26)$$

where $\partial_t E_{\nu}(\mathbf{k}) \approx e(\mathbf{E}(t) \cdot \nabla_{\mathbf{k}})(\mathbf{p}_S \cdot \nabla_{\mathbf{k}})\varepsilon(\mathbf{k})$ is approximated by expanding the band dispersions in powers of the center-of-mass momentum $\mathbf{p}_S$. Equation (26) demonstrates that the non-equilibrium normal modes and light-induced pseudo-spin canting are determined by the competition between condensate momentum and order parameter relative phase dynamics. In particular, $\partial_t E_{\nu}(\mathbf{k})$ drives pseudo-spin canting via difference-frequency Raman processes $\omega_{A,B} - \omega_{A,B} \sim 0$ and sum-frequency Raman processes $\omega_{A,B} + \omega_{A,B} \sim 2\omega_0 > \omega_{H,1}$, which drive pseudo-spin canting at frequencies determined by the laser pulse. The time-dependence of $|\Delta_{\nu}|^2 \delta\theta_{\nu}(t)$, on the other hand, is determined by the amplitude and phase collective modes of the driven system.

Supplementary Fig. 1 shows the time dependence of (a) the SC order parameter amplitude $2|\Delta_{\nu=1}|$ ($\nu = 1$ denotes the hole band) and (c) the interband phase difference $\Delta\theta$ for high $E_0 = 700$ kV/cm driving. The corresponding spectra are shown in Supplementary Figs. 1b and 1d. The SC order parameter amplitude mostly shows a $\omega \approx 0$ light-induced quantum quench, whose coherent physical origin was discussed in Ref. [13]. This quench characterizes the light-induced modulation of the superfluid density and dominates in the order parameter amplitude spectrum, Supplementary Fig. 1b, over the weak Higgs oscillations marked by the black dashed line. On the other hand, the interband phase difference dynamics changes between the three different nonlinear regimes I–III discussed in the main text. In regimes I and II, corresponding to driving fields up to ~ 400 kV/cm in our calculation, the phase fluctuations do not play a dominant role. In contrast to that, for the highest fields used in the experiment, the nonlinear threshold field-dependence of $\mathbf{p}_S$ and the phase-amplitude collective mode leads to non-adiabatic pseudo-spin canting dominated by the phase oscillations close to the Higgs frequency $\omega_{H,1}$. This frequency is well below the Leggett mode frequency that determines the phase collective excitation mode of the equilibrium SC state. The phase oscillations become pronounced in regime III due to strong phase-amplitude light-induced coupling in the collective mode of the light-driven non-equilibrium SC state (Supplementary Fig. 1c). These oscillations are characterized by the Fourier transform $\Delta\theta(\omega)$, Supplementary Fig. 1d, which is dominated by two peaks: a strong peak at $\omega_{H,1}$ (black dashed line), and a weaker peak slightly above (green dashed curve). This two-peak structure of the phase spectrum signifies the non-perturbative dependence of the non-equilibrium SC state and its collective mode on the driving field.

We conclude that the emergence of a distinct non-linear regime III observed in the experiment, witnessed by the drastic change in the THz-MDCS spectral profile above critical field, results from the sharp time-dependence of the order parameter phase due to the coupled phase-amplitude collective mode of the non-equilibrium driven state above critical driving. The calculated phase fluctuations of the phase-amplitude non-equilibrium state collective mode significantly differ from the Leggett mode excitation of the equilibrium SC state (Supplementary Fig. 3). In particular, the strong light-induced phase-amplitude coupling leads to strong phase oscillations at the Higgs mode frequency $\omega_{H,1}$, which drives pseudo-spin canting from the equilibrium directions determined by the phase of the $s_{\pm}$ order parameter.

The light-induced pseudo-spin canting described by Eq. (26) may be thought of as determining non-equilibrium normal modes of the two coupled x and y pseudo-spin highly nonlinear oscillators in different bands. Due to the strong nonlinearity, it may also be thought of as parametrically driving a non-equilibrium SC state determined by the pseudo-spin time-dependent canting angles between different bands. While our calculation does not include any dissipation, the latter can stabilize such non-equilibrium state into a stationary state. Either way, long-lived phase and superfluid momentum dynamics drives a pseudo-spin canting contribution to the THz-MDCS spectra at frequencies determined by the time-dependence of $[\partial_t E_{\nu}(\mathbf{k}) - 4|\Delta_{\nu}|^2 \delta\theta_{\nu}(t)] \Delta\rho_1^{(\nu)}$. When the quasi-particle excitations are resonantly driven by the pulse $\mathbf{E}^2$ -spectrum, as it is the case for the broad pulses used here, the $\tilde{\rho}_1^{(\nu)}(\mathbf{k})$ spectra are dominated by a momentum-dependent peak centered at the quasi-particle excitation energy, $E_{\mathbf{k}}^{(1)} = 2\sqrt{[\varepsilon_1(\mathbf{k}) + \mu_{\text{eff}} + \mu_F^{(1)}]^2 + |\Delta_{1,\infty}|^2}$, with quenched order parameter asymptotic value $|\Delta_{1,\infty}|$. This is illustrated in Supplementary Fig. 2, where an example of the calculated dynamics and spectrum of $\tilde{\rho}_1^{(\nu=1)}(\mathbf{k})$ is shown for one wavevector $\mathbf{k}$. The spectrum (Supplementary Fig. 2b) shows a strong peak at the quasi-particle excitation energy (vertical dashed red line), while the contribution at the Higgs mode energy (vertical black dashed line) is



Supplementary Figure 2. (a) Dynamics and (b) spectrum of $\tilde{\rho}_1^{(\nu=1)}(\mathbf{k})$ for one $\mathbf{k}$ pseudo-spin. The Higgs mode energy is indicated by a vertical dashed black line, while the quasi-particle excitation energy is marked by a vertical dashed red line.

negligible for the used pulses. The dominant contribution to $\Delta\tilde{\rho}_1^{(\nu)}(\mathbf{k})$ comes from quasi-particle excitations close to the excitation energy minimum, which is located close to the Higgs mode energy $\omega_{H,1}$. As a result, $\Delta\tilde{\rho}_1^{(\nu)}(\mathbf{k})$ mainly oscillates close to $\omega_{H,1}$. We thus obtain, through the nonlinear coupling Eq. (26), THz-MDCS sidebands centered at the sum of the frequencies of $\Delta\theta_\nu(t)$ oscillations (phase-amplitude collective mode frequency close to $\omega_{H,1}$) and $\Delta\rho_1^{(\nu)}$ oscillations (quasi-particle excitations close to $\omega_{H,1}$). Above critical driving, this nonlinear coupling is amplified both by the light-induced quench of the superfluid-density (Supplementary Fig. 4d) and by the phase-amplitude collective mode, which gives a pronounced $\Delta\theta_\nu(\omega)$ peak at $\omega \sim \omega_{H,1}$ above critical driving (Supplementary Fig. 4b).

As discussed above, $\Delta\rho_1^{(\nu)}$ and $\Delta\rho_2^{(\nu)}$ couple to $\Delta P_2^{(\nu)}(\mathbf{k})$, which suggests that the non-perturbative effects discussed above may be alternatively viewed by transforming to the rotated frame defined by the instantaneous angle $\Delta\theta_\nu(t)$ in each band:

$$\begin{aligned} P_1^{(\nu)}(\mathbf{k}) &= \tilde{\rho}_1^{(\nu)}(\mathbf{k}) \cos \Delta\theta_\nu - \tilde{\rho}_2^{(\nu)}(\mathbf{k}) \sin \Delta\theta_\nu, \\ P_2^{(\nu)}(\mathbf{k}) &= \tilde{\rho}_1^{(\nu)}(\mathbf{k}) \sin \Delta\theta_\nu + \tilde{\rho}_2^{(\nu)}(\mathbf{k}) \cos \Delta\theta_\nu. \end{aligned} \quad (27)$$

In this rotated frame, the pseudo-spin dynamics is described by the equations of motion

$$\begin{aligned} \frac{\partial}{\partial t} \tilde{\rho}_0^{(\nu)}(\mathbf{k}) &= -e \mathbf{E}(t) \cdot \nabla_{\mathbf{k}} \tilde{\rho}_3^{(\nu)}(\mathbf{k}) - |\Delta_\nu| \left[P_2^{(\nu)}(\mathbf{k}_-) - P_2^{(\nu)}(\mathbf{k}_+) \right], \\ \frac{\partial}{\partial t} P_1^{(\nu)}(\mathbf{k}) &= -(E_\nu(\mathbf{k}) + \partial_t \Delta\theta_\nu) P_2^{(\nu)}(\mathbf{k}), \\ \frac{\partial}{\partial t} P_2^{(\nu)}(\mathbf{k}) &= (E_\nu(\mathbf{k}) + \partial_t \Delta\theta_\nu) P_1^{(\nu)}(\mathbf{k}) - |\Delta_\nu| N_\nu(\mathbf{k}), \\ \frac{\partial}{\partial t} \tilde{\rho}_3^{(\nu)}(\mathbf{k}) &= -e \mathbf{E}(t) \cdot \nabla_{\mathbf{k}} \tilde{\rho}_0^{(\nu)}(\mathbf{k}) - |\Delta_\nu| \left[P_2^{(\nu)}(\mathbf{k}_-) + P_2^{(\nu)}(\mathbf{k}_+) \right]. \end{aligned} \quad (28)$$

By taking the second derivative, we derive the following nonlinear oscillator equation of motion for $\Delta P_2^{(\nu)}$, which directly determines $\tilde{\rho}_0^{(\nu)}(\mathbf{k})$ and the nonlinear current:

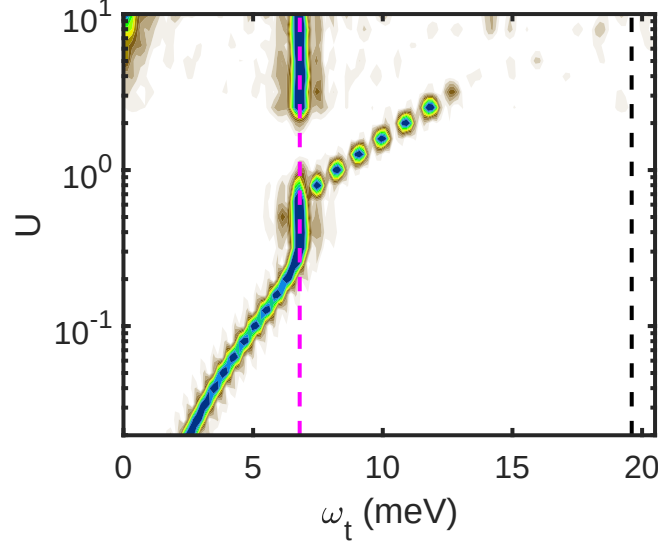
$$\partial_t^2 \Delta P_2^{(\nu)}(\mathbf{k}) + \left[(E_\nu(\mathbf{k}) + \partial_t \Delta\theta_\nu)^2 + 4|\Delta_\nu|^2 \right] \Delta P_2^{(\nu)}(\mathbf{k}) - \left[\partial_t E_\nu(\mathbf{k}) + \partial_t^2 \Delta\theta_\nu \right] \Delta P_1^{(\nu)}(\mathbf{k}) = S_\nu(\mathbf{k}) + \partial_t |\Delta_\nu| N_\nu(\mathbf{k}),$$

while the coupling to $\Delta P_1^{(\nu)}(\mathbf{k})$ is given by

$$\partial_t \Delta P_1^{(\nu)}(\mathbf{k}) = -(E_\nu(\mathbf{k}) + \partial_t \Delta\theta_\nu) \Delta P_2^{(\nu)}(\mathbf{k}). \quad (29)$$

The source term is

$$S_\nu(\mathbf{k}) = \left[\partial_t E_\nu(\mathbf{k}) + \partial_t^2 \Delta\theta_\nu \right] P_1^{(\nu),0}(\mathbf{k}) - |\Delta_\nu| \left[e \mathbf{E} \cdot \nabla_{\mathbf{k}_+} (\tilde{\rho}_0^{(\nu)}(\mathbf{k}_+) + \tilde{\rho}_3^{(\nu)}(\mathbf{k}_+)) + e \mathbf{E} \cdot \nabla_{\mathbf{k}_-} (\tilde{\rho}_0^{(\nu)}(\mathbf{k}_-) - \tilde{\rho}_3^{(\nu)}(\mathbf{k}_-)) \right], \quad (30)$$



Supplementary Figure 3. Dependence of $\Delta\theta$ spectrum on the interband interaction strength U for $E_0 = 25.0$ kV/cm excitation. Dashed magenta (black) line indicates $\omega_{H,1}$ ($\omega_{H,2}$).

where the second term describes quantum transport effects. The relative phase dynamics is obtained from

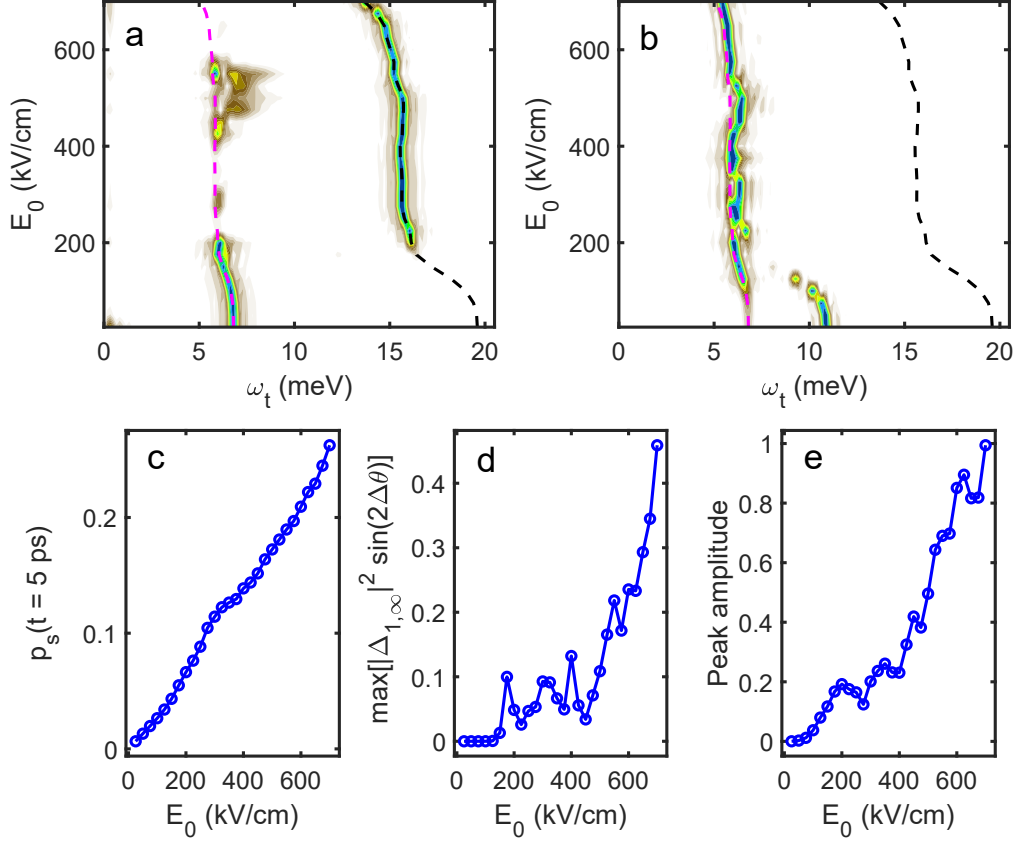
$$\partial_t \Delta\theta_\nu = \partial_t \left(\frac{\Delta''_\nu}{|\Delta_\nu|} \right) = \frac{1}{|\Delta_\nu|} \left[\partial_t \Delta''_\nu - \Delta''_\nu \frac{\partial_t |\Delta_\nu|}{|\Delta_\nu|} \right]. \quad (31)$$

Parametric driving of the above oscillator by the modulation of its frequency by $\partial_t \Delta\theta_\nu$ in the rotated frame leads to sidebands in the THz-MDCS spectra, in a way analogous to Floquet sidebands.

Supplementary Note 4: Phase–Amplitude Collective Mode and Bi–Higgs Frequency Sidebands

To compare the predicted relative phase dynamics with earlier studies on multi-band superconductors with weak interband interactions, $g_{\lambda,\nu \neq \lambda} << g_{\lambda,\lambda}$, Supplementary Fig. 3 shows the dependence of the $\Delta\theta$ -spectrum on the interband interaction strength $U = g_{\lambda,\nu \neq \lambda}/g_{\lambda,\lambda}$ for a weak excitation field of $E_0 = 25$ kV/cm. For small interband U , a Leggett phase mode is located below the excitation energy gap determined by $\omega_{H,1}$ (dashed magenta line), which is in agreement with earlier studies on multi-band superconductors with dominant intraband interaction [15]. With increasing U , we find here that the Leggett mode moves towards $\omega_{H,1}$ and crosses $\omega_{H,1}$ around $U \sim 0.5$. A further increase of U leads to a further blue shift of the mode towards $\omega_{H,2}$ (dashed black line). The Leggett phase mode is located around ~ 12 meV for $U = 3$ used in the simulations and is expected to be overdamped, as it overlaps with the quasi-particle continuum. It does not produce the bi-Higgs frequency sideband signals if weak laser excitation is used, where the low order susceptibility expansion applies.

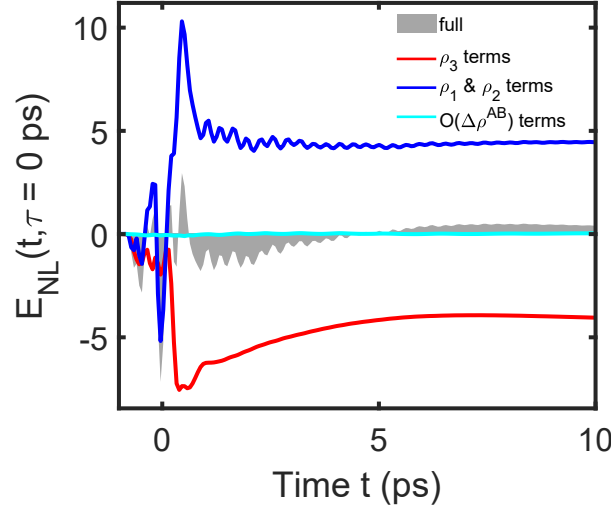
To clarify the role of the phase–amplitude collective mode emerging for strong laser fields in enhancing the parametric pseudo–spin driving by the phase dynamics, Supplementary Fig. 4 shows the field strength dependence of (a) the order parameter amplitude spectrum $|\Delta_1(\omega)|$ and (b) the spectrum of the relative phase $\Delta\theta(\omega)$ for strong Coulomb interband coupling as in the iron-based SC studied here. At low fields, the order parameter amplitude spectrum is dominated by a peak at $\sim \omega_{H,1}$ (dashed magenta line). With increasing field E_0 , the higher Higgs mode arising from the contribution of the electron pocket, i. e., the $\omega_{H,2}$ -mode discussed in Ref. [6] (dashed black line), emerges due to strong interband coupling. This higher Higgs mode amplitude exceeds the $\omega_{H,1}$ -peak amplitude at high E_0 , in agreement with previous studies [6]. Compared to that, for low fields, $\Delta\theta_\nu(\omega)$ shows a peak located within the quasi-particle continuum, around 12 meV in Supplementary Fig. 4b, which corresponds to the previously studied Leggett mode. This is consistent with previous results obtained by using susceptibility expansions [14]. With increasing driving field, however, the relative phase mode moves towards $\omega_{H,1}$ due to the nonlinear light–induced contributions, which strongly couple phase and



Supplementary Figure 4. (a), (b) Field strength dependence of the SC order parameter amplitude spectrum $|\Delta_1(\omega)|$ and the spectrum of the interband phase difference $\Delta\theta(\omega)$. Dashed magenta (black) lines indicate Higgs mode $\omega_{H,1}$ ($\omega_{H,2}$). (c), (d) Field strength dependence of the THz-light induced superfluid momentum $\mathbf{p}_s$ and the maximum of the $|\Delta_1|^2 \sin 2\Delta\theta$ spectrum. The increase of the latter exceeds the increase of $\mathbf{p}_s$ at elevated field strengths. (e) E_0 -dependence of $\omega_t = 2\omega_{H,1} - \omega_0$ peaks in the THz-MDCS spectrum.

amplitude to create phase-amplitude collective modes. Depending on E_0 , Supplementary Fig. 4b clearly shows that either the $\omega_{H,1}$ - or the Leggett-mode peak dominates the $\Delta\theta$ -spectrum. The emergence of a strong phase peak at the Higgs frequency $\omega_{H,1}$ demonstrates the strong nonlinear coupling between the amplitude Higgs mode and the phase Leggett mode that determine the low-order response for weak fields. This strong nonlinear coupling results in a light-induced phase-amplitude collective mode at $\omega_{H,1}$. This collective mode displays strong phase oscillations at the Higgs frequency $\omega_{H,1}$, which allows for resonant parametric driving of the coupled nonlinear parametric harmonic oscillator equations (23) as discussed above. The resulting time-dependent pseudo-spin canting, as the pseudo-spins non-adiabatically adjust to the time-dependent phase deviations from their equilibrium values that determine the $s_{\pm}$ order parameter pseudo-spin directions, leads to sideband signals at twice the Higgs energy $\omega_{H,1}$, due to phase-quasi-particle nonlinear coupling discussed in Supplementary Note 3.

To clarify the transition from Higgs collective mode to coupled phase-amplitude mode at $\omega_{H,1}$, observed in the experimental and theoretical THz-MDCS spectra in Figs. 2 and 3 in the main text, Supplementary Fig. 4c shows the field strength-dependence of the light-induced persisting superfluid momentum $\mathbf{p}_s$. This Cooper pair center-of-mass momentum breaks the equilibrium inversion symmetry and characterizes the strength of the Higgs mode signals at $\omega_t = \omega_{H,1}$ in the THz-MDCS spectra within regime II. Supplementary Fig. 4d shows the field-dependence of the maximum of the $|\Delta_1|^2 \sin 2\Delta\theta$ spectrum that determines the strength of the pseudo-spin canting in response to the phase angle time-dependent changes, which leads to the nonlinear oscillator "normal modes". At low driving fields, the increase of $\mathbf{p}_s$ is proportional to E_0^3 , since in this regime it is generated to lowest order by third-order nonlinear processes that determine $J(t)$ and the effective driving field $E(t)$, Eq. (17), when light-wave propagation effects are included [8]. This initial excitation regime is, however, followed by another excitation regime, where, in a two-band SC, the quench of the SC gap is only slightly modified as the driving field increases as observable in Supplementary Fig. 4a.



Supplementary Figure 5. Nonlinear transmitted electric field as a function of gate time t for $\tau = 0$ ps and 700 kV/cm high excitation. The total nonlinear transmission (shaded area) is shown together with the results where only (i) the quantum transport term $\propto \tilde{\rho}_3$ (first line Eq. (33), red line), (ii) the terms $\propto \tilde{\rho}_{1,2}$ (2nd–5th lines of Eq. (33), blue line), and (iii) the nonlinear contributions resulting from the interference between SC excitations of pulses A and B (6th line of Eq. (33), cyan line) are included in the simulations.

This behavior is unlike the one-band case [8, 12] and results from the strong interband coupling between electron and hole pockets leading to the formation of a hybrid-Higgs collective mode [6]. In this non-perturbative excitation regime, the contribution of Higgs collective effects to the nonlinear response dominates over quasi-particle excitations, which results in the different nonlinear increase of $\mathbf{p}_S$ as compared to the initial regime seen in Supplementary Fig. 4c. Above 600 kV/cm driving, a further increase of the driving field leads to a complete quench of the SC gap (results are only shown up to an order parameter quench of 25 % in Supplementary Fig. 4) which results in a stronger nonlinear increase of $\mathbf{p}_S$ compared to the one in the initial excitation regime seen in Supplementary Fig. 4c. This behavior is in agreement with the results in one-band superconductors discussed in Refs. [8, 12].

Compared to that, the maximum of the $|\Delta_1|^2 \sin 2\Delta\theta$ spectrum presented in Supplementary Fig. 4d is zero in the perturbative excitation regime, as in susceptibility expansion approaches. In the nonlinear regimes I and II, parametric time-periodic driving of pseudo-spin canting by the phase dynamics is negligible, and we recover there previously obtained results without any bi-Higgs frequency sidebands. However, above critical laser field, we obtain a (two-step) increase with growing field strength in $|\Delta_1|^2 \sin 2\Delta\theta$. In particular, the coupled phase-amplitude mode emerges around $E_0 = 150$ kV/cm, when the relative phase mode gets close to $\omega_{H,1}$ (Supplementary Fig. 4b). The spectrum only slightly increases up to $E_0 = 400$ kV/cm, while $\omega_{H,1}$ is only slightly modified by the growing driving field. A further increase of E_0 leads to a strong increase of the maximum of $|\Delta_1|^2 \sin 2\Delta\theta$ spectrum above a critical field $E_0 > 400$ kV/cm (Supplementary Fig. 4d), where the non-perturbative bi-Higgs frequency sidebands emerge in the THz-MDCS spectra (Supplementary Fig. 4e). In this high excitation regime, the SC order parameter becomes further quenched, which leads to a stronger increase of the relative phase oscillation amplitude enhanced by $1/|\Delta_1|$ and increases the light-induced change in superfluid density. The strong nonlinear increase of the $|\Delta_1|^2 \sin 2\Delta\theta$ spectral peak above driving field threshold exceeds the corresponding increase of the light-induced DC current, so that the THz-MDCS signals generated by the coupled phase-amplitude mode at $\omega_t = 2\omega_{H,1} - \omega_0$ and $\omega_t = 2\omega_{H,1} - 2\omega_0$ dominate over the Higgs collective mode signals at $\omega_t = \omega_{H,1}$. Important for our proposed interpretation is that the two-step increase of $|\Delta_1|^2 \sin 2\Delta\theta$ spectral peak, determined by both amplitude and phase dynamics, coincides with the increase of the $\omega_0 = 2\omega_{H,1} - \omega_0$ -peaks in the calculated THz-MDCS spectra (Supplementary Fig. 4e). This result confirms our theoretical prediction that the bi-Higgs frequency non-perturbative sideband peaks observed in the experiment are mainly parametrically driven by the interband phase-amplitude mode of a light-induced time-dependent SC state characterized by canted pseudo-spins deviating from the equilibrium $s_{\pm}$ directions. Such time-dependent canted pseudo-spin state is not realized close to equilibrium or for perturbative driving.

Supplementary Note 5: THz-MDCS Nonlinear Spectra

Based on Eqs. (18)–(19), the THz-MDCS nonlinear spectra are determined by the dynamics of $\tilde{\rho}_0^{(\nu),\text{NL}}(\mathbf{k}) = \tilde{\rho}_0^{(\nu),\text{AB}}(\mathbf{k}) - \tilde{\rho}_0^{(\nu),\text{A}}(\mathbf{k}) - \tilde{\rho}_0^{(\nu),\text{B}}(\mathbf{k})$, where $\tilde{\rho}^{(\nu),\text{AB}}(\mathbf{k})$ denotes the density matrix of the non-equilibrium state driven by both pulses, while $\tilde{\rho}^{(\nu),\text{A}}(\mathbf{k})$ ($\tilde{\rho}^{(\nu),\text{B}}(\mathbf{k})$) is the density matrix that describes the quantum state driven by pulse A (B) alone. To separate the nonlinear processes of main interest here from the processes arising from pump-probe interference discussed in Ref. [13], which lead to THz-MDCS peaks displaced along the vertical ω_τ axis, we decompose the density matrix $\tilde{\rho}^{(\nu),\text{AB}}(\mathbf{k})$ as

$$\tilde{\rho}^{(\nu),\text{AB}}(\mathbf{k}) = \tilde{\rho}^{(\nu),\text{A}}(\mathbf{k}) + \tilde{\rho}^{(\nu),\text{B}}(\mathbf{k}) + \Delta\tilde{\rho}^{(\nu),\text{AB}}(\mathbf{k}), \quad (32)$$

where $\Delta\tilde{\rho}^{(\nu),\text{AB}}(\mathbf{k})$ is generated by interference between SC excitations of both pulses A and B. From the equation of motion for $\tilde{\rho}_0^{(\nu),\text{NL}}(\mathbf{k})$ we then obtain

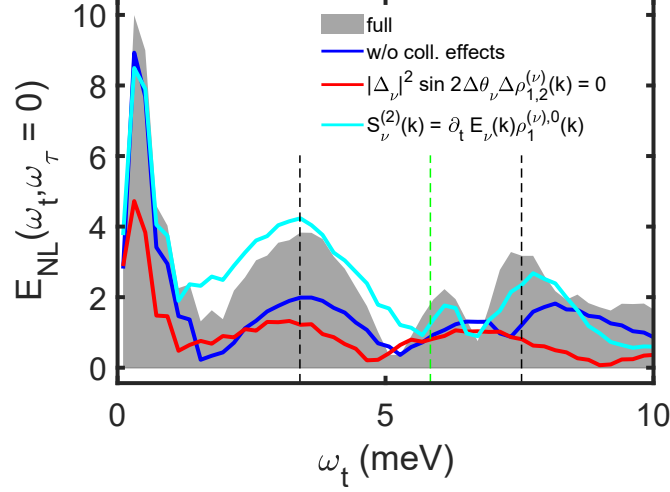
$$\begin{aligned} \frac{\partial}{\partial t} \tilde{\rho}_0^{(\nu),\text{NL}}(\mathbf{k}) = & -e \mathbf{E}_A(t) \cdot \nabla_{\mathbf{k}} \tilde{\rho}_3^{(\nu),\text{B}}(\mathbf{k}) \\ & - |\Delta_\nu^A| \left[(\cos \delta\theta_\nu^A + \cos \delta\theta_\nu^B) (\tilde{\rho}_2^{(\nu),\text{B}}(\mathbf{k}_-^{\text{AB}}) - \tilde{\rho}_2^{(\nu),\text{B}}(\mathbf{k}_+^{\text{AB}})) \right] \\ & - |\Delta_\nu^A| \left[(\cos \delta\theta_\nu^A + \cos \delta\theta_\nu^B) (\tilde{\rho}_2^{(\nu),\text{A}}(\mathbf{k}_-^{\text{AB}}) - \tilde{\rho}_2^{(\nu),\text{A}}(\mathbf{k}_+^{\text{AB}})) \right] \\ & - |\Delta_\nu^A| \left[(\sin \delta\theta_\nu^A + \sin \delta\theta_\nu^B) (\tilde{\rho}_1^{(\nu),\text{B}}(\mathbf{k}_-^{\text{AB}}) - \tilde{\rho}_1^{(\nu),\text{B}}(\mathbf{k}_+^{\text{AB}})) \right] \\ & - |\Delta_\nu^A| \left[(\sin \delta\theta_\nu^A + \sin \delta\theta_\nu^B) (\tilde{\rho}_1^{(\nu),\text{A}}(\mathbf{k}_-^{\text{AB}}) - \tilde{\rho}_1^{(\nu),\text{A}}(\mathbf{k}_+^{\text{AB}})) \right] \\ & + \mathcal{O}(\Delta\tilde{\rho}^{(\nu),\text{AB}}) + \text{A} \leftrightarrow \text{B}, \quad \mathbf{k}_\pm^{\text{AB}} = \mathbf{k} \pm \mathbf{p}_S^A \pm \mathbf{p}_S^B. \end{aligned} \quad (33)$$

This correlated nonlinear signal describes contributions along $(\omega_t, 0)$, i. e. along the frequency vector of pulse A, $\omega_A = (\omega_0, 0)$, and along $(\omega_t, -\omega_t)$, i. e., along the frequency vector of pulse B, $\omega_B = (\omega_0, -\omega_0)$, when the processes arising from pump-probe interference are negligible. The contributions of the different terms of Eq. (33) to the total nonlinear differential transmission are studied in Supplementary Fig. 5 where the total nonlinear differential transmission for fixed $\tau = 0$ ps (shaded area) is shown together with the results where only (i) the quantum transport term $\propto \tilde{\rho}_3$ (first line Eq. (33), red line), (ii) the terms $\propto \tilde{\rho}_{1,2}$ (2nd–5th lines of Eq. (33), blue line), and (iii) the nonlinear contributions resulting from the interference between SC excitations of pulses A and B (6th line of Eq. (33), cyan line) are included in the simulations. The quantum transport terms mainly lead to inversion symmetry breaking, since the contribution to the nonlinear response shows a large DC current, but no collective mode oscillations after both pulses, i. e. for $t > 2$ ps. Compared to that, the result of $\propto \tilde{\rho}_{1,2}$ contributions also shows a large DC current, which compensates the one of the transport term, but, most importantly, also exhibits collective mode oscillations after both pulses. This demonstrates that the Higgs mode peaks as well as the sideband signals at twice of the Higgs energy are mainly generated by the $\propto \tilde{\rho}_{1,2}$ contributions, in agreement with the discussion in Supplementary Note 3. Finally, we note that the contribution of the nonlinear terms resulting from the interference between SC excitations of pulses A and B to the nonlinear differential transmission are not important for the proposed effects, for the two strong broad pulses considered in this paper.

Supplementary Note 6: Field Dependence of the THz-MDCS Signals

We start with the nonlinear processes that dominate at higher fields. From Eq. (33) we obtain that the non-adiabatic pseudo-spin canting results in THz-MDCS satellite peaks at $(2\omega_{\text{H},1} - \omega_0, 0)$ and $(2\omega_{\text{H},1} - \omega_0, -2\omega_{\text{H},1} + \omega_0)$. These strong bi-Higgs frequency sideband signals arise to lowest order from the ninth-order nonlinear processes $2\omega_{\text{A},\text{B}} - 2\omega_{\text{A},\text{B}} + 2\omega_{\text{H},1}^{\text{B},\text{A}} - \omega_{\text{B},\text{A}}$, as discussed in more detail below. In the presence of light-wave propagation effects inside the SC system, which lead to DC current generation (Supplementary Note 7), these same processes lead to inversion-symmetry breaking peaks at $(2\omega_{\text{H},1} - 2\omega_0, 0)$ and $(2\omega_{\text{H},1} - 2\omega_0, -2\omega_{\text{H},1} + 2\omega_0)$. These bi-Higgs frequency sideband peaks are generated by the nonlinear processes $2\omega_{\text{A},\text{B}} - 2\omega_{\text{A},\text{B}} + \omega_{\text{H},1}^{\text{B},\text{A}} + (\omega_{\text{H},1}^{\text{B},\text{A}} - 2\omega_{\text{B},\text{A}})$.

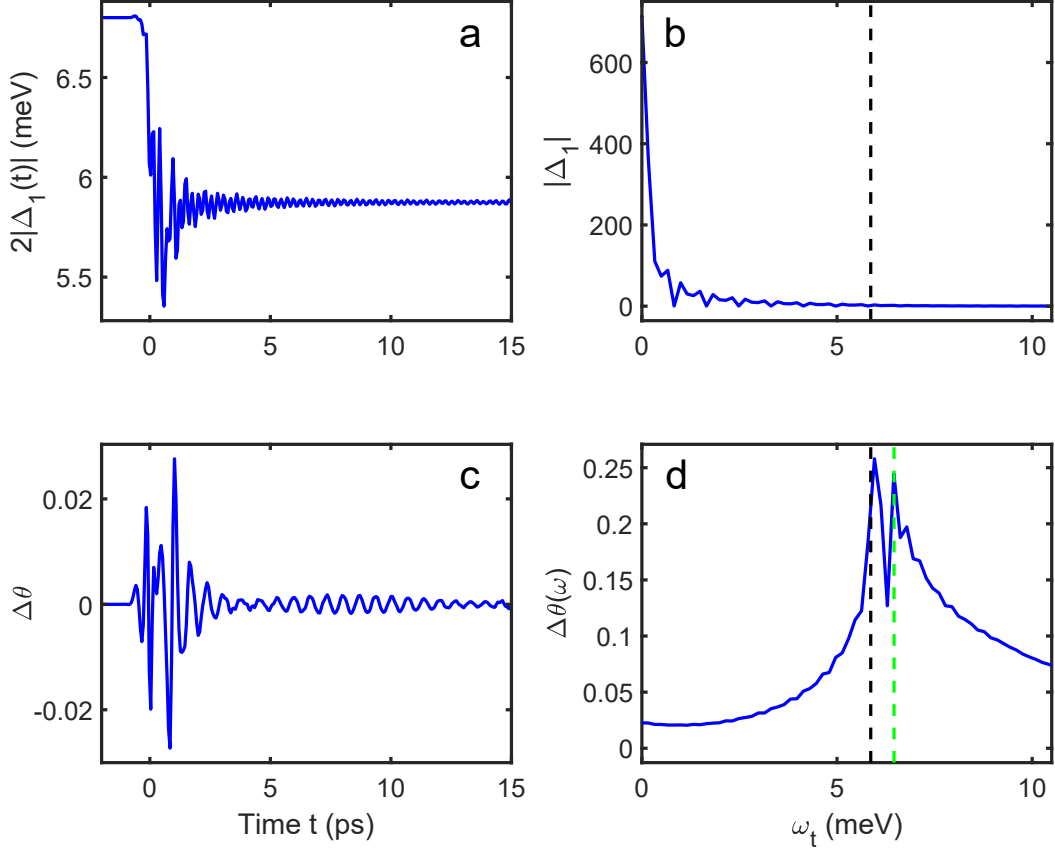
To verify that the sideband signals are indeed mainly generated by the $\propto |\Delta_1|^2 \sin 2\Delta\theta \Delta\tilde{\rho}_{1,2}^{(\nu)}$ dynamical coupling of the pseudo-spin components $\Delta\tilde{\rho}_1^{(\nu)}$ and $\Delta\tilde{\rho}_2^{(\nu)}$ in the equations of motion (23), Supplementary Fig. 6 shows the nonlinear differential transmission $E_{\text{NL}}(\omega_t, \omega_\tau = 0)$ for 500 kV/cm excitation. The full calculation (shaded area) is compared with calculations where (i) collective modes are switched off (2nd terms on the rhs of Eqs. (23)) (blue line),



Supplementary Figure 6. Nonlinear differential transmission $E_{\text{NL}}(\omega_t, \omega_\tau = 0)$ for 500 kV/cm excitation. The full calculation (shaded area) is compared with calculations where (i) collective effects are switched off (2nd terms on the rhs of Eqs. (23) are switched off, blue line) (ii) the term $|\Delta_1|^2 \sin 2\Delta\theta \Delta\tilde{\rho}_{1,2}^{(\nu)}$ driving pseudo-spin canting is switched off (red line), and (iii) all contributions of the source terms (24), except for the field-dependent source term $\partial_t E_\nu(\mathbf{k}) \tilde{\rho}_1^{(\nu),0}(\mathbf{k})$, which drives pseudo-spin precession in the third-order response, are switched off (cyan line). Vertical dashed black lines indicate $2\omega_{\text{H},1} - \omega_0$ and $2\omega_{\text{H},1} - 2\omega_0$ signals while the peak at $\omega_{\text{H},1}$ is marked by a vertical dashed green line.

(ii) the coupling term $|\Delta_1|^2 \sin 2\Delta\theta \Delta\tilde{\rho}_{1,2}^{(\nu)}$ is switched off (without relative phase-driven non-adiabatic pseudo-spin canting, red line), and (iii) all contributions of the source terms (24), except for the field-dependent source term $\partial_t E_\nu(\mathbf{k}) \tilde{\rho}_1^{(\nu),0}(\mathbf{k})$ already known to drive pseudo-spin precession in the third-order response, are switched off (cyan line). First, switching of all source terms (24) except for the field-dependent source term $\partial_t E_\nu(\mathbf{k}) \tilde{\rho}_1^{(\nu),0}(\mathbf{k})$ considered before has no significant impact on the sideband peaks at twice the Higgs energy. In contrast, the signals at $2\omega_{\text{H},1} - \omega_0$ and $2\omega_{\text{H},1} - 2\omega_0$ (vertical dashed black lines) are strongly suppressed when either collective effects or the coupling $\propto |\Delta_1|^2 \sin 2\Delta\theta \Delta\tilde{\rho}_{1,2}^{(\nu)}$ are switched off. This result shows that the strong sideband signals are generated by the phase–amplitude collective mode via the nonlinear dynamical coupling $\frac{1}{2}|\Delta_1|^2 \sin 2\Delta\theta \Delta\tilde{\rho}_{1,2}^{(\nu)} = \Delta'_1 \Delta''_1 \Delta\tilde{\rho}_{1,2}^{(\nu)}$, which depends on both light-induced amplitude (Δ'_1) and phase (Δ''_1) changes and parametrically drives pseudo-spin canting in the non-equilibrium state via the changes of the relative phase from its equilibrium value.

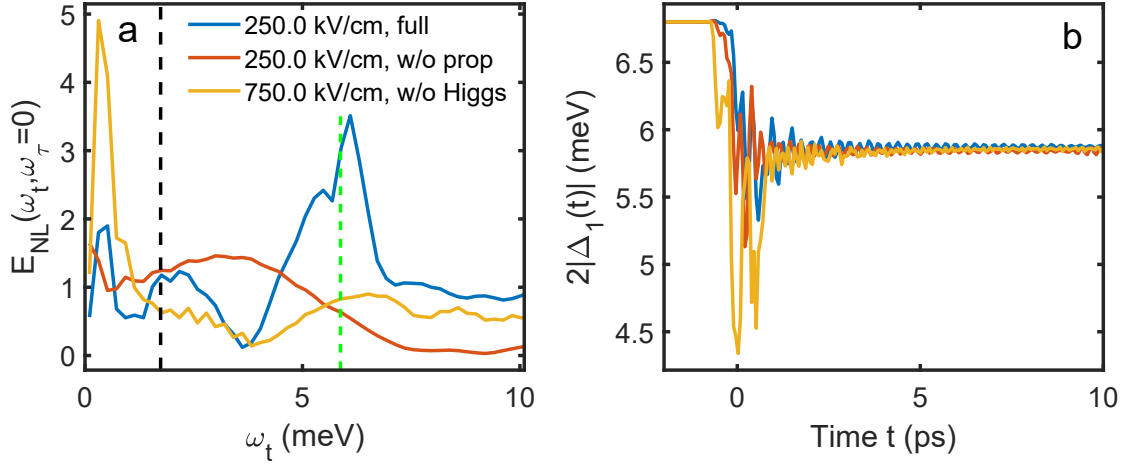
We now discuss the nonlinear contributions to the THz–MDCS signal for the *lower* fields considered here. Supplementary Figs. 7a and 7c show the dynamics of the SC order parameter amplitude $|\Delta_1|$ and the interband phase difference between electron and hole pockets, $\Delta\theta$, for 250 kV/cm excitation below the critical field required to observe the bi-Higgs frequency sidebands. The order parameter is quenched by the strong single cycle pulse, which leads to a strong $\omega = 0$ -peak in the $|\Delta_1|$ spectrum (Supplementary Fig. 7b). The latter dominates over the $\omega_{\text{H},1}$ -peak (black dashed line). As a result, $|\Delta_1^A|$ in the second term of Eq. (33) is driven by the difference-frequency Raman process $2\omega_A - 2\omega_A$, as discussed in Ref. [13]. At the same time, the $\Delta\theta$ spectrum (Supplementary Fig. 7d) shows a peak at $\omega_{\text{H},1}$ (black dashed line) and a slightly weaker peak above $\omega_{\text{H},1}$ (dashed green line). However, the $\Delta\theta$ signal is weak, such that $\delta\theta$ in Eq. (33) can be approximated by its equilibrium value $\delta\theta^0 \sim \pi$ and thus $\cos \delta\theta \sim -1$. By expanding the second term of Eq. (33) in powers of $\mathbf{p}_S$, we obtain $|\Delta_\nu^A| \left[\cos \delta\theta^{A,B} (\tilde{\rho}_2^{(\nu),B}(\mathbf{k}_-^{\text{AB}}) - \tilde{\rho}_2^{(\nu),B}(\mathbf{k}_+^{\text{AB}})) \right] \approx |\Delta_\nu^A| (\mathbf{p}_S^A + \mathbf{p}_S^B) \cdot \nabla_{\mathbf{k}} \tilde{\rho}_2^{(\nu),B}(\mathbf{k}) + \mathcal{O}(\mathbf{p}_S^3)$ such that the term (26) dominantly drives ninth-order nonlinear processes leading to peaks at $(2\omega_A - 2\omega_A) + \omega_{\text{H},1}^B + (\omega_B - \omega_B) - \omega_B = (\omega_{\text{H},1} - \omega_0, -\omega_{\text{H},1} + \omega_0)$. These peaks are observed in the THz–MDCS spectra in Figs. 2 and 3 in the main text at lower fields. Analogously, exchanging $A \leftrightarrow B$ leads to a peak at $(\omega_{\text{H},1} - \omega_0, 0)$. Note that the above peaks are shifted from the Higgs frequency by ω_0 and do not explain the experimentally observed peaks centered at the either Higgs or bi-Higgs frequencies, which are absent for the above weaker driving field.



Supplementary Figure 7. Dynamics of (a) the SC order parameter $2|\Delta_1|$ and (c) the interband phase difference $\Delta\theta$ for 250 kV/cm excitation. The corresponding spectra are shown in (b) and (d). The Higgs mode energy is indicated by a vertical dashed black line while the Leggett mode, which is located within the quasi-particle continuum, is marked by a vertical dashed green line.

Supplementary Note 7: Inversion-Symmetry-Breaking Nonlinear Processes

The origin of the hybrid-Higgs collective mode characterizing multi-band FeSCs with strong interband coupling was discussed in Ref. [6]. This Higgs collective mode leads to a distinct peak in the THz-MDCS spectra when the THz-driven inversion-symmetry breaking persists after the pulse. This peak is photogenerated by higher-order processes beyond the third-order response, via the dynamical interplay of THz-driven nonlinear SC response with lightwave electromagnetic propagation inside the SC system. The latter interplay leads to coherent photogeneration of a nonlinear DC supercurrent through difference-frequency Raman processes, as shown in Ref. [8]. The persisting inversion-symmetry breaking also leads to gapless non-equilibrium SC states and equilibrium-symmetry-forbidden spectral peaks [8], which have been experimentally observed in Refs. [11, 12]. Here, dynamical inversion-symmetry breaking allows the photogeneration of high-order nonlinear signals centered at the Higgs frequency $\omega_{H,1}$ within non-linear regime II. To demonstrate that the calculated signal at $\omega_t = \omega_{H,1}$ is indeed generated by nonlinear interactions of the Higgs collective mode, we compare in Supplementary Fig. 8a $E_{NL}(\omega_t, \omega_\tau = 0)$ obtained by the full calculation with electromagnetic propagation effects ($\mathbf{p}_S \neq 0$ after the pulse, blue line) with the calculation without propagation ($\mathbf{p}_S = 0$ after the pulse, red line) and the calculation with propagation effects but without the Higgs collective contribution to Eq. (23) ($\mathbf{p}_S \neq 0$ after the pulse but no collective mode). To be able to directly compare the different simulations, the field strengths are chosen such that $\omega_{H,1} = 2\Delta_{1,\infty} \sim 5.8$ meV in all cases (Supplementary Fig. 8b). The result of the full calculation shows a weak high-order pump-probe peak at $\omega_t = \omega_{H,1} - \omega_0$ (black dashed line), as well as a strong ninth-order inversion-symmetry-breaking nonlinear signal at $\omega_{H,1}$ (green dashed line). The latter high-order nonlinear signal vanishes when propagation effects are switched off and is strongly suppressed without collective effects. This result demonstrates that the inversion-symmetry breaking signals at $\omega_t = \omega_{H,1}$ are generated by high-order nonlinear processes involving strong coupling of the Higgs collective mode excitations, which dominate



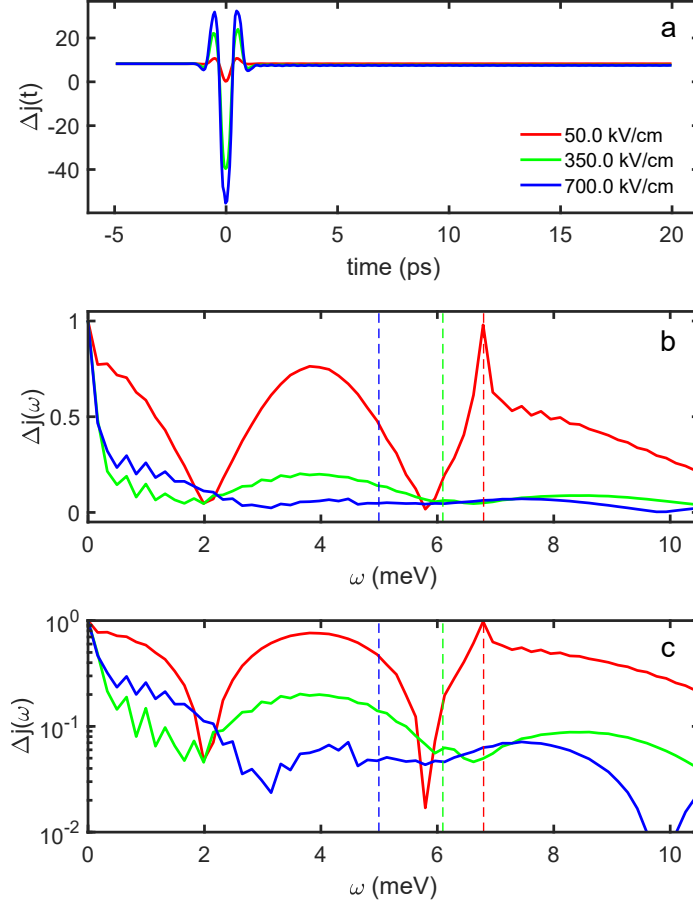
Supplementary Figure 8. Origin of inversion-symmetry breaking peaks at $\omega_t = \omega_{H,1}$ in the THz-MDCS spectra. **(a)** The nonlinear response $E_{NL}(\omega_t, \omega_\tau = 0)$ is shown for the full calculation with propagation effects (blue line), for a calculation without propagation effects (red line), and for a calculation with propagation effects but without Higgs collective mode (yellow line). It is clear from this figure that both light-induced persisting symmetry breaking and Higgs collective effects must be invoked to explain the experiment. $\omega_t = \omega_{H,1} - \omega_0$ ($\omega_t = \omega_{H,1}$) is indicated with a vertical dashed black (green) line. **(b)** The corresponding dynamics of the SC order parameter amplitude $2|\Delta_1|$.

over the traditional third- or fifth-order perturbative responses.

We now discuss the nonlinear processes that generate the THz-MDCS peaks at $\omega_t = \omega_{H,1}$. In the presence of light-wave propagation effects, our calculations show a photo-generated long-lived DC current determined by the superfluid momentum $\mathbf{p}_S$. As a result of the interplay of SC nonlinearity and electromagnetic propagation effects, the photocurrent develops a static $\omega = 0$ -component, in addition to the oscillating component at the pulse frequency ω_0 that shifted the Higgs frequency peaks in the above analysis. Thus, the higher order difference-frequency Raman processes assisted by quasi-particle excitations discussed in the previous section drive a new inversion-symmetry forbidden peak at $\omega_t = \omega_{H,1}$ in the THz-MDCS spectra, in addition to the signals at $\omega_t = \omega_{H,1} - \omega_0$, as observed experimentally in Fig. 2 in the main text. More specifically, inversion-symmetry forbidden peaks arise at $(\omega_{H,1}, 0)$ and $(\omega_{H,1}, -\omega_{H,1})$ in the THz-MDCS spectra, both dominated by the Higgs collective mode, as demonstrated in Supplementary Fig. 8a. Based on the above detailed analysis, we conclude that our THz-MDCS experiments and the observation of distinct peaks at $(\omega_{H,1}, 0)$ in two-dimensional frequency space allow for quantum sensing of the Higgs collective modes of a light-induced finite-momentum-pairing non-equilibrium SC state, $\mathbf{p}_S \neq 0$, which lives longer than the pulse.

It is important to note that the above sharp THz-MDCS peaks come from higher order nonlinear processes. The contribution of such processes is masked within the quasi-particle continuum if a DC external current is applied to break the equilibrium inversion symmetry instead of using the interplay between SC nonlinearity and electromagnetic propagation. To demonstrate the advantage of the latter purely laser-induced process that makes the proposed effects observable experimentally, we performed a simulation of the response obtained with a DC external current and a single THz pump pulse. Supplementary Fig. 9 shows the dynamics (Supplementary Fig. 9a) and spectrum (Supplementary Figs. 9b and 9c) of the differential current Δj obtained by subtracting the total current without symmetry-breaking DC current from the one with DC current applied. For the lowest studied THz field (red line), Δj shows a sharp peak at the Higgs frequency (dashed vertical line). For such low driving field, the Higgs frequency peak exceeds the fundamental emission peak at $\omega_0 = 1$ THz. With increasing THz field, however, the signal at the Higgs frequency (dashed vertical lines) is suppressed as compared to the peak at ω_0 . The Higgs mode is hardly observable in the differential current spectrum for the highest studied field (blue line). In contrast, the THz-MDCS results, Figs. 3c and 3d in the main text, show a strong Higgs resonance for high fields. Importantly, this Higgs resonance gives way to dominant bi-Higgs frequency satellite peaks above excitation threshold. These signals, observed for the first time here, are not detectable with single-pulse one-dimensional imaging in the presence of a DC current in Supplementary Fig. 9, due to the broad ω_0 and second harmonic emission peaks. On the other hand, traditional pump-probe signals [13] are expected to dominate for low excitation without sufficiently strong symmetry breaking, in which case a DC current is advantageous.

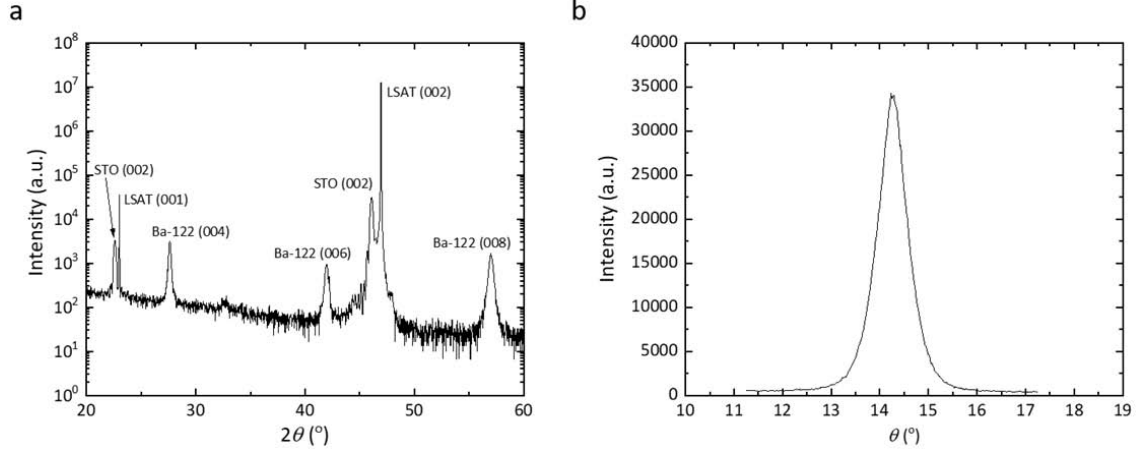
We next discuss similarities and differences in the finite-momentum pairing achieved with parametric driving and



Supplementary Figure 9. (a) Dynamics of the differential photocurrent obtained by subtracting the total current without symmetry-breaking DC current from the one with DC current applied. The result are shown for three different THz pump field strengths. (b), (c) The corresponding spectra in linear and semi-logarithmic scales. Unlike with THz dynamical symmetry breaking, the Higgs mode (vertical dashed lines) can only be clearly resolved at low pump field strengths (red curves).

the one created in a superconductor with an applied DC current. In one-band superconductors, we have shown in Refs. [8, 11] that the finite-momentum pairing states obtained all-optically by THz dynamical symmetry breaking lead at long times to three different kinds of finite-momentum-pairing states: (i) SC states with finite quasiparticle excitation energy and finite order parameter, (ii) gapless SC states with finite order parameter but zero quasiparticle excitation energy, and (iii) gapless quasiparticle states with zero order parameter. There are practical experimental differences between all-optical and transport methods, but these finite-momentum pairing states comparable to Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) states could also be obtained by using a DC static current to impart a sufficiently strong static finite momentum to the SC state. However, here we showed different states obtained by two-phase-locked-pulse excitation of multi-band superconductors above critical threshold, not observable in one-band superconductors. The difference arises from the dynamical interplay between order parameter relative phase dynamics and finite momentum pairing, which requires strong THz driving beyond the Higgs mode resonance regime seen with DC current in Supplementary Fig. 9. In particular, above critical THz field strength, we demonstrated here a transition from the finite momentum pairing states with hybrid-Higgs collective modes to new phase-driven states characterized by bi-Higgs frequency satellite peaks dominating over Higgs resonances. To parametrically drive the new states, we need strong THz light-induced phase-amplitude coupling to move the Leggett mode phase oscillation frequency from well within the continuum to the Higgs frequency of the amplitude oscillations. Our two-phase-locked-pulse excitation scheme allows us to access and image with two-dimensional frequency resolution these states, which are achieved in the non-perturbative excitation regime above threshold.

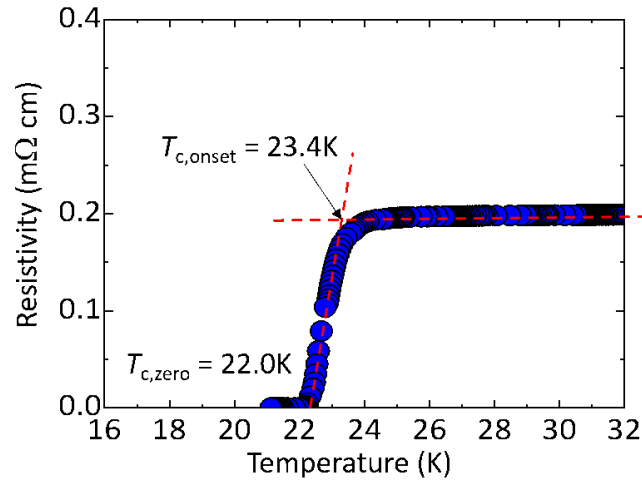
Supplementary Note 8: Iron Pnictide epitaxial thin films and magnetic/electronic/crystalline/superconducting quality



Supplementary Figure 10. (a) Out-of-plane θ - 2θ XRD patterns of Co-doped BaFe_2As_2 films grown on SrTiO_3 buffered (001)-oriented $(\text{La;Sr})(\text{Al;Ta})\text{O}_3$ (LSAT) single-crystal substrates. (b) Rocking curve and FWHM for (004) reflection of Ba-122 films.

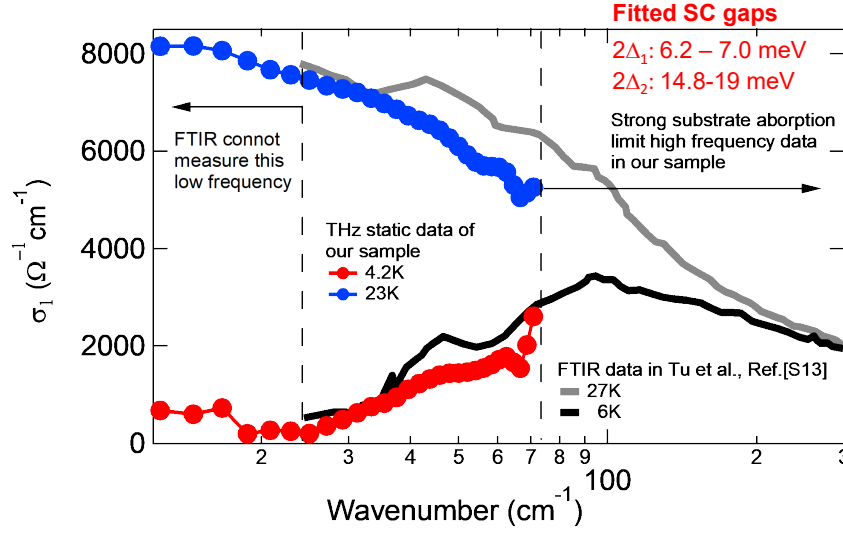
Co-doped BaFe_2As_2 (Ba-122) epitaxial thin films were grown on 40 nm thick SrTiO_3 (STO) buffered (001)-oriented $(\text{La;Sr})(\text{Al;Ta})\text{O}_3$ (LSAT) single-crystal substrates [16–18]. The LSAT substrates are double-side polished for optical measurement. The base pressure is below 3×10^{-5} Pa and the films were synthesized by pulsed laser deposition with a KrF (248 nm) ultraviolet excimer laser in a vacuum of 3×10^{-4} Pa at 730°C (growth rate: 2.4 nm/sec). The Co-doped Ba-122 target was prepared by solid-state reaction with a nominal composition of $\text{Ba/Fe/Co/As} = 1:1.84:0.16:2.2$. This composition was determined by wavelength-dispersive X-ray spectroscopy (WDS) measurements to produce 8% optimal doping in the grown films.

The epitaxial and crystalline quality of the optimally doped BaFe_2As_2 thin films was measured by four-circle X-ray diffraction (XRD). Supplementary Fig. 10a shows the out-of-plane θ - 2θ scans of the films on STO buffered (001)-oriented LSAT single-crystal substrates. The XRD patterns show that the film 001 reflections dominate indicating c -axis growth normal to the substrate. As shown in Supplementary Fig. 10b, the full width half maximum (FWHM) of the (004) reflection rocking curve of the films on STO/LSAT is as narrow as 0.7° , which means high quality epitaxial thin films.



Supplementary Figure 11. Superconducting transition of Co-doped Ba-122 films; $T_{c,\text{onset}}$ and $T_{c,\text{zero}}$ of the film on STO buffered LSAT are shown.

We have also performed chemical, structural and electrical characterizations of epitaxial Co-doped BaFe₂As₂ (Ba-122) superconducting thin films. We determined the chemical composition of Ba122 thin films by wavelength dispersive spectroscopy (WDS) analyses. The chemical composition of the thin film is found to be Ba(Fe_{0.92},Co_{0.08})₂As_{1.8}, which is close to the stoichiometry of Ba122 with 8 % (atomic %) optimal Co-doping. The PLD targets were made in the same way using the same nominal composition of Ba(Fe_{0.92},Co_{0.08})₂As_{2.2} as reported in our previous papers [16–18]. We measured temperature-dependent electrical resistivity for superconducting transitions by four-point method (Supplementary Fig. 11). Onset T_c and T_c at zero resistivity are as high as 23.4 K and 22.0 K, respectively, and ΔT_c is as narrow as 1.4 K, which are the highest and narrowest values for Ba-122 thin films. In our prior papers, one can also check a zero-field-cooled magnetization T_c and it clearly shows a diamagnetic signal by superconducting quantum interference device (SQUID) magnetometer measurements.



Supplementary Figure 12. A comparison between THz conductivity data of our sample (circles) at 4.2 K and 23 K and prior FTIR conductivity of single crystal samples (solid lines) [19].

It has already been established that up to five superconducting energy gaps can exist in FeSCs and can be organized into two energy scales, i.e., $2\Delta_1 \sim 6.2\text{--}7\text{ meV}$ and $2\Delta_2 \sim 15\text{ meV}$ [19]. The comparison of our equilibrium conductivity data (Supplementary Fig. 12) with the literature [19] shows the very high quality of both our characterization techniques in comparison with the literature and quality of our thin film samples used. Our equilibrium data is fully consistent with the reported properties of FeSCs in the literature. An example is shown in Supplementary Fig. 12. First, we can obtain the plasma frequency ω_p , obtained by fitting the normal state conductivity spectra with the Drude model, which gives the plasma frequency to be $\sim 194\text{ THz}$ ($\sim 804\text{ meV}$) and the scattering rate $\sim 2.5\text{ THz}$ ($\sim 10\text{ meV}$). These measurements are in excellent agreement with bulk single crystal samples at optimal doping: a normal state Drude plasma frequency of 972 meV , scattering rate 15 meV was obtained there. Second, some other equilibrium thermodynamic quantities can also be obtained, e.g., the London penetration depth $\lambda_L = 378\text{ nm}$, corresponding to a condensed fraction of $\sim 50\%$. These are again consistent with the prior measurements of high quality bulk samples, which show $\sim 50\%$ of the free carriers participating in superfluidity below T_c and a penetration depth of 300 nm . Third, our sample exhibits a relatively long mean field path, comparable to the coherence length, $l/\xi = \pi\tau\Delta_{SC}/\hbar \sim 1$, which indicates that our sample lies in the intermediate regime between the clean and dirty limits.

A key electronic property of FeSCs is the strong Coulomb coupling between electron and hole pockets that is well established in iron-based superconductors [20]:

- The theoretical predictions, if we assume larger intraband than interband interaction, provide the WRONG pairing symmetry, i.e., s_{++} instead of s_{+-} , and the electron-phonon interaction is too small to account for the high critical temperatures demonstrated. One of the first phase-sensitive tests of the symmetry of the superconducting order parameter have revealed a sign change, which indicates the dominance of interband interaction U over intraband interaction V . In addition, such a s_{+-} pairing is directly corroborated by the

observation of a resonance peak in the neutron scattering spectra at the SDW wave vector connecting the interband portions of the Fermi surface with the opposite signs of the superconducting order parameter. This SDW resonant peak has indeed been seen in almost all known FeSCs, which clearly show the dominance of the interband U .

- Opposite band shifts for hole- and electron-like pockets as a function of doping are a direct consequence of the multiband character of FeSCs with a dominant interband interaction U .
- The pairing mechanism in FeSCs is believed to be SDW fluctuations which relate closely to the antiferromagnetic/nesting wave vector between e- and h-bands, i.e., interband instead of intraband, at the Fermi surface.
- The dominance of interband coupling U between e-h pockets over intraband is widely accepted by now also due to some other complementary ultrafast measurements, e.g., spin-exciton modes in ultrafast THz conductivity [21]. These have been the foundational facts, being tested extensively in the community in the past 10 years, which lead to the conclusion of the unconventional nature of the pairing due to a dominant interband interaction in Fe-based superconductivity.

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