

Supplementary materials for “Terahertz field-induced giant symmetry modulations in a van der Waals antiferromagnet”

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Infrared spectrum

Far-infrared measurements were performed at the National High Magnetic Field Laboratory, using a Bruker Vertex 80v vacuum Fourier Transform Infrared (FTIR) spectrometer coupled to a vertical-bore superconducting 17.5 T magnet. Transmission spectra of a single crystal of MnPS_3 were recorded in the spectral range from 10 cm^{-1} to 205 cm^{-1} , with a resolution of 0.3 cm^{-1} .

Broadband far-infrared radiation, generated by a mercury lamp, was guided through an evacuated beamline connecting the spectrometer to the top of a brass lightpipe. A 90° off-axis parabolic mirror located at the bottom of the lightpipe directed the beam toward a second, identical confocal mirror, which collimated the radiation through a short secondary lightpipe ending at a Si bolometer detector. The sample, mounted at the focal point of the mirrors, fully covered a clear aperture of 3 mm and was maintained at a fixed temperature of approximately 5.5 K.

The magnetic field was applied in the plane of the sample and perpendicular to the propagation direction of the incident radiation (Voigt geometry). A cold low-pass filter blocked infrared radiation above 200 cm^{-1} . The transmission spectra were acquired in 0.5 T magnetic field increments and are presented as an intensity colormap in Supplementary Fig. 1a while corresponding horizontal line cuts, taken at every 3 T, are shown in Supplementary Fig. 1b. A dip in transmission intensity was observed at $\sim 4.5\text{ THz}$ (150 cm^{-1}), matching the frequency of an IR-active mode. To improve the signal-to-noise ratio, each measurement was repeated twice at every field step. The reproducibility between repeated scans was better than 0.5%, though slightly degraded near phonon peak regions due to reduced intensity.

To isolate field-dependent spectral features from field-independent background effects, each spectrum was divided by a reference spectrum, defined as the average of all measured spectra with statistical outliers removed. This normalization effectively suppressed instrumental artifacts and yielded a flat baseline, while preserving field-responsive changes.

The resulting normalized spectra were presented as a colormap in Supplementary Fig. 1c, with black and yellow representing the minimum and maximum deviations from the reference, respectively. White regions indicate frequencies where the spectral reproducibility exceeded 1%, typically coinciding with diminished transmission intensity. A broad purple-black band below 100 cm^{-1} reflects a known $\sim 3\%$ reduction in source intensity under high magnetic fields in this experimental configuration.

Raman spectrum

For low-temperature Raman spectroscopy measurements at National High Magnetic Field Laboratory, a 0.6 W 532 nm laser excitation was employed with a 2400 grooves/mm grating in a 0.75 FL spectrometer. To ensure better spectral resolution over a spectral window centered at 180 cm^{-1} , a $30\text{ }\mu\text{m}$ entrance slit was used. For each set of measurement, high signal-to-noise ratio was obtained upon averaging over 3 acquisitions (360 s acquisition time). Moreover, the averaging would also eliminate the cosmic ray effects. The experiments were performed under unpolarized light conditions using a polarization scrambler. To perform

high-temperature (> 60 K) measurement, the laser power and grating were changed to 0.2 W and 1200 grooves/mm, respectively. In addition, the spectral window was centered at 470 cm^{-1} .

Supplementary Fig. 1d plots the temperature-dependent Raman spectrum under zero magnetic field. A sharp peak is visible at 4.5 THz ($\sim 150\text{ cm}^{-1}$), consistent with previous studies [1–3]. Interestingly, as the temperature is lowered, a broadband feature around 3 THz ($\sim 100\text{ cm}^{-1}$) and a sharp feature at 3.5 THz ($\sim 117\text{ cm}^{-1}$) appear below 60 K, potentially suggesting an onset of inversion symmetry-breaking. Upon applying an in-plane magnetic field, no change in the Raman spectrum at 5 K was recorded as described in the 2D colormap in Supplementary Fig. 1e, ruling out the possibilities of magnon or magneto-phonon coupling.

Phenomenological fit of the SHG-RA patterns

For a normally incident probe beam, the SHG intensity as a function of the analyzer angle φ is given by the expression

$$I_{SH} = |A\cos^2(\varphi)\sin(\varphi) + B\sin^3(\varphi)|^2, \quad (\text{S1})$$

where A and B are phenomenological fit parameters, and can be written as a linear combination of the susceptibility tensor elements: $A = \chi_{xyy} + \chi_{yyx}$, $B = \chi_{xxx}$. All other components of the SHG tensor vanish within the electric dipole approximation as a consequence of the mirror plane perpendicular to y -axis [4]. For convenience, we take A to be a real number while B is a complex quantity, i.e., $B = B_{real} + iB_{im}$ [4, 5]. Using this formulation allows for a reasonable fit of the equilibrium SHG-RA patterns. However, this model breaks down for pumped SHG-RA patterns since A and B alone are unable to capture the THz field-induced large symmetry modulations as seen in Fig. 3d. To resolve this, we add extra terms in (S1):

$$I_{SH} = |A\cos^2(\varphi)\sin(\varphi) + B\sin^3(\varphi) + C\sin^2(\varphi)\cos(\varphi) + D\cos^3(\varphi)|^2. \quad (\text{S2})$$

Here, $C = C_{real} + iC_{im} = \chi_{yxx} + \chi_{xxy} + \chi_{xyx}$ and $D = D_{real} + iD_{im} = \chi_{yyy}$. Eq. (S2) enables us to fit the nonequilibrium SHG-RA patterns as a function of pump-probe delay time (Fig. 3e). A full derivation of Eqs. (S1)-(S2) is provided in the next section. To avoid complications, we restrict our analysis to the nonequilibrium SHG-RA patterns at time delays well beyond the TFISH response (see the phenomenological fitting movies in the Supplementary Materials).

For the pump polarization described in Supplementary Fig. 2a (THz is generated from a DSTMS source), the temporal evolution of the real and imaginary parts of the fitting parameters A, B, C and D are displayed in Supplementary Figs. 2a and 2c, respectively. The corresponding Fourier transform spectra are shown in Supplementary Figs. 2b and 2d, revealing pronounced phonon peaks at 1.7 and 4.5 THz. These results are consistent with other pump polarizations (Supplementary Fig. 2e–h) as well as different THz generation crystal (OH1, Supplementary Figs. 9–10).

Alternatively, instead of fitting the data with Eq. (S2), we can Fourier decompose the nonequilibrium signal in the following form:

$$I_{SH} = a_0 + a_2 \cos(2\varphi) + a_4 \cos(4\varphi) + a_6 \cos(6\varphi) + b_2 \sin(2\varphi) + b_4 \sin(4\varphi) + b_6 \sin(6\varphi), \quad (\text{S3})$$

where $a_0, a_2, a_4, a_6, b_2, b_4, b_6$ are the Fourier decomposition coefficients. Now, equating Eqs. (S2) and (S3) yields the following relations:

$$a_0 = \frac{1}{32} \left(2A^2 + 10|B|^2 + 2|C|^2 + 10|D|^2 + 4A \operatorname{Re}(B) + 4 \operatorname{Re}(CD^*) \right) \quad (\text{S4})$$

$$a_2 = \frac{1}{32} \left(A^2 - 15|B|^2 - |C|^2 + 15|D|^2 - 2A \operatorname{Re}(B) + 2 \operatorname{Re}(CD^*) \right) \quad (\text{S5})$$

$$a_4 = \frac{1}{32} \left(-2A^2 + 6|B|^2 - 2|C|^2 + 6|D|^2 - 4A \operatorname{Re}(B) - 4 \operatorname{Re}(CD^*) \right) \quad (\text{S6})$$

$$a_6 = \frac{1}{32} \left(-A^2 - |B|^2 + |C|^2 + |D|^2 + 2A \operatorname{Re}(B) - 2 \operatorname{Re}(CD^*) \right) \quad (\text{S7})$$

$$b_2 = \frac{1}{32} \left(6A \operatorname{Re}(C) + 10A \operatorname{Re}(D) + 10 \operatorname{Re}(BC^*) + 6 \operatorname{Re}(BD^*) \right) \quad (\text{S8})$$

$$b_4 = \frac{1}{32} \left(8A \operatorname{Re}(D) - 8 \operatorname{Re}(BC^*) \right) \quad (\text{S9})$$

$$b_6 = \frac{1}{32} \left(-2A \operatorname{Re}(C) + 2A \operatorname{Re}(D) - 2 \operatorname{Re}(BD^*) + 2 \operatorname{Re}(BC^*) \right) \quad (\text{S10})$$

Equations (S4)–(S10) imply that the Fourier coefficients $a_0, a_2, a_4, a_6, b_2, b_4, b_6$ can be reconstructed from the complex fit parameters A, B, C, D . For the THz pump polarized along a lobe, the Fourier coefficients, obtained directly from the data and reconstructed from the fit parameters using Eqs. (S4)–(S10), are shown in Supplementary Figs. 3b and 3c, respectively. A similar analysis is presented in Supplementary Figs. 3e and 3f, where the THz pump is polarized along a node. From the figures, it is clear that the coefficients acquired from both methods exhibit strikingly similar trends, supporting the validity of our phenomenological fit analysis as well as the accuracy of the fit parameters.

SHG intensity derivation: symmetry-allowed tensor components

Although the atomic positions in MnPS_3 are centrosymmetric, the onset of magnetic order breaks inversion symmetry, enabling a c -type SHG response [4–6]. Below the Néel temperature T_N , the magnetic point group reduces to $2'/m$, equivalent to monoclinic $m = C_{1h}$ [7, 8]. Assuming the mirror plane lies in the ac plane, the non-vanishing elements of the second-order susceptibility tensor $\hat{\chi}$ include:

$$\chi_{xxx}, \chi_{xyy}, \chi_{xzz}, \chi_{xxz}, \chi_{xzx}, \chi_{yyz}, \chi_{yzy}, \chi_{yxy}, \chi_{yyx}, \chi_{zxx}, \chi_{zyy}, \chi_{zzz}, \chi_{zzx}, \chi_{zxx}.$$

Symmetry constraints further impose that $\chi_{xxy} = \chi_{xyx} = \chi_{yxx} = \chi_{yyy} = 0$. In the contracted 3×6 matrix notation used for in-plane excitation, the effective susceptibility

tensor becomes:

$$\hat{\chi} = \begin{pmatrix} \chi_{xxx} & \chi_{xyy} & \chi_{xzz} & \chi_{xyz} & \chi_{xzx} & 0 \\ 0 & 0 & \chi_{yzz} & \chi_{yyz} & \chi_{yzx} & \chi_{yxy} \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & \chi_{zyz} & \chi_{zzx} & \chi_{zxy} \end{pmatrix}.$$

We consider a normally incident electric field polarized at an angle φ with respect to the y -axis

$$\vec{E} = \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} = E_0 \begin{pmatrix} \sin(\varphi) \\ \cos(\varphi) \\ 0 \end{pmatrix}.$$

For convenience, we use $E_0 = 1$. The components of second-order polarization $\vec{P}(2\omega)$ can be written as,

$$P_i = \sum_{j,k} \chi_{ijk} E_j E_k. \quad (\text{S11})$$

where $i, j, k \in \{x, y, z\}$. Using the above relation, the SHG polarization is expressed as

$$\vec{P}(2\omega) = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \hat{\chi} \begin{pmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_y E_z \\ 2E_z E_x \\ 2E_x E_y \end{pmatrix} = \begin{pmatrix} \chi_{xxx} & \chi_{xyy} & \chi_{xzz} & \chi_{xyz} & \chi_{xzx} & 0 \\ 0 & 0 & \chi_{yzz} & \chi_{yyz} & \chi_{yzx} & \chi_{yxy} \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & \chi_{zyz} & \chi_{zzx} & \chi_{zxy} \end{pmatrix} \begin{pmatrix} \sin^2(\varphi) \\ \cos^2(\varphi) \\ 0 \\ 0 \\ 0 \\ 2\sin(\varphi)\cos(\varphi) \end{pmatrix}. \quad (\text{S12})$$

From (S12), we obtain

$$P_x = \chi_{xxx} \sin^2(\varphi) + \chi_{xyy} \cos^2(\varphi), \quad (\text{S13})$$

$$P_y = 2\chi_{yxy} \sin(\varphi) \cos(\varphi) = (\chi_{yxy} + \chi_{yyx}) \sin(\varphi) \cos(\varphi), \quad (\text{S14})$$

$$P_z = \chi_{zxx} \sin^2(\varphi) + \chi_{zyy} \cos^2(\varphi) + (\chi_{zxy} + \chi_{zyx}) \sin(\varphi) \cos(\varphi). \quad (\text{S15})$$

Here, we used the convention $\chi_{ijk} = \chi_{ikj}$. Assuming the detector is aligned with the incident polarization direction

$$\hat{e}_{\text{det}} = \begin{pmatrix} \sin(\varphi) \\ \cos(\varphi) \\ 0 \end{pmatrix},$$

the detected SHG signal is thus the projection of the SHG polarization $\vec{P}(2\omega)$ along the detector direction $\hat{e}_{\text{det}}$ which gives

$$\vec{P}(2\omega) \cdot \hat{e}_{\text{det}} = P_x \sin(\varphi) + P_y \cos(\varphi) \quad (\text{S16})$$

$$= \chi_{xxx} \sin^3(\varphi) + \chi_{xyy} \cos^2(\varphi) \sin(\varphi) + (\chi_{yxy} + \chi_{yyx}) \cos^2(\varphi) \sin(\varphi) \quad (\text{S17})$$

$$= \chi_{xxx} \sin^3(\varphi) + (\chi_{xyy} + \chi_{yxy} + \chi_{yyx}) \cos^2(\varphi) \sin(\varphi). \quad (\text{S18})$$

Therefore, the SHG intensity becomes

$$I_{SH} = |\vec{P}(2\omega) \cdot \hat{e}_{\text{det}}|^2 = \left| \chi_{xxx} \sin^3(\varphi) + (\chi_{xyy} + \chi_{yxy} + \chi_{yyx}) \cos^2(\varphi) \sin(\varphi) \right|^2 \quad (\text{S19})$$

$$= \left| A \cos^2(\varphi) \sin(\varphi) + B \sin^3(\varphi) \right|^2, \quad (\text{S20})$$

where $A = \chi_{xyy} + \chi_{yxy} + \chi_{yyx}$ and $B = \chi_{xxx}$. We note that Eq. (S20) resembles Eq. (S1), providing a full derivation of the phenomenological fitting function for the equilibrium SHG-RA patterns.

SHG intensity derivation: lower symmetry case

In the photoinduced case, we consider a symmetry-lowered scenario where all χ_{ijk} elements may be nonzero. The susceptibility tensor is expressed as

$$\hat{\chi} = \begin{pmatrix} \chi_{xxx} & \chi_{xyy} & \chi_{xzz} & \chi_{xyz} & \chi_{xxz} & \chi_{xxy} \\ \chi_{yxx} & \chi_{yyy} & \chi_{yzz} & \chi_{yyz} & \chi_{yzx} & \chi_{yyx} \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & \chi_{zyz} & \chi_{zzx} & \chi_{zxy} \end{pmatrix}.$$

Following the similar mathematical operations discussed earlier, we obtain the SHG polarization

$$P_x = \chi_{xxx} \sin^2(\varphi) + \chi_{xyy} \cos^2(\varphi) + (\chi_{xxy} + \chi_{xyx}) \sin(\varphi) \cos(\varphi), \quad (\text{S21})$$

$$P_y = \chi_{yxx} \sin^2(\varphi) + \chi_{yyy} \cos^2(\varphi) + (\chi_{yyx} + \chi_{yyx}) \sin(\varphi) \cos(\varphi). \quad (\text{S22})$$

The detected signal can be written as

$$\vec{P}(2\omega) \cdot \hat{e}_{\text{det}} = P_x \sin(\varphi) + P_y \cos(\varphi) \quad (\text{S23})$$

$$= \chi_{xxx} \sin^3(\varphi) + \chi_{xyy} \cos^2(\varphi) \sin(\varphi) + (\chi_{xxy} + \chi_{xyx}) \sin^2(\varphi) \cos(\varphi) \quad (\text{S24})$$

$$+ \chi_{yxx} \sin^2(\varphi) \cos(\varphi) + \chi_{yyy} \cos^3(\varphi) + (\chi_{yyx} + \chi_{yyx}) \cos^2(\varphi) \sin(\varphi). \quad (\text{S25})$$

Now, we compute the SHG intensity

$$I_{SH} = |\vec{P}(2\omega) \cdot \hat{e}_{\text{det}}|^2 = \left| \chi_{xxx} \sin^3(\varphi) + (\chi_{xyy} + \chi_{yxy} + \chi_{yyx}) \cos^2(\varphi) \sin(\varphi) \right. \\ \left. + (\chi_{yxx} + \chi_{xxy} + \chi_{xyx}) \sin^2(\varphi) \cos(\varphi) + \chi_{yyy} \cos^3(\varphi) \right|^2 \quad (\text{S26})$$

$$= \left| A \cos^2(\varphi) \sin(\varphi) + B \sin^3(\varphi) + C \sin^2(\varphi) \cos(\varphi) + D \cos^3(\varphi) \right|^2. \quad (\text{S27})$$

Here, $C = \chi_{yxx} + \chi_{xxy} + \chi_{xyx}$ and $D = \chi_{yyy}$. The SHG intensity expression in Eq. (S27) mirrors Eq. (S2). This correspondence confirms that the fitting parameters C and D effectively capture the dynamical symmetry modulations to the SHG-RA patterns as observed experimentally.

THz pump – magneto-optic probe measurements

Using the same laser source as tr-SHG measurements, we performed dynamic magneto-optic experiments under THz excitation. These measurements, which track changes in the polarization state of a transmitted 800 nm probe, include both THz-induced ellipticity change ($\Delta\eta$) and polarization rotation ($\Delta\theta$). A quarter-wave plate (QWP) and a half-wave plate (HWP) were used to measure $\Delta\eta$ and $\Delta\theta$, respectively. In both configurations, a Wollaston prism was placed after the waveplates in the beam path, splitting the beam into orthogonally-polarized components to be detected by two Thorlabs DET100A Si-based balanced detectors (Supplementary Fig. 4a-c). We note that for each temperature and experimental configuration, 60 individual measurements were acquired and averaged to improve the signal-to-noise ratio.

The time trace of THz-induced ellipticity change is shown in Supplementary Fig. 4d at below (9K, blue) and above (90 K, red) the T_N . A DSTMS crystal was used for THz generation. The signals are vertically offset for clarity. A sharp peak appears near time zero which is followed by fast oscillations. The peak feature is ascribed to THz Kerr effect. Fourier transform of the oscillatory signal at 9 K reveals two Raman-active phonons at 3.5 THz and 4.5 THz (Supplementary Fig. 4e). At 90 K, both modes exhibit a blueshift and a marked reduction in amplitude, consistent with prior Raman measurements [2], and indicative of their coupling to the AFM order. In addition, temperature-dependent THz-induced polarization rotation signals are shown in Supplementary Fig. 4f, with the associated FFT spectra presented in Supplementary Fig. 4g. While the signal amplitude is notably weaker compared to the ellipticity response, both phonon modes are still resolved at 9 K. The phonon features also diminish in strength and exhibit a blueshift at 90 K, in tandem with the ellipticity change data.

Similar measurements were performed using a THz pump generated from an OH1 crystal (Supplementary Fig. 4h-k), yielding results consistent with the DSTMS data. The same Raman-active phonons at 3.5 THz and 4.5 THz were observed in both ellipticity change and polarization rotation channels, with comparable temperature-dependent behavior.

Effect of an external field and emergence of the 1.7 THz hidden mode

A static in-plane electric field would lower the crystal symmetry, as also supported by earlier results [6]. The reduced symmetry originates from field-induced electric or magnetic dipole transitions which can potentially change the optical activity of a phonon mode, e.g., rendering the 1.7 THz mode IR- or Raman-active. We argue that the effect of magnetic dipole transitions can largely be ruled out since no 1.7 THz mode was visible in our equilibrium IR and Raman measurements under strong magnetic field (Supplementary Fig. 1). Thus, electric dipole transitions owing to the applied electric field are the plausible origin of the reduced symmetry. This argument is congruent with our proposed mechanism where a THz electric field-driven charge transfer renders the 1.7 THz mode weakly IR-active.

This can be theoretically understood from a simple coupled-mode picture. We start with the coupled-mode potential energy for two oscillators Q_R (the hidden mode, $\omega_R = 1.7$ THz)

and Q_{IR} (the IR-active mode, $\omega_{IR} = 4.5$ THz):

$$U = \frac{1}{2}\omega_R^2 Q_R^2 + \frac{1}{2}\omega_{IR}^2 Q_{IR}^2 + g Q_R Q_{IR} - Z^* E Q_{IR}. \quad (\text{S28})$$

In the zero-field ground state, the centrosymmetric MnPS₃ structure imposes $g \rightarrow 0$, consistent with our DFT phonon results which show only very small IR and Raman intensities for the 1.7 THz mode. Using Newton's second law $\ddot{Q}_i = -\partial U / \partial Q_i$ with a phenomenological damping term $\gamma_i \dot{Q}_i$, the equations of motion are:

$$\ddot{Q}_R + \gamma_R \dot{Q}_R + \omega_R^2 Q_R = -g Q_{IR}, \quad (\text{S29})$$

$$\ddot{Q}_{IR} + \gamma_{IR} \dot{Q}_{IR} + \omega_{IR}^2 Q_{IR} = -g Q_R + Z^* E. \quad (\text{S30})$$

Here $Z^* E$ is the direct driving force from the electric field on the IR-active mode, and $-g Q_R$ is the back-action from Q_R . Note that Q_R has no direct coupling to E — it is IR-silent by symmetry when $g = 0$.

Assuming a monochromatic probe field $E(t) = E_0 e^{-i\omega t}$ and steady-state solutions of the same form, and defining the response denominators

$$D_R \equiv \omega_R^2 - \omega^2 - i\gamma_R \omega, \quad D_{IR} \equiv \omega_{IR}^2 - \omega^2 - i\gamma_{IR} \omega, \quad (\text{S31})$$

the equations of motion reduce to the 2×2 linear system:

$$D_R Q_R + g Q_{IR} = 0, \quad (\text{S32})$$

$$D_{IR} Q_{IR} + g Q_R = Z^* E_0. \quad (\text{S33})$$

Solving Eqs. (S32)–(S33) yields:

$$Q_{IR} = \frac{Z^* D_R}{D_R D_{IR} - g^2} E_0, \quad Q_R = \frac{-g Z^*}{D_R D_{IR} - g^2} E_0. \quad (\text{S34})$$

Since the IR polarization is $P = Z^* Q_{IR}$, the susceptibility is:

$$\chi(\omega) \equiv \frac{P}{E_0} = \frac{Z^{*2} D_R}{D_R D_{IR} - g^2}. \quad (\text{S35})$$

The IR absorption spectrum is proportional to $\text{Im}[\chi(\omega)]$.

At $E_{DC} = 0$, $g = 0$, and Eq. (S35) reduces to

$$\chi = \frac{Z^{*2}}{D_{IR}}, \quad (\text{S36})$$

which is a single Lorentzian centered at $\omega_{IR} = 4.5$ THz. Note that no 1.7 THz mode is visible, consistent with equilibrium IR and Raman measurements. Under a static in-plane field $E_{DC} \neq 0$, the field drives a charge redistribution between Mn and S atoms, modifying Mn–S hybridization and breaking inversion symmetry. This activates a finite $g_{\text{eff}}(E_{DC}) \neq 0$, allowing the modes to mix so that $Q_R \propto g_{\text{eff}} E_{DC}$, and the 1.7 THz mode acquires a small

induced effective charge $\sim g_{\text{eff}} Z^*/\omega_{IR}^2$. As a result, a peak at $\omega_R = 1.7$ THz emerges in the IR absorption spectrum (Supplementary Fig. 13). This is supported by previous studies showing that a DC field breaks inversion symmetry and activates IR or Raman modes that are silent in zero field [9–11].

The coupled-mode picture and the charge transfer mechanism described in the main text are complementary descriptions of the same physics at different levels. The 4.5 THz mode is IR-active in zero field because it carries a nonzero Born effective charge Z^* , and is therefore always visible as a Lorentzian regardless of any applied field. The 1.7 THz hidden mode, by contrast, has no direct coupling to the electric field ($Z_R^* = 0$) in the centrosymmetric ground state. Under E_{DC} , charge redistribution between Mn and S atoms — the same mechanism identified in our THz experiments — activates g_{eff} , and a peak at 1.7 THz emerges growing linearly with E_{DC} . The toy model therefore captures the symmetry argument (broken inversion $\rightarrow g_{\text{eff}} \neq 0 \rightarrow 1.7$ THz IR activity), while the charge transfer framework provides the microscopic justification for why inversion symmetry is broken.

Movies showing temporal evolution of SHG-RA patterns

We provide four movies visualizing the time evolution of SHG-RA patterns under strong-field THz excitation (peak field strength ~ 500 kV/cm) at 9 K, using a DSTMS crystal for THz generation:

- **Movie S1:** THz field is polarized along a lobe (equivalent to $E_{\perp}$) of the static SHG-RA pattern, displayed with a fixed radial scale (capped at 1×10^{-5}) to enable direct temporal comparison.
- **Movie S2:** THz field is polarized along a node (equivalent to $E_{\parallel}$), also shown with a fixed radial scale for consistent comparison across delay times.
- **Movie S3:** Same configuration as Movie S1 (THz field polarized along a lobe), but using a dynamic radial scale that adjusts to the signal magnitude in each frame.
- **Movie S4:** Same configuration as Movie S2 (THz field polarized along a node), also displayed with a dynamic radial scale.

All four movies are provided as individual .mp4 files.

Movies showing dynamical phenomenological fitting

Two additional movies present time-resolved phenomenological fitting of SHG-RA patterns at 9 K under THz excitation:

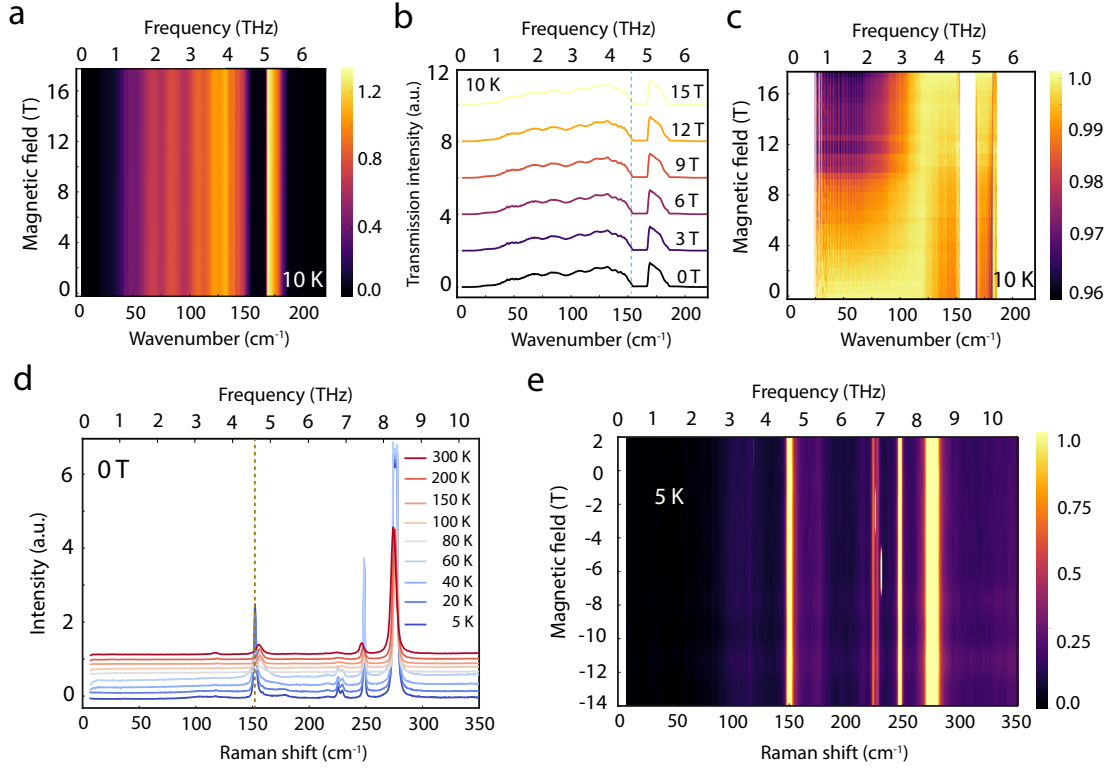
- **Movie S5:** THz field is polarized along a lobe. Experimental SHG-RA patterns (solid blue circles) are fitted at each time step using the expression in Eq. (S27) in Supplementary Materials, with red curves representing the phenomenological fits using complex fitting parameters A , B , C , and D . For better visibility, the fixed radial scale is capped at 8×10^{-6} .

- **Movie S6:** THz field is polarized along a node, with experimental data and fitting displayed in the same format as in Movie S5.

These fitting dynamics are also provided as separate .mp4 files.

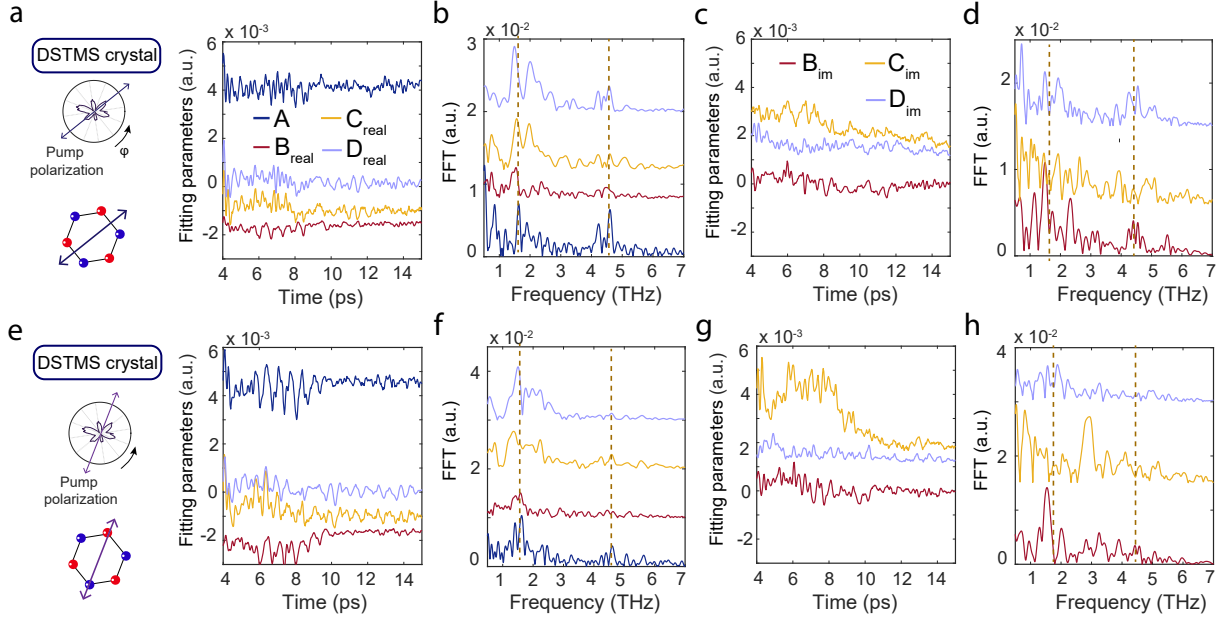
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Infrared and Raman characterizations



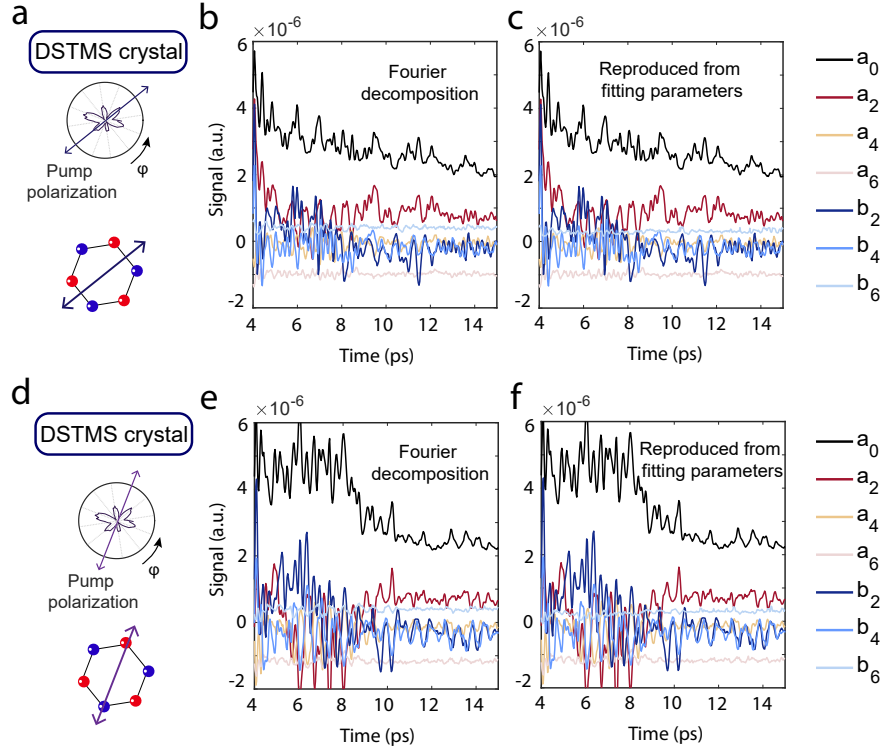
Supplementary Fig. 1. Infrared and Raman spectra. **a**, 2D colormap of IR spectra at 10 K as a function of applied in-plane magnetic field, showing a sharp dip at ~ 4.5 THz (150 cm^{-1}). **b**, Horizontal linecuts at select magnetic fields, the blue dashed line at 4.5 THz represents a phonon. Vertical offsets are applied for better visibility. **c**, Magnetic field-dependent spectra (normalized with the spectrum at 0 T) showing negligible field-induced changes. **d**, Temperature-dependent Raman spectra. The 4.5 THz phonon is marked in brown dashed line. **e**, Raman spectra at 5 K as a function of in-plane magnetic field shown in a 2D colormap. No spectral change due to magnetic field was recorded.

Dynamical complex fitting parameters for SHG-RA patterns



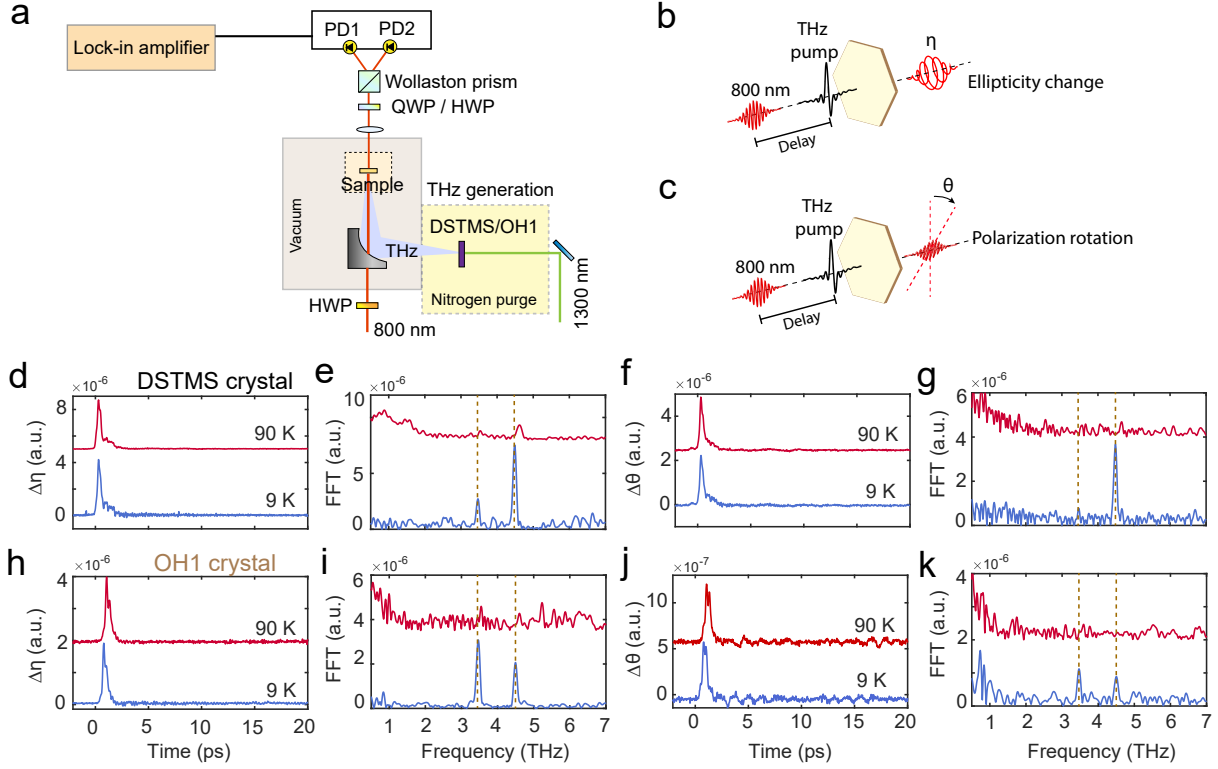
Supplementary Fig. 2. Time evolution of complex fitting parameters for the SHG-RA patterns. **a–d**, Real (**a**) and imaginary (**c**) parts of the SHG fit parameters A , B , C , and D , and their corresponding Fourier transforms (**b**, **d**) at 9 K. The THz pump is generated from a DSTMS crystal, and is polarized along a lobe relative to the SHG-RA pattern (dark blue arrow). THz polarization relative to the crystal orientation is shown for clarity. Vertical dashed lines at 1.7 THz and 4.5 THz highlight dominant coherent modes. **e–h**, Same analysis with the pump polarization along a node (purple arrow), showing changes in the amplitude and frequency content of the fitted components. The FFTs are separated by vertical offsets for clarity.

Analysis of the SHG-RA patterns using phenomenological fit and Fourier decomposition approaches



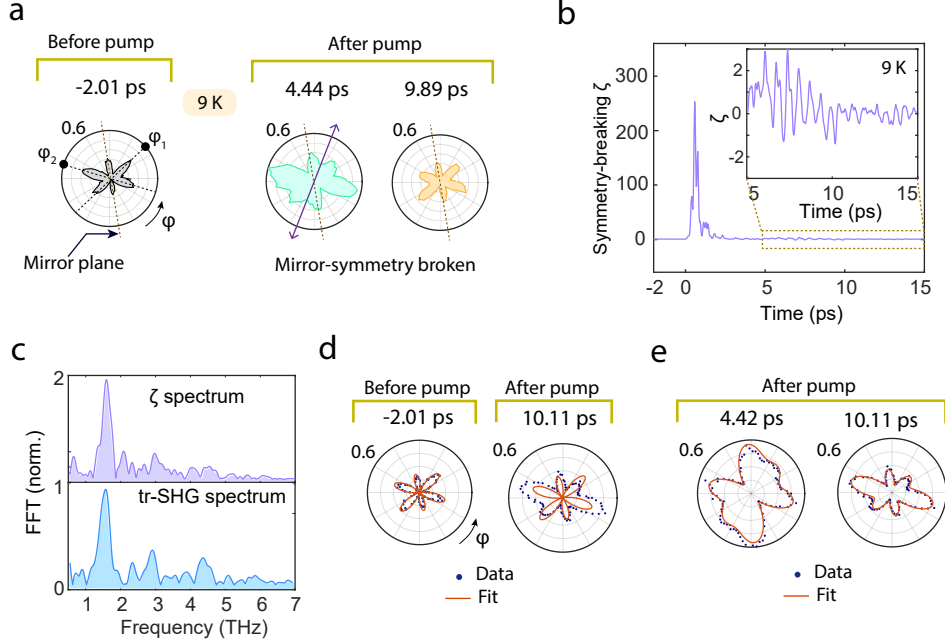
Supplementary Fig. 3. Quantitative analysis of SHG-RA patterns. **a**, The THz pump is polarized along a lobe of the SHG-RA pattern (dark blue arrow). Pump polarization relative to the crystal orientation is shown for clarity. The THz is generated from a DSTMS crystal. **b**, Fourier decomposition coefficients directly extracted from tr-SHG data. Temperature is set at 9 K. **c**, Fourier coefficients reconstructed from the phenomenological complex fit parameters A, B, C and D , using Eqs. (S4)–(S10). **d**, THz is polarized along a node of the SHG-RA pattern (purple arrow). **e**, Fourier decomposition coefficients directly extracted from tr-SHG data. **f**, Fourier coefficients reconstructed from the phenomenological complex fit parameters A, B, C and D , using Eqs. (S4)–(S10).

THz pump – magneto-optic probe measurements



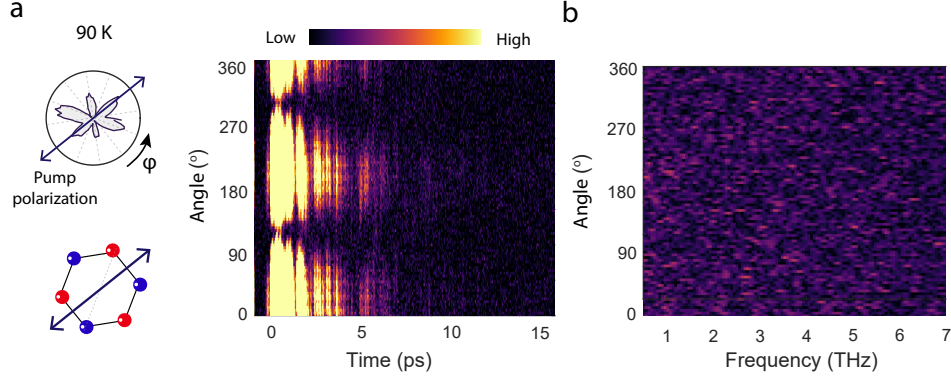
Supplementary Fig. 4. THz pump-induced ellipticity change and polarization rotation dynamics. **a**, Experimental configuration. HWP: half-wave plate, QWP: quarter-wave plate, PD: photodiode. The QWP is used for measuring ellipticity change, while the HWP is used for polarization rotation measurements. **b–c**, Schematic illustrations of the measurement geometry. The THz pump is polarized along a lobe of the static SHG-RA pattern. **d**, Temporal evolution of THz-induced ellipticity change $\Delta\eta$ at temperatures below (9 K, blue) and above (90 K, red) T_N . Traces are vertically offset for clarity. DSTMS crystal is used for THz generation. **e**, Corresponding Fourier transform spectra, revealing coherent Raman-active modes at 3.5 THz and 4.5 THz (brown dashed lines). Although weaker in amplitude, both modes exhibit a blueshift above T_N . **f–g**, Temperature-dependent dynamics of THz-induced polarization rotation $\Delta\theta$ and its Fourier spectrum. **h–i**, $\Delta\eta$ dynamics and corresponding FFT spectra at 9 K and 90 K (OH1 as the THz generation crystal), showing the 3.5 THz and 4.5 THz modes. **j–k**, $\Delta\theta$ dynamics and FFT spectra under the same pumping conditions.

Symmetry modulation analysis when THz is polarized along a node



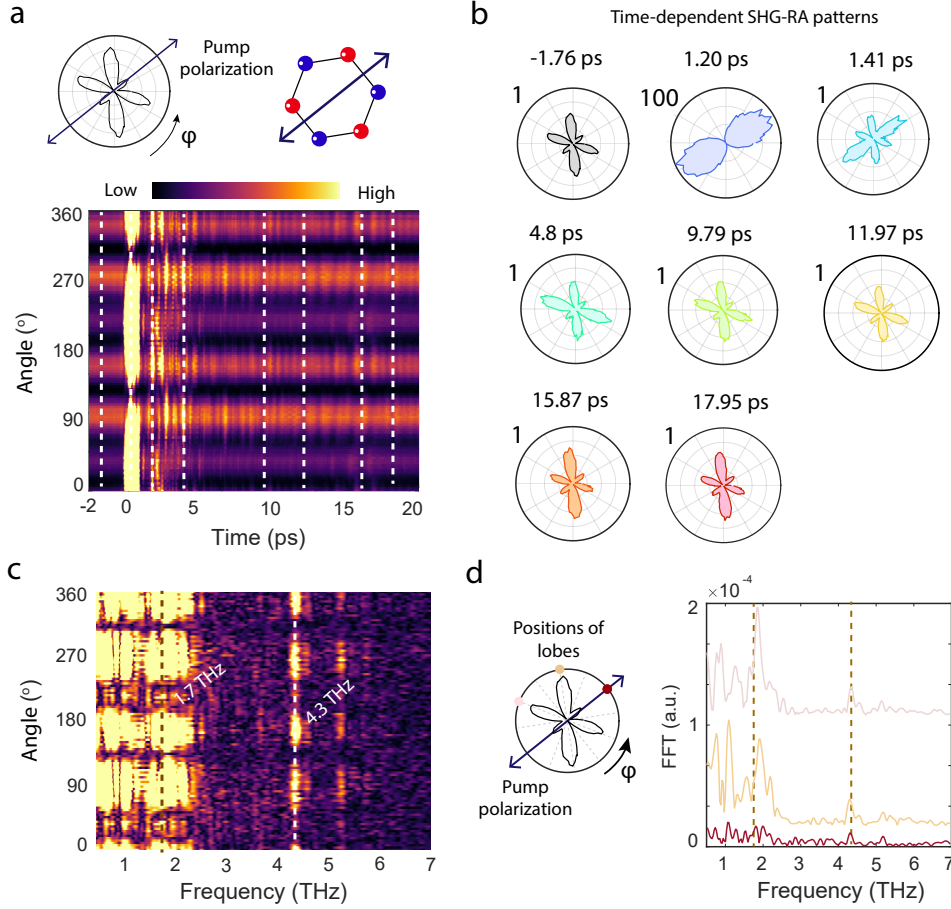
Supplementary Fig. 5. THz field-induced long-lived mirror symmetry modulations when THz is along a node (DSTMS crystal). **a**, SHG-RA patterns in equilibrium (black), and at different pump-probe time delays upon THz excitation (teal and yellow) at 9 K. Photoexcited SHG-RA patterns exhibit a notable symmetry modulation relative to the equilibrium mirror plane (brown dashed line). The THz pump field is polarized along a node (purple arrow). **b**, Time-evolution of symmetry-breaking parameter ζ , unmasking coherent oscillations at later times (inset). **c**, Fourier transform of ζ (top), compared with tr-SHG spectrum (bottom), demonstrating peaks at 1.7 THz and 4.5 THz. **d**, Equilibrium SHG-RA pattern at $t = -2.01$ ps fitted with complex parameters A and B ; this model does not reproduce the photoinduced patterns after THz excitation (i.e., $t = 10.11$ ps). **e**, Close agreement between nonequilibrium data and phenomenological fitting using complex parameters A, B, C and D . The radial scale of each polar plot is normalized, with the outer circle corresponding to an amplitude of 0.6.

Time-resolved SHG dynamics above the AFM transition temperature



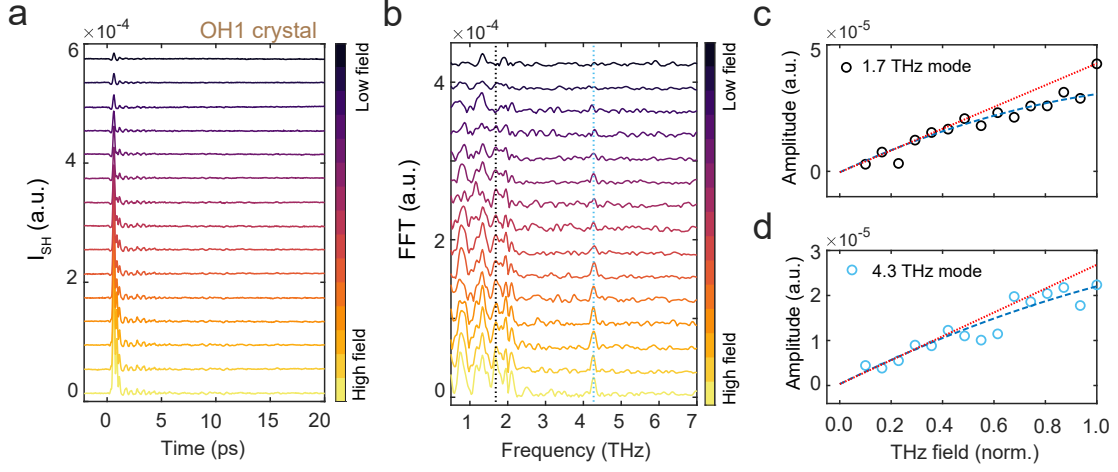
Supplementary Fig. 6. Time- and angle-resolved SHG dynamics upon strong-field THz excitation at 90 K. **a**, Pump-induced SHG as a function of pump-probe delay time t and polarizer analyzer angle (φ) at 90 K. THz pump generated from DSTMS crystal with field strength of ~ 500 kV/cm is polarized along a lobe of the static SHG-RA pattern (dark blue arrow). Pump polarization relative to the crystal orientation is shown for clarity. The THz is generated from a DSTMS crystal. The signal is dominated by TFISH effect with no coherent oscillations. **b**, Fourier transform spectrum of the pump-probe signal, no coherent modes are detected.

Dynamics with THz pump generated from OH1 crystal



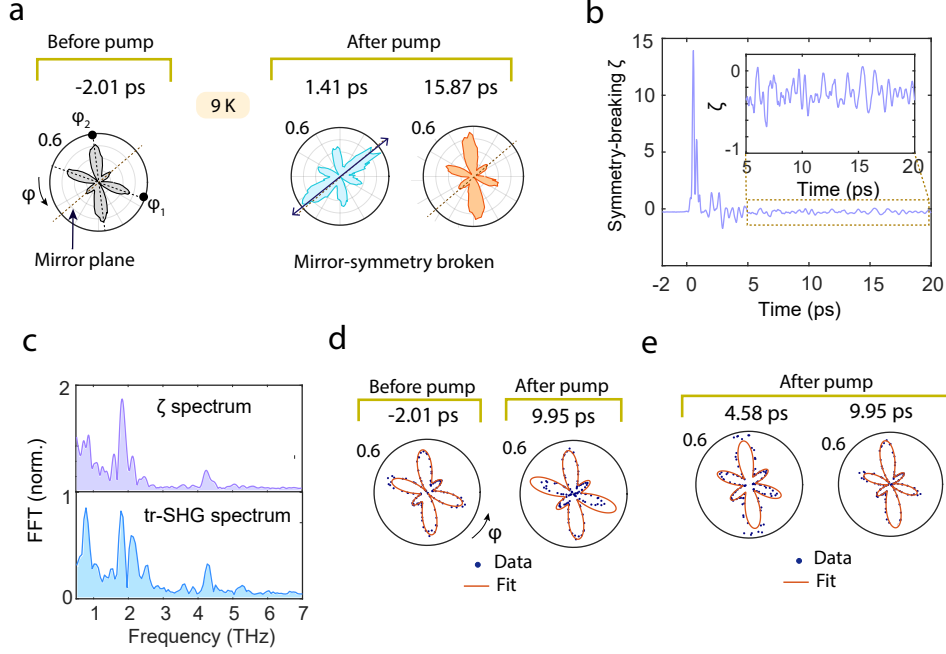
Supplementary Fig. 7. Time- and angle-resolved SHG dynamics upon strong-field THz excitation (OH1 crystal). **a**, Pump-induced SHG as a function of pump-probe delay time t and polarizer analyzer angle (φ) at 9 K. THz pump with field strength of ~ 200 kV/cm is polarized along a lobe of the static SHG-RA pattern (dark blue arrow). THz polarization direction relative to the crystal orientation is shown for clarity. The later time dynamics is dominated by a long-lived oscillatory signal, suggesting coherent phonons. **b**, SHG-RA patterns at different pump-probe delays, obtained from vertical linecuts in **a** (dashed white lines). The radial scale of each polar plot is normalized, with the outer circle corresponding to an amplitude of 1. **c**, Fourier transform spectrum of the pump-probe signal, multiple prominent peaks are observed. **d**, Horizontal linecuts showing FFT spectra at lobe positions (indicated by colored circles in the SHG-RA pattern), showing coherent modes predominantly at 1.7 THz and 4.3 THz. The linecuts are vertically offset for better visibility.

Field dependence of the coherent modes when THz is generated from OH1 crystal



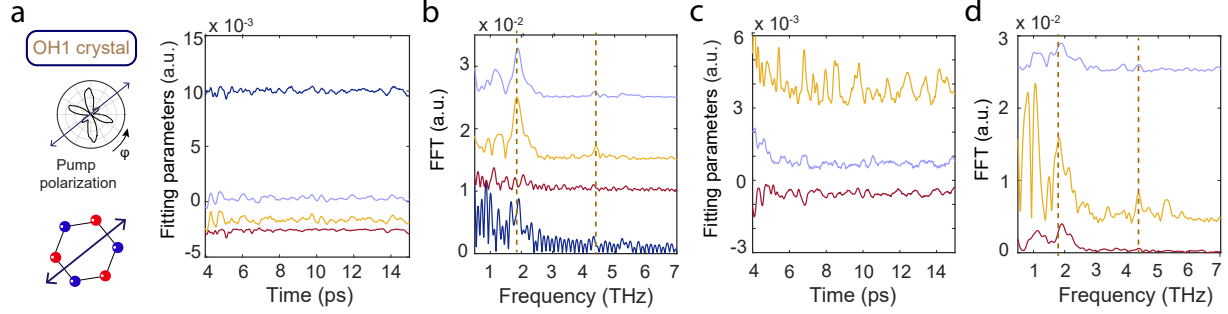
Supplementary Fig. 8. tr-SHG dynamics as a function of THz pump field. **a**, The tr-SHG dynamics along a lobe as a function of THz field generated from a OH1 crystal (peak field ~ 200 kV/cm) at 9 K. **b**, Corresponding FFT spectra showing pronounced peak features at 1.7 THz and 4.3 THz (vertical dashed lines). The signals are vertically offset for clarity. **c–d**, Mode amplitude plotted as a function of normalized pump field for 1.7 THz (**c**, black open circles) and 4.3 THz (**d**, blue open circles) modes. Both modes exhibit predominantly linear scaling with field. Red and blue dashed lines indicate linear and sublinear fits, respectively.

Symmetry modulation analysis when THz is generated from OH1 crystal



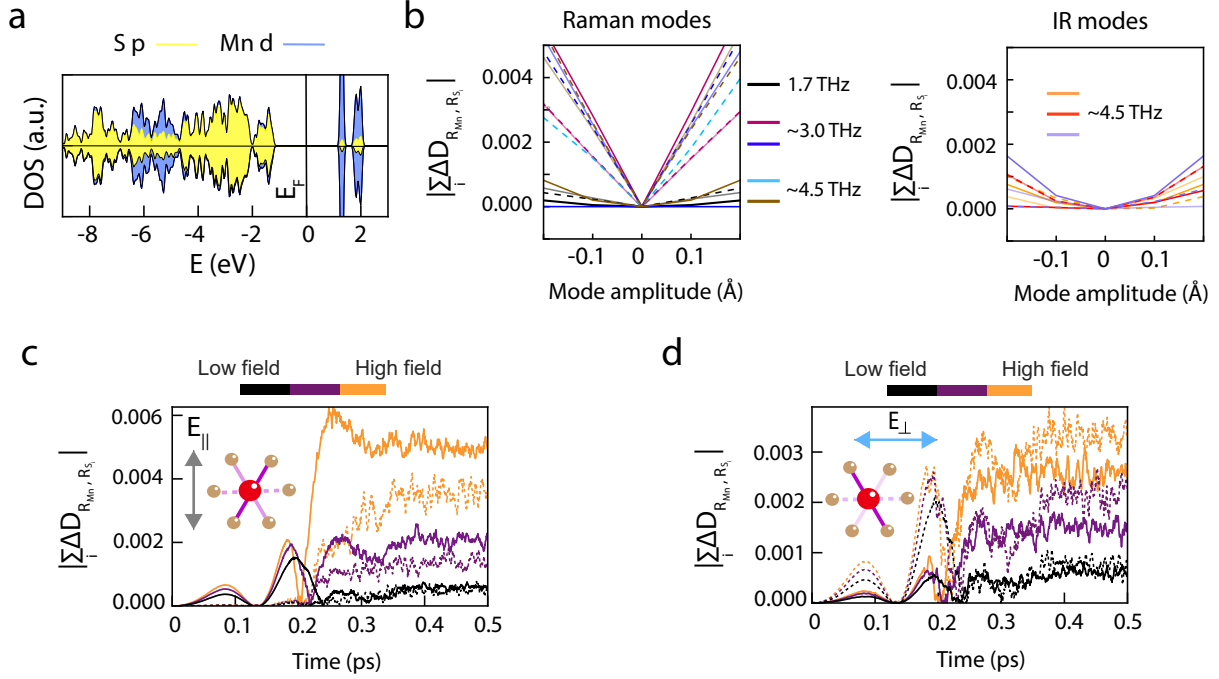
Supplementary Fig. 9. Terahertz field-induced long-lived mirror symmetry modulations (OH1 crystal). **a**, SHG-RA patterns in equilibrium (black), and at different pump-probe time delays upon THz excitation (light blue and orange) at 9 K. Photoexcited SHG-RA patterns exhibit a notable symmetry modulation relative to the equilibrium mirror plane (brown dashed line). The THz pump field is polarized along a lobe. **b**, Time-evolution of symmetry-breaking parameter ζ , unmasking coherent oscillations at later times (inset). **c**, Fourier transform of ζ (top), compared with tr-SHG spectrum (bottom), demonstrating peaks at 1.7 THz and 4.3 THz. **d**, Equilibrium SHG-RA pattern at $t = -2.01$ ps fitted with complex parameters A and B ; this model does not reproduce the photoinduced patterns after THz excitation (i.e., $t = 9.95$ ps). **e**, Close agreement between nonequilibrium data and phenomenological fitting using complex parameters A, B, C and D . The radial scale of each polar plot is normalized, with the outer circle corresponding to an amplitude of 0.6 .

Dynamics of phenomenological fitting parameters (OH1 generation crystal)



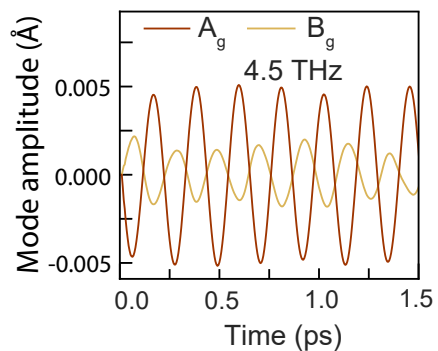
Supplementary Fig. 10. Time evolution of complex fitting parameters for the SHG-RA patterns. **a–d**, Real (**a**) and imaginary (**c**) parts of the SHG fit parameters A , B , C , and D , and their corresponding Fourier transforms (**b**, **d**) at 9 K. The THz pump is generated from an OH1 crystal, and is polarized along a lobe relative to the SHG-RA pattern (dark blue arrow). THz polarization relative to the crystal orientation is shown for clarity. Vertical dashed lines at 1.7 THz and 4.3 THz highlight dominant coherent modes. The FFTs are separated by vertical offsets for clarity.

THz-induced modification of bond strength derived from tight-binding model calculation



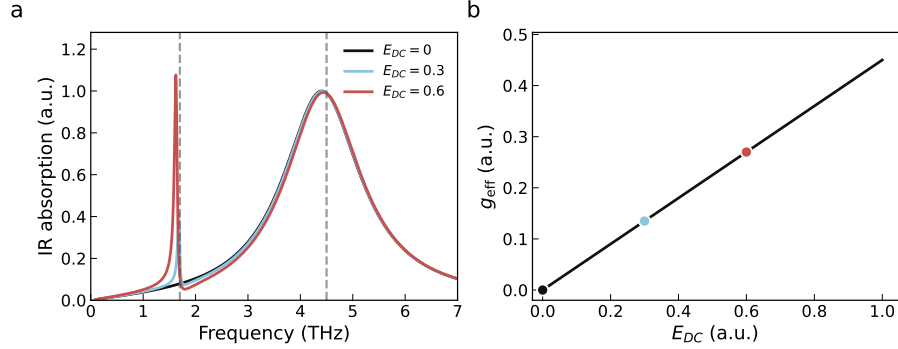
Supplementary Fig. 11. Tight-binding model-based calculations. **a**, Density of states of the ground-state of MnPS₃ calculated from the tight-binding model projected on S p (yellow) and Mn d orbitals. Projected DOS are stacked on top of each other. The two spin channels are shown with opposite signs. The THz pump field is polarized along a lobe. **b**, Phonon induced modifications in Mn-S bond strength around Mn atoms. Solid, dashed, and transparent lines represent Mn-S bonds oriented along three different directions. **c-d**, Evolution of Mn-S bonding strength $D_{R_{Mn}, R_{Si}}$ under the THz field from the model-based rt-TDDFT simulations for $E_{\parallel}$ (**c**) and $E_{\perp}$ (**d**) polarizations. Solid, dashed, and transparent lines denote Mn-S bonds in three different directions around Mn atoms, as shown in the inset.

Constrained DFT simulation of 4.5 THz Raman mode driving under charge transfer condition



Supplementary Fig. 12. Simulation of 4.5 THz Raman mode under THz-induced charge transfer. Molecular dynamics simulations with a fixed electronic structure and a 0.2% excited state population, initialized with atomic velocity distribution corresponding to $T = 9$ K, revealing the dynamics of the 4.5 THz Raman modes with A_g (maroon) and B_g (beige) symmetries.

Effect of external field on the optical activity of the 1.7 THz mode



Supplementary Fig. 13. Coupled-mode toy model of field-induced IR activity of the 1.7 THz hidden mode. **a**, IR absorption spectrum $\text{Im}[\chi(\omega)]$ computed from the coupled linear response of the hidden mode Q_R ($\omega_R = 1.7$ THz) and the IR-active mode Q_{IR} ($\omega_{IR} = 4.5$ THz), for three values of the applied DC field E_{DC} . At $E_{DC} = 0$ (black), inversion symmetry is preserved, $g_{\text{eff}} = 0$, and only the intrinsic 4.5 THz IR-active mode is visible. As E_{DC} increases, field-induced charge redistribution between Mn and S atoms breaks inversion symmetry, activating $g_{\text{eff}} > 0$ and giving rise to a peak at 1.7 THz, while the 4.5 THz mode remains as a reference. **b**, g_{eff} grows linearly with E_{DC} , vanishing exactly at $E_{DC} = 0$ in the centrosymmetric ground state. Colored dots correspond to the three field values shown in **a**. All quantities are in arbitrary units; $\gamma_R = 0.04$ THz and $\gamma_{IR} = 1.8$ THz are the phenomenological linewidths of the two modes.