Supporting Information

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Nanoscale-Confined Terahertz Polaritons in a van der Waals Crystal

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Note S1: Sample preparation and α-MoO$_3$ polaritonic response verification

Throughout this work, we used commercially available α-MoO$_3$ crystals (purity >99.9999%, 2Dsemiconductors Inc., USA) exfoliated onto double-side polished, THz-grade, high-resistivity float-zone silicon substrate (Tydex LCC, Russia). The substrate was thoroughly cleaned with deionized water, acetone and isopropyl alcohol. Following a drying process (nitrogen air blow), the substrate surface was plasma treated (O\textsubscript{2}, 1 mbar, 5 min.) in a low-energy plasma cleaning chamber (Pico, Diener electronic GmbH + Co. KG, Germany). The latter treatment was performed in order to remove any organic residual, and to increase the surface energy of the substrate temporarily. A large α-MoO$_3$ crystal (> 1 mm) was placed onto an adhesive tape (Nitto Denko Co., SPV 224P), and was exfoliated multiple times before deposition over the substrate. The last exfoliation step and deposition was done immediately after removing the substrate from the O\textsubscript{2} plasma chamber.

The crystal structure of the layered semiconductor α-MoO$_3$ is shown in Figure S1a. Its main growth direction takes place along the c-axis ([001]), and the van der Waals (vdW) stacking direction is along the b-axis ([010]). The α-MoO$_3$ vdW layer is composed of a double layer of deformed octahedras (bottom right in Figure S1a), wherein molybdenum atoms are covalently bonded to four oxygen atoms. Three classes of oxygen atoms are found, depending on its oxidation state: single- (O\textsuperscript{(1)}, along [010]), double- (O\textsuperscript{(2)}, along [100]), or tri-coordinated (O\textsuperscript{(3)}, along [001]). Different Mo-O bond lengths results from the different coordination state, giving rise to an orthorhombic crystal structure (Pnma 62, α-phase), with unit cell parameters $a = 0.396$ nm, $b = 1.382$ nm, and $c = 0.373$ nm. Figure S1b,c show optical microscopy images of the sample used throughout this work. As the latter was prepared from a single crystal, the deposited flakes’ relative crystal orientation is maintained throughout the substrate area. We confirmed the crystallographic direction of the (typically longer) geometrical flake direction.
with polarization-dependent Raman spectroscopy (see Section S3) by observing the 158 cm\(^{-1}\) rigid chain translation vibration mode\(^{[1]}\) along [001].

To confirm the polaritonic response of the \(\alpha\)-MoO\(_3\) used in this work, we performed near-field nanoimaging with continuous-wave gas laser (CO\(_2\)) in mid-infrared regime. The optical microscopy image of Figure S1c shows the 131 nm flake discussed in main text (yellow). The near-field image shown in Figure S1d has been taken at 26.55 THz (11.29 \(\mu\)m, 885.61 cm\(^{-1}\)), where \(\alpha\)-MoO\(_3\) is anticipated to support in-plane hyperbolic phonon polariton modes.\(^{[3]}\) A wide variety of polaritonic response is observed, including tip and edge launched polaritons, propagating solely along the [001] axis, thus validating the sample for our study.

**Figure S1.** (a) Illustration showing an \(\alpha\)-MoO\(_3\) flake, and its crystal structure generated with the Materials project tool (www.materialsproject.org, Ref.\(^{[2]}\)). (b,c) Optical microscopy images of the sample used throughout this work. (d) Near-field intensity image recorded at 26.55 THz with a continuous-wave gas laser. Tip-sample excitation was slightly defocused, thus enhancing the launching efficiency and visibility of edge-polaritons.
Note S2: Polariton dispersion, group velocities and lifetimes

The polariton group velocities and lifetimes for each of the $\alpha$-MoO$_3$ flakes studied were extracted following procedures described in detail in previous reports.$^{[3-5]}$ In summary, the near-field polariton interferometry profile $S_{2\Omega}(x)$ with $x = 0$ at the flake edge was Fourier filtered (high-pass) in order to remove the DC signal offset. Subsequently, the profile was multiplied by a correction factor $\sqrt{x}$ in order to compensate for the geometrical spreading of the polariton wave. The resulting data was fitted to a damped sinusoidal function $S = S_o + Ae^{-t_0 \sin \left( \pi \frac{x-x_c}{p} \right)}$, where $S_o$ is the signal offset, $x_c$ the spatial offset, $t_0$ decay constant, $A$ the amplitude and $p$ a half cycle. For tip-launched polaritons, the decay length as well as the polariton wavelength are immediately obtained with $L_{\text{tip}} = 2t_o$ and $\lambda_{\text{tip}} = 4p$, respectively. The magnitude of the polariton wavevector is then obtained as $k = 2\pi/\lambda_{\text{ph}}$. This procedure was repeated for all combinations of flake thicknesses and FEL frequencies, resulting in the polariton dispersion curve shown in Figure 3a (main text). Note that for edge-launched polaritons, the above-mentioned equations would be modified to $L_{\text{edge}} = t_o$ and $\lambda_{\text{edge}} = 2p$.

Figure S2. Polariton group velocities as function of frequency. Data calculated/extracted from the dispersion of Fig. 3a of main text. Red-shaded symbols represent the data of the polaritons along the [001] crystallographic direction, whereas the blue-shaded symbols shows the data for the polaritons along the [100] crystallographic direction. The different flake thicknesses are indicated in the label.
In order to calculate the polariton lifetimes $\tau$, knowledge of their associated group velocities $v_g$ is still required. To this end, we take the derivative of a generic power law function ($y = ax^b$) fitted to our experimental data ($\tilde{v}$-k), and calculate the group velocities with $v_g = 2\pi c \frac{d\tilde{v}}{dk}$, wherein $c$ is speed of light, $\tilde{v}$ the spatial frequency in cm$^{-1}$ units, and $k$ the momentum in cm$^{-1}$ units. The resulting group velocities as function of frequency and flake thicknesses is depicted in Figure S2. Polariton lifetimes are then obtained with $\tau = L/v_g$, and is plotted in Figure S3.

We note that polariton lifetime estimation is highly susceptible to experimental errors in THz nanoimaging. The high average-power FEL shows inherently elevated, time-varying spectral noise in addition to power drifts, consequently complicating the imaging process. In addition, we used self-homodyne detection technique, which is known to not fully suppress background far-field contribution in s-SNOM.[6] Furthermore, detector sensitivities at these THz frequencies are low as compared to its MIR/visible counterparts, therefore $S_{2\omega}$ signals obtained are typically near the measurement noise level. In practice, the general low-signal to noise ratios impart that the above-mentioned fitting procedure leads to non-negligible errors in the extraction of $\text{Im}(k)$, and hence strong variation of lifetime estimation. This variability is observed in the experimental lifetime $\tau$ plot of Figure S3 (symbols), as $\tau$ should be nearly independent of flake thickness for a specific illumination frequency, and for the limit in which the substrate does not impart significant losses. Notwithstanding the $\tau$ estimation variability, the collective dataset provides a sufficient level of certainty for the estimates presented.
Figure S3. THz polariton decoherence lifetimes for PhP[001] (red-shaded symbols) and PhP[100] (blue-shaded symbols), as extracted from the polariton interferometry experiments. The analytical lifetimes were derived from Eq. S8, for representative α-MoO₃ slab of thickness d = 100 nm. Note that although thickness dependence is expected for τ due to substrate interaction, it is negligible for the low-loss RHFZ Si used.

In the main text, we report quality factors (Q) for the polariton propagation that were obtained with the complex k-vector values obtained with the fitting procedure described above. An alternative method is to evaluate the Fourier transform of the real-space polariton profiles, thereby obtaining the real (proportional to the spatial frequency coordinate of the polariton peak maxima) and imaginary (proportional to the half-width at half-maximum, HWHM, of the polariton peak) components of the k vector. To this end, we fast-Fourier-transform our experimental data, and fit it to a Lorentzian function, as shown in Figure S4. Here we evaluate the same profiles shown in Figure 3d (main text) and obtain quality factors (annotated in viewgraphs of Figure S4) that are very similar to those reported in the main text.
Figure S4. Alternative method for the polaritons’ quality-factor extraction. The polariton interferometry profiles of Fig. 3d (main-text) were fast Fourier transformed (FFT) and fitted with Lorentzian functions to extract the spatial frequency \([α \text{Re}(k)]\), and the polariton peak’s half-width at half-maximum (HWHM, \(α \text{Im}(k))\). (top) FFT of the profile for a 131 nm flake at 11.17 THz, and (bottom) FFT of the profile for a 53 nm flake at 9.22 THz. The extracted polariton propagation quality factors are given in the subfigures.

Note S3: Polarization-resolved Raman spectroscopy

In order to verify the characteristics of the commercially obtained \(α\)-MoO\(_3\) we have performed polarization-resolved micro-Raman spectroscopy (Horiba LabRAM HR Evolution). A 633 nm pump laser was operated at 17 mW and used in combination with a 1800 lines/mm grating and a CCD detector (Syncerity CCD, Horiba Scientific), enabling a spectral resolution of 0.014 nm. A rotatable sample holder was used for variation of \(β\) from 0° to 90° (see inset of Figure S5a), as this range contains all information due to the crystal symmetry.\(^1\) The obtained Raman-spectra for the whole infrared range are shown in Figure S5a, for pump polarization along the [001] axis (\(β = 0°\)) and along the [100] axis (\(β = 90°\)). The crystal orientation is assigned with respect to the flake geometry by the highly anisotropic Raman-active mode 158 cm\(^{-1}\), which is known to show its maxima along the [001] axis.\(^1\)
Figure S5. (a) Raman spectra for pump polarization along [100] (black curve, $\beta = 90^\circ$), and along [001] (red curve, $\beta = 0^\circ$). Optical micrograph of the sample used ($\alpha$-MoO$_3$ on MgO) is shown in inset, wherein the pump polarization (red arrow) and its relative angle to the crystal axes are illustrated. (b) Polarization-dependent Raman shifts for selected THz vibration modes within the frequency range of this study for $\beta$ angles varying from 0 to 90°. Data scaled accordingly to facilitate visualization, as indicated in the plot.

For the THz Raman-peaks within spectral interval covered in the main-text, we do a more detailed polarization-dependence study. These peaks were fitted using Lorentzian functions and their angle-dependent relative intensities are plotted in Figure S5b. Peaks at 291, 337 and 365 cm$^{-1}$ each show intensity maxima for pump polarization parallel to the crystal [001] axis and minima along [100] axis, resulting in a 180° periodicity and assignment as $A_g$ modes.$^7$ The peak at 283 cm$^{-1}$ displays minima parallel to both axis and maxima at approximately 45° between each axis and is therefore assigned as $B_{2g}$ mode.$^7$ Furthermore, we also note that the line-widths of the Raman peaks are also very narrow (Table S1), with FWHM of 1.07 cm$^{-1}$ for the narrowest 995.3 cm$^{-1}$ peak, demonstrating high crystal order quality.
Table S1. Intensity and linewidth of the peaks extracted from Raman-spectra of Fig. S5a. The parameters were obtained for pump excitation polarized along the [001] axis (left), and along [100] axis (right).

|          | Long Axis [001] |          | Short Axis [100] |
|----------|----------------|----------|-----------------|
| λ (µm)   | ν (THz)        | Ram. Shift (cm⁻¹) | Intensity (a.u.) | FWHM (cm⁻¹) | λ (µm)   | ν (THz)        | Ram. Shift (cm⁻¹) | Intensity (a.u.) | FWHM (cm⁻¹) |
| 50.600   | 5.92           | 197.63   | 0.44            | 2.34         | 50.592     | 5.93       | 197.66         | 0.72            | 2.19          |
| 46.062   | 6.51           | 217.10   | 0.60            | 2.82         | 46.111     | 6.50       | 216.87         | 0.04            | 3.64          |
| 35.272   | 8.50           | 283.51   | 1.67            | 4.74         | 35.271     | 8.50       | 283.52         | 3.07            | 4.89          |
| 34.331   | 8.73           | 291.28   | 0.26            | 4.48         | 34.390     | 8.72       | 290.78         | 0.13            | 4.28          |
| 29.660   | 10.11          | 337.15   | 1.11            | 2.76         | 29.661     | 10.11      | 337.14         | 0.48            | 2.69          |
| 27.399   | 10.94          | 364.98   | 0.42            | 6.02         | 27.399     | 10.94      | 364.98         | 0.01            | 161.15        |
| 12.210   | 24.55          | 818.98   | 3.64            | 7.57         | 12.213     | 24.55      | 818.82         | 6.58            | 7.46          |
| 10.047   | 29.84          | 995.31   | 2.93            | 1.15         | 10.047     | 29.84      | 995.33         | 1.83            | 1.07          |

Note S4: Dielectric function for high-resistivity float-zone silicon substrate

The α-MoO₃ calculations presented in the main text, and described in the Supplementary Note 07, take into account substrate (HRFZ Si) and superstrate (air) effects for an accurate modelling of the dispersion. To the best of our knowledge there is no experimental report of the HRFZ Si dielectric function for the spectral range studied here, namely 7.5 – 12 THz (250.17 - 400.27 cm⁻¹). However, such data has been reported for the deep THz[8] and mid-infrared regimes,[9] and is shown in Figures S6a,b. It is also known that non-doped silicon possesses a spectrally flat response for frequencies lower than 12 THz. Hence, in order to extract the dielectric function for our given spectral range, we have interpolated (continuous curves in Figures S6a,b) the experimentally reported data, and calculated the real and imaginary parts of the dielectric function (shown in Figures S6c). Note that variations of the Re(ε) of silicon can be considered negligible, as compared to the strong variations of encountered in the reststrahlenbands of α-MoO₃.
Figure S6. (a) Experimental refractive indexes (n) and (b) extinction coefficients (k) for deep THz (< 5 THz, Ref. [8]) and far-/mid-infrared range (> 400 cm\(^{-1}\), Ref. [9]) for silicon. The continuous curves are generated with spline interpolation, filling the interval where experimental characterization is absent. The complex dielectric function, shown in (c), is calculated from (a,b).

Note S5: Description of ab-initio calculations and vibrational mode assignment

The dielectric function of \(\alpha\)-MoO\(_3\) is calculated fully ab-initio as reported in ref. \([10]\) by making use of density functional theory (DFT) within the Perdew, Burke, and Ernzerhof parametrization of the exchange-correlation functional.\([11]\) The dielectric tensor, which becomes diagonal in orthorhombic crystals, is calculated within perturbation theory.\([12]\) In this framework, the dielectric tensor for Cartesian directions \(\alpha\) and \(\beta\) is given by

\[
\varepsilon_{\alpha\beta}(\omega) = \varepsilon_{\alpha\beta}^{\infty} + 4\pi\chi_{\alpha\beta}(\omega),
\]

where \(\varepsilon_{\alpha\beta}^{\infty}\) is the electronic contribution to the dielectric tensor (the high-frequency limit) and \(\chi_{\alpha\beta}(\omega)\) is the susceptibility, expressed in atomic units as

\[
\chi_{\alpha\beta}(\omega) = -\frac{1}{\Omega} \sum_{i} \frac{2\omega_{i} M_{i}^{\alpha} M_{i}^{\beta}}{\omega^{2} - \omega_{i}^{2} - 2\omega_{i} \Pi_{i}(\omega_{i})},
\]

where \(\Omega\) is the unit cell volume, \(\omega_{i}\) the phonon frequency of the \(i\)-th mode (the sum over \(i\) is restricted to phonon modes at the \(\Gamma\) point), \(\Pi_{i}(\omega_{i})\) the \(i\)-th phonon mode’s self-energy due to phonon-phonon interaction taken at the phonon frequency, and \(M_{i}^{\alpha}\) is the contribution of the \(i\)-th mode to the dipole moment.
\[ M_i^\alpha = \sum_{\beta s} z_s^{\alpha \beta} e_{is}^\beta \sqrt{2M_s \omega_i} \]  

(S3)

In Equation (S3), \( z_s^{\alpha \beta} \) is the effective-charge tensor for atom \( s \), \( M_s \) the mass of atom \( s \), and \( e_{is}^\beta \) the polarization vector of mode \( i \) for atom \( s \) along the Cartesian direction \( \beta \).

Phonon frequencies, polarization vectors, effective charges, and the high-frequency limit of the dielectric function are calculated making use of density functional perturbation theory (DFPT)\(^{[13]}\) as implemented in Quantum Espresso.\(^{[14,15]}\) An 80 Ry energy cutoff was used for the plane-wave basis and a 800 Ry cutoff for the density. Electronic integrations were performed on an 8 x 2 x 8 grid. The phonon self-energy was calculated just including the so-called bubble contribution:\(^{[16,17]}\)

\[
\Pi_i(\omega) = -\frac{1}{2N_q} \sum_{\mathbf{q}|k} \Phi_{ijk}(0, \mathbf{q}, -\mathbf{q}) \left\{ \frac{2(\omega_{ijq} + \omega_{k-q})[1 + n_B(\omega_{ijq}) + n_B(\omega_{k-q})]}{\omega_{ijq} + \omega_{k-q} - (\omega + i\delta)^2} + \frac{2(\omega_{ijq} - \omega_{k-q})[n_B(\omega_{k-q}) - n_B(\omega_{ijq})]}{(\omega_{k-q} - \omega_{ijq})^2 - (\omega + i\delta)^2} \right\}. 
\]

(S4)

In Equation (S4) \( \omega_{ijq} \) represents the \( j \)-th mode at the \( \mathbf{q} \) point of the Brillouin zone, \( N_q \) the number of \( \mathbf{q} \) points in the sum, \( n_B(\omega) \) is the Bose-Einstein occupation factor, \( \delta \) is a small number (10 cm\(^{-1}\) in our case), and \( \Phi_{ijk}(0, \mathbf{q}, -\mathbf{q}) \) are the anharmonic third-order force constants transformed to the phonon mode basis.\(^{[17]}\) The third-order anharmonic force-constants are calculated by finite-differences calculating atomic forces on displaced supercells created by the ShengBTE code.\(^{[18,19]}\) The third-order force constants are calculated in a 2 x 1 x 2 supercell including interaction terms up to 5 nearest-neighbors. The self-energy is then calculated at 300 K by including in the sum over the \( \mathbf{q} \) points a 16 x 4 x 16 phonon grid. The phonon frequencies and third-order force constants in this grid are obtained by Fourier interpolation. The dynamical matrices are calculated originally in a 6 x 2 x 6 \( \mathbf{q} \) point grid. The \textit{ab-initio} damping factors of the phonon mode \( \omega_i \) is given by the imaginary part of the phonon self-energy taken at the phonon frequency:

\[ \gamma_i = -\text{Im} \Pi_i(\omega_i). \]

(S5)
In addition, we illustrate in Figure 3b (main text) the atomic vibrations associated with the PhP\(_{[001]}\) at \(v_{\text{adjusted}} = 7.85\) THz (left-panel, \(v_{\text{ab-initio}} = 6.89\) THz) and with the PhP\(_{[100]}\) at \(v_{\text{adjusted}} = 11.004\) THz (right-panel, \(v_{\text{ab-initio}} = 10.04\) THz), as extracted the ab-initio calculations. For the PhP\(_{[001]}\), we observe atomic displacements along the [001] (Fig. 3b, left-panel), and can attribute this infrared-active mode to the pronounced bending of the O\(^{(2)}\)-Mo-O\(^{(2)}\) motifs, wherein both the light oxygen atoms and the heavy Mo atoms vibrate, wagging in the [001] direction, giving rise the strong terahertz in-plane anisotropic hyperbolic band of main-text. This vibration agrees well with the wagging B\(_{1u}\) symmetry mode assignment of Py et al.\(^{[20]}\) Note that the stretching vibration of this same lattice motif along [100] also gives rise to the hyperbolic bands in the mid-infrared.\(^{[10]}\) For the PhP\(_{[100]}\), we observe atomic displacements associated along [100] that can be attributed to the out-of-plane bending deformation (of B\(_{3u}\) symmetry\(^{[21]}\)) of the O\(^{(3)}\) oxygen atoms with respect to the MoO\(_3\) planes formed along the [001] direction. At this frequency, it is also evident displacements of the O\(^{(2)}\) atoms along the [010] axis. However, the dipole moments associated with this vibration cancels out in the unit cell (i.e. not IR-active), and is not observable in our experiments.

**Note S6: Terahertz \(\alpha\)-MoO\(_3\) dielectric function extraction from correlative far- and near-field experiments and ab-initio calculations**

To properly interpret our imaging results, an accurate dielectric function model for \(\alpha\)-MoO\(_3\) in the THz range (so far unknown) is required. We thus adapt the strategy followed in our previous work in ref.\(^{[10]}\) to the THz range and perform correlative far- and near-field experiments together with ab-initio calculations. To do so, we first have to take into account that: i) \(\alpha\)-MoO\(_3\) is a biaxial crystal where the three principal components of the dielectric tensor \(\hat{\varepsilon}(\vec{\nu})\) (with \(\vec{\nu} = \nu/c\)) —namely, \(\varepsilon_x(\vec{\nu}), \varepsilon_y(\vec{\nu})\) and \(\varepsilon_z(\vec{\nu})\), corresponding to the [100], [001] and [010] crystal directions of \(\alpha\)-MoO\(_3\), respectively—are different in general:
\[
\varepsilon(\tilde{\nu}) = \begin{pmatrix}
\varepsilon_x(\tilde{\nu}) & 0 & 0 \\
0 & \varepsilon_y(\tilde{\nu}) & 0 \\
0 & 0 & \varepsilon_z(\tilde{\nu})
\end{pmatrix},
\]  

(S6)

and, ii) \(\alpha\)-MoO\(_3\) is a polar dielectric where each of the principal components of the dielectric function can be modelled as a Lorentz (or TO-LO) oscillator:\[^{10}\]

\[
\varepsilon_i(\tilde{\nu}) = \varepsilon_i^{\infty} \left( \frac{(\tilde{\nu}_i^{LO})^2 - \tilde{\nu}_i^2 - i\gamma_i}{(\tilde{\nu}_i^{TO})^2 - \tilde{\nu}_i^2 - i\gamma_i} \right), \quad i = x, y, z,
\]  

(S7)

where \(\varepsilon_j(\tilde{\nu})\) denotes the i-th principal component of the permittivity (\(i = x, y, z\) stand for the three principal components, along the [100], [001], and [010] crystal directions of \(\alpha\)-MoO\(_3\), respectively); \(\varepsilon_i^{\infty}\) represents the high-frequency dielectric constant, \(\tilde{\nu}_i^{LO}\) and \(\tilde{\nu}_i^{TO}\) stand for the LO and TO phonon frequencies; and \(\gamma_{ij}\) refers to the damping the Lorentz oscillator.

Figure S7. Dielectric function of \(\alpha\)-MoO\(_3\) at THz frequencies along the three crystallographic axes [001] (red curve), [100] (blue curve) and [010] (green curve), extracted from ab-initio calculations.

We start calculating the parameters in Equation (S7) through an \textit{ab-initio} model (Figure S7). However, as is well-known, spectral shifts in the TO and LO phonon frequencies are typically obtained in \textit{ab-initio} models for semiconductor oxides with functional semi-local exchange-correlation.\[^{22}\] Therefore, we adapt the \textit{ab-initio} frequencies to those from prior reports of far-
field measurements of $\alpha$-MoO$_3$ in the THz range.$^{[7,10,21]}$ Subsequently, the whole set of parameters in Equation (S7) —this is. the TO and LO phonon frequencies, $\nu_l^{TO}$ and $\nu_l^{LO}$, respectively, and the phonon damping $\gamma_l$ — are refined by comparing the experimental dispersion and damping of PhPs, uncovered by polariton interferometry using s-SNOM on several flakes of $\alpha$-MoO$_3$, with analytical calculations. To this end, we employ the analytical dispersion of polaritons propagating in a biaxial slab embedded between two semi-infinite media:$^{[23]}$

$$k(\nu) = \frac{\rho}{d} \left[ \arctan \left( \frac{\epsilon_1 \rho}{\epsilon_x} \right) + \arctan \left( \frac{\epsilon_3 \rho}{\epsilon_z} \right) + \pi l \right], \quad l = 0, 1, 2, \ldots, \quad (S8)$$

where $k$ is the in-plane momentum ($k^2 = k_x^2 + k_y^2$), forming an angle $\alpha$ with the x axis, $\epsilon_1$ and $\epsilon_3$ are the permittivities of the superstrate and substrate, respectively, $d$ is the thickness of the $\alpha$-MoO$_3$ slab and $\rho = i \sqrt{\epsilon_z / (\epsilon_x \cos^2 \alpha + \epsilon_y \sin^2 \alpha)}$. By these correlative attempts, excellent quantitative agreement is achieved for slabs of different thicknesses (see Figure 3 in the main text). The resulting dielectric function is shown in Figure 1c of the main text, and the parameters are shown in Table S2.

| Axis | $\epsilon_\infty$ | $\nu^{TO}$ (cm$^{-1}$) | $\nu^{LO}$ (cm$^{-1}$) | $\gamma$ (cm$^{-1}$) |
|------|----------------|----------------|----------------|----------------|
| [100] | 5.78 | 367 | 390 | 3 |
| [001] | 6.07 | 262 | 367 | 4 |
| [010] | 4.47 | 337 | 363 | 1 |
Note S7: The effect of pulse frequency bandwidth and temporal pulse width on lifetime estimations

Polariton interferometry with a pulsed light source leads to a non-trivial, time-dependent near-field signal formation. For s-SNOM imaging, this effect becomes critical, as the polariton roundtrip time may be convoluted by the illumination temporal pulse width itself.

Free-electron lasers (FEL) are known to generate nearly Fourier-transform-limited pulses, with the exception of FELs based on self-amplified spontaneous emission (e.g. X-ray FELs; not applicable in our case). Moreover, the FEL pulse envelope is known to show an approximate Gaussian temporal profile. As the time-bandwidth-product \((= \tau_{FEL} \cdot \Delta \nu)\) of the Gaussian pulse is known, we can obtain a direct estimate of the lower limit of the temporal pulse width. In our experiments, we tuned the FEL to obtain the narrowest/longest possible pulse, yielding estimated pulse widths of around > 5 ps (see Table S3), having taken a conservative bandwidth at the full-width at half-maxima (FWHM) value.

| Frequency (THz) | Wavelength (µm) | Wavenumber (cm\(^{-1}\)) | Bandwidth \(\Delta \nu\) (cm\(^{-1}\)) | Pulse width \(\tau_{FEL}\) (ps) |
|----------------|-----------------|--------------------------|-----------------------------|------------------|
| 11.459         | 26.16           | 382.26                   | 2.75                        | 5.35             |
| 11.403         | 26.29           | 380.37                   | 2.05                        | 7.18             |
| 11.321         | 26.48           | 377.64                   | 3.67                        | 4.01             |
| 11.169         | 26.84           | 372.58                   | 1.96                        | 7.51             |
| 11.103         | 27.00           | 370.37                   | 3.55                        | 4.14             |
| 9.603          | 31.22           | 320.31                   | 2.66                        | 5.53             |
| 9.436          | 31.77           | 314.76                   | 2.80                        | 5.25             |
| 9.224          | 32.50           | 307.70                   | 1.75                        | 8.41             |
| 9.041          | 33.16           | 301.57                   | 2.57                        | 5.72             |
| 8.899          | 33.69           | 296.82                   | 2.70                        | 5.45             |
| 8.553          | 35.05           | 285.31                   | 2.87                        | 5.13             |

Table S3. FEL pulse characteristics for the frequencies used in our experiment. The center frequency, bandwidth and temporal pulse width were extracted from the FEL spectra (Fig. 1b, main text) obtained with a grating spectrometer assuming a Gaussian spectral distribution and temporal profile. The pulse width is calculated assuming a Fourier-transform-limited pulse, with \(\Delta \nu\) taken at FWHM.
We perform direct self-homodyne (SH) s-SNOM measurements, which entails that the scattered near-field signal is interferometrically amplified by background radiation for detection. While this phenomenon is well understood in experiments with CW laser sources, the interpretation of near-field signal formation in SH mode with a pulsed light source and with time-dependent processes, becomes rather complex. In the context of the (time-dependent) polariton interferometry technique, it requires that near-field signal scattering takes place within the timescale of the excitation pulse. That is, assuming that the near-field signal cannot be detected without SH amplification, the observable maximum propagation length (and polariton lifetime) should be intrinsically limited, whenever the polariton lifetime is significantly longer than the exciting pulse.

In this context, we can invoke a maximal measurable polariton lifetime of approximately \( \sqrt{2} \cdot \tau_{FEL} \), as defined by the convolution between the polariton and FEL pulses (assuming a Gaussian pulse profile). In this limiting case, the near-field signal formation is defined as the cross-correlation between the leading edge of the polariton pulse with trailing edge of the FEL pulse. For \( \alpha \)-MoO\(_3\) THz polaritons propagating along the [001] and [001] crystallographic axes (with estimated lifetimes of \( \tau_{[001]}^{0.22\,THz} = 3 \pm 0.4 \, ps \) and \( \tau_{[100]}^{11.17\,THz} = 9 \pm 4 \, ps \), respectively), the estimated \( \sqrt{2} \cdot \tau_{FEL} \) lifetime upper-limit is not reached (i.e. \( \sim 11.9 \, ps \) and \( \sim 10.6 \, ps \), respectively). Hence, we conclude that the polariton lifetime estimations reported in the main-text have an acceptable degree of accuracy. It is important to stress that the estimation of FEL pulse width via the time-bandwidth product provides a lower limit value, only. Hence, the measurement time window may be significantly broader.
In contrast, the FEL pulse frequency bandwidth is expected to have a rather non-negligible effect in the lifetime estimation if the RB bandwidth is relatively narrow (see in Figure S8 the modelled polariton interferometry profiles for the broadband RB\textsubscript{1} (left) and the narrowband RB\textsubscript{3} (right), calculated for different FEL pulse bandwidths $\Delta\nu_{\text{FEL}}$). The monochromatic cases with bandwidth $\Delta\nu_{\text{FEL}} = 0$, are also plotted as a reference. The lifetime values in our model calculations are expected to be underestimated for all cases, namely by a factor of around 0.83x

![Figure S8](image)

Figure S8. The effect of THz pulse bandwidth (BW) on the measured polariton interferometry profile. (left) Evaluation of the FEL pulse BW effect for the broad PhP\textsubscript{[001]} band. (right) Evaluation of the FEL pulse BW effect for the narrow PhP\textsubscript{[100]} band. Black dashed curves are the modelled polariton profile, while the solid red lines are the damped sinusoidal fittings.

(for PhP\textsubscript{[001]} within RB\textsubscript{1}) and 0.47x (for PhP\textsubscript{[100]} within RB\textsubscript{3}) for bandwidths of $\Delta\nu_{\text{FEL}} = 0.65\%_{\text{FWHM}}$ and $\Delta\nu_{\text{FEL}} = 0.53\%_{\text{FWHM}}$, respectively.

Note moreover that, as emphasized in Supplementary Note 2, the determination of lifetimes is drastically affected by the low signal-to-noise ratio of our THz nanoimaging measurements. Therefore, the polariton lifetime values reported in our manuscript are only an approximate estimation.
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