Supplementary Material for "Optical control of non-equilibrium phonon dynamics"

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Fig. S1 | Quantum and Classical Molecular Dynamics Simulations. a, Schematic of the supercell for QMD simulations. Periodic boundary conditions imposed along all three directions are used to model a bulk 2H-phase $MoTe_2$ crystal. b, Schematic of the photoexcitation process,

which involves instantaneous promotion of one electron from the VBM (i.e. the HOMO state) to the CBM. This simulates the band-edge (BE) excitation by the 800 nm pulse. At 400 nm, electron is promoted to a higher-energy state to simulate photogeneration of a hot electron. TD-DFT is used to track the time evolution of KS energy levels after electronic excitation. These eigenlevels also respond to atomic motion at the characteristic frequency of lattice vibration modes. **c**, Schematic of the laterally-large bulk simulation cell used in classical molecular dynamics simulations used to model the influence of phonon modes on the changes of UED patterns (i.e. peak and diffuse intensities). **d**, Phonon modes are selectively excited by applying an instantaneous force on atoms along the eigenvector of the phonon mode. This induces normal-mode vibrations in the lattice, whose magnitude can be tracked by following the local mean-square displacement of atoms, $\langle u^2 \rangle$.



Fig. S2 | **Differential Diffuse Scattering.** (a), Upon 400 nm excitation and (b) Upon 800 nm optical excitation.

3. Forcefield Parameterization

Molecular dynamics simulations were performed with an empirical Stillinger-Weber forcefield. Containing 2- and 3-body interaction terms, this forcefield has been used previously in MD simulations and studies of thermal and elastic phenomena in transition metal dichalcogenide (TMDC) materials ^{1–3}. Forcefield parameters for MoTe₂ crystals were optimized using density functional theory calculations of structural properties like lattice constants and vibrational properties like the phonon dispersion curve. Forcefield parameterization was performed with the GULP code which uses the Broyden-Fletcher-Goldfarb-Shanno algorithm to minimize the objective function ^{4,5}

$$F(x) = \sum_{i=1}^{N} w_i \left[f_i^{SW}(x) - f_i^{exp-DFT} \right]^2$$

Here, the vector x denotes the Stillinger-Weber parameters, f_i^{obs} is the *i*th observable quantity, such as lattice constant and vibrational frequency obtained from first-principles DFT calculations. $f_i^{calc}(x)$ is the corresponding value calculated using the Stillinger Weber forcefield with parameters defined by x and w_i is an empirically chosen weight which represents the relative importance of the observable quantity, $f_i^{exp-DFT}$. Fig. S3 compares the phonon dispersion spectra produced by the MoTe₂ Stillinger-Weber forcefields to those generated from DFT simulations. This figure demonstrates that lattice vibrations, especially those of low-energy acoustic modes are captured accurately in the Stillinger Weber force field.



Fig. S3 | Goodness of SWFF for bulk MoTe₂. Stillinger Weber forcefields are constructed to reproduce the entire phonon dispersion (a) and vibrational density of states (b) of the bulk 2H-phase MoTe₂ crystal.

4. Sample rotation during photoexcitation



Fig. S4 | Peak position drift. There is negligible drift in the position of the center of mass of each of the six (100) lattice peaks, indicating no significant change in the orientation of the MoTe₂ sample due to optical excitation.

Optical excitation	Peak	τ (ps)	ΔI (%)	
400 nm pump	100	1.458 ± 0.047	$0.600 \pm 1.3 { imes} 10^{-6}$	
Fluence = 0.86 mJ/cm^2	110	1.570 ± 0.008	$-2.553 \pm 3.3 \times 10^{-6}$	
	200	1.733 ± 0.011	$\textbf{-4.507} \pm 1.1 {\times} 10^{\text{-5}}$	
	220	1.584 ± 0.003	$-15.686 \pm 5.2 \times 10^{-5}$	
	300	1.638 ± 0.003	$-12.638 \pm 3.1 \times 10^{-5}$	
	120	1.709 ± 0.004	$-8.667 \pm 2.0 \times 10^{-5}$	
	130	1.727 ± 0.003	$-15.756 \pm 4.2 {\times} 10^{\text{-5}}$	
	M-point	1.411 ± 0.018	$3.931 \pm 2.3 { imes} 10^{-5}$	
	K-point	1.101 ± 0.027	$3.728 \pm 3.6 {\times} 10^{\text{-5}}$	
	Λ -point	3.559 ± 0.112	$5.755 \pm 9.5 {\times} 10^{\text{-5}}$	
800 nm pump	100	0.807 ± 162.4	$-0.037 \pm 1.5 \times 10^{-5}$	
Fluence = 2.54 mJ/cm^2	110	1.407 ± 0.106	$-1.349 \pm 2.5 \times 10^{-5}$	
	200	1.360 ± 0.098	$-1.887 \pm 5.9 \times 10^{-5}$	
	220	1.133 ± 0.013	$-6.291 \pm 1.3 \times 10^{-4}$	
	300	$\overline{1.283\pm0.012}$	$-4.987 \pm 6.2 \times 10^{-5}$	
	120	1.555 ± 0.047	$-3.629 \pm 9.4 \times 10^{-5}$	

5. Time constants for intensity of lattice planes and diffuse regions

130	1.101 ± 0.024	$-5.329 \pm 1.7 { imes} 10^{-4}$
M-point	0.680 ± 0.034	$1.980 \pm 6.5 { imes} 10^{-5}$
K-point	0.745 ± 0.137	$1.803 \pm 9.0 \times 10^{-5}$
Λ-point	1.619 ± 1.293	$0.934 \pm 2.0{\times}10^{\text{-4}}$

Table S1	Measured	dvnamics o	f peak and	diffuse inter	sities in	UED ex	periments
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6. Debye-Waller Model

Quantitatively, variations in the lattice plane intensity, I(q), can be explained due to variations in the Debye-Waller parameter, W, which depends upon the lattice disorder through the RMS displacements of atoms in the crystal, $\langle u^2 \rangle$, through the Equations 1(a) and 1(b).

$$I_q = I_0 \times W$$
 Eqn. 1(a)

 $W = \exp(-q^2 \langle u^2 \rangle)$ Eqn. 1(b)

Figures 2d and 2g show a semilog plot of measured normalized peak intensities of different $\{hkl\}$ planes as a function of the reciprocal vector, q. The linear dependence of log I(q) on q^2 indicates that lattice disordering/thermalization explains the variation of all lattice peak intensities.

7. Electronic Band Structure of Bulk 2H-phase MoTe₂



Fig. S5 | Electronic structure of bulk MoTe₂. Valence and conduction band edges of bulk MoTe₂ showing the indirect band gap between the highest occupied state at the Γ point in the valence band and the lowest unoccupied Λ point state in the conduction band.

8. Sample preparation and characterization



Fig. S6 | **Experimental sample characterization. a**, Raman spectra of MoTe₂ film shows several modes at E_{2g}^{1} (~231 cm⁻¹), A_{1g} (~171 cm⁻¹) and B_{2g}^{1} (~286 cm⁻¹). **b**, (002), (004), (006) and (008) planes are detected in the XRD patterns. XPS spectra of (**c**) Mo 3d and (**d**) Te 3d. The main peaks are observed at 231.2 eV (Mo 3d_{3/2}), 228.0 eV (Mo 3d_{5/2}) and 583.3 eV (Te 3d_{3/2}), 572.9 eV (Te 3d_{5/2}). (**e**), AFM measurement is conducted near the edge. (**f**), The depth profile shows the film has a thickness of ~10 nm. (**g**) TEM image and (**h**) corresponding Fast Fourier transform (FFT) image confirm the MoTe₂ film has a hexagonal crystal structure.

9. Temperature increase in UED experiments and efficiency of electron-phonon coupling at different excitation energies

Stronger electron-phonon coupling at higher excitation energies is also supported by the measured increase in sample temperature during optical excitation by 400 nm and 800 nm pulses. The stronger Debye-Waller response due to 400 nm excitation is consistent with the complete conversion of absorbed optical energy into lattice motion, while the relatively weaker Debye-Waller response due to 800 nm excitation indicates that only intraband relaxation (i.e. relaxation of carriers to the conduction band edge) couples to lattice motion.

Experimental sample

MoTe₂ bulk, band gap, $E_g = 1.1 \text{ eV}$ Sample thickness, $t = 9 (\pm 1) \text{ nm} = 0.009 \,\mu\text{m}$ Sample density is 7.7 g/cm³ and molar mass of MoTe₂ is 351.14 g/mol. Specific heat, $C_v(300 \text{ K}) = 18.38 \frac{\text{cal}}{\text{mol}-\text{K}} = 0.2189 \frac{\text{J}}{\text{g-K}}$ (41)

<u>Predicted Temperature Jump at 400 nm Excitation at Pump Fluence of 0.86 mJ/cm²</u>. Photon energy hv = 3.1 eV

Beam diameter of the optical pulse = 910 μ m (i.e. 2 ω)) Pumped volume = $\pi \omega^2 t = 5.854 \times 10^{-9} \text{ cm}^3$ Total energy in pump, $Q_{pump} = 1.33 \mu J$

Absorption efficiency, $\eta_{abs} = 0.43$, including the absorption cross section and on the substrate and saturable absorber effect.

Total absorbed energy, $Q_{in}=Q_{pump}\times\eta_{abs}=0.57~\mu J$

Estimated ΔT for complete conversion of absorbed energy into thermal energy:

$$\Delta T = \frac{0.57 \,\mu\text{J}}{5.85 \times 10^{-9} \,\times \,7.7 \,\times \,0.2189} = 58 \,\text{K}$$

This suggests that full absorbed photon energy will lead to ~60 K temperature of the MoTe₂ at current pump energy.

Temperature Jump Calculation from UED Experimental Results at 400 nm Excitation.

The temperature jump in experimental samples can be estimated from the measured change in mean square displacement of atoms using the following Debye-Waller expressions.

$$\Delta \langle u^2 \rangle_{\Delta T} = \langle u^2 \rangle_T - \langle u^2 \rangle_{298K}$$
(2a)

$$\langle u^2 \rangle_T = \frac{3\hbar^2}{mk_B \theta_D} \left[\left(\frac{T}{\theta_D} \right)^2 P_{(\theta_D/T)} + \frac{1}{4} \right]$$
(2b)

$$P_{(\theta_D/T)} = \int_0^{\frac{\theta_D}{T}} \frac{x}{e^{x} - 1} dx \cong 1.6449(1 - e^{-0.64486\frac{\theta_D}{T}})$$
(2c)

where $\Delta \langle u^2 \rangle_{\Delta T}$, \hbar , m, k_B, and θ_D are means-square displacement, reduced Planck's constant, reduced mass, Boltzmann constant and Debye Temperature, respectively. The Debye temperature of bulk 2H-phase MoTe₂ is 165 K (corresponding to the 3.5 THz maximum frequency of the acoustic bands in bulk 2H-MoTe₂). Figs. S7 shows a fitting to obtain mean-square displacement from UED measurement (i.e. slope). According to the Eqs. 2b and 2c, we obtained ~70 K temperature jump of lattice temperature at 400 nm excitation. This suggests complete conversion of absorbed optical energy (i.e. 58 K vs. 70 K).



Fig. S7 | **Temperature measurement in UED experiments.** The atomic mean square displacement obtained from fitting UED intensities to Debye-Waller expression provides an estimated temperature jump of ~70 K.

Predicted Temperature Jump at 800 nm Excitation at Pump fluence of 2.5 mJ/cm²

Photon energy hv = 1.55 eVBeam diameter of the optical pulse is 510 µm (i.e. 2 ω) Pumped volume = $\pi\omega^2 t = 1.8385 \times 10^{-9} \text{ cm}^3$

Pumped volume = $\pi\omega^2 t = 1.8385 \times 10^{-9} \text{ cm}^3$

Total energy in pump, $Q_{pump} = 2.59 \ \mu J$ Absorption efficiency, $\eta_{abs} = 0.175$, based on the substrate and saturable absorber effect Reflection efficiency of the mirror, $\eta_{refl} = 0.64$ Total absorbed energy, $Q_{in} = Q_{pump} \times \eta_{abs} \times \eta_{refl} = 0.29 \ \mu J$

Estimated ΔT for complete conversion of absorbed energy into thermal energy:

$$\Delta T = \frac{0.29 \,\mu\text{J}}{1.8385 \times 10^{-9} \times 7.7 \times 0.2189} = 93.6 \,\text{K}$$

Estimated ΔT for conversion of above-band-gap energy into thermal energy:

$$\Delta T = \frac{0.29 \,\mu\text{J} \times (1.55 - 1.1) \,\text{eV}}{1.8385 \times 10^{-9} \times 7.7 \times 0.2189 \times 1.55 \,\text{eV}} = 27.17 \,\text{K}$$

Temperature Jump Calculation from UED Experimental Results at 800 nm Excitation.

Using the same calculation procedure as shown above for 400 nm, we are able to obtain temperature jumps in MoTe₂ crystals pumped by a 800 nm optical pulse at three different fluence values, 1.4 mJ/cm², 2.5 mJ/cm² and 3.2 mJ/cm² corresponding to the resulting carrier density of 3.5×10^{20} , 6.3×10^{20} and 8.1×10^{20} cm⁻³, respectively. For all three carrier densities, the measured temperature rise from UED (Figures S8(a) and S8(b)) are only ~30% of the expected temperature rise due to complete conversion of optical energy into lattice thermal disorder. This ratio is consistent with the fraction of optical energy above the 1.1 eV band gap, (i.e. $\frac{1.55-1.1}{1.55} \approx 30\%$),

suggesting that only intraband relaxation of excited electrons to the conduction band edge occurs on the timescale of our UED experiments for 800 nm excitation.



Fig. S8 | Temperature measurement for 800 nm excitation. (a) The atomic mean square displacements obtained from fitting UED intensities to Debye-Waller expression for three pump fluence values results in temperature jumps significantly lower than values predicted for complete conversion of optical energy to thermal energy (b).



Fig. S9 | Calculated intensity of {100} and {110} peaks from classical MD simulation. The 200-fs instrument response time in UED experiments prohibits the observation of high-frequency coherent oscillations. Classical MD simulations are performed at time steps of 2 fs and can be used to resolve coherent lattice motion that accompanies the E_{2g}^1 , A_{1g} , and LA(M) phonon modes.

10. Fourier transform analysis of Kohn-Sham eigen levels for identification of vibrational frequencies

Fourier transforms shown in Figure 4 are performed for the 10 highest-occupied Kohn-Sham eigenlevels lying ~ 0.75 eV below the valence band maximum. For both the 1.3 eV and 2.8 eV excitations, Fourier analysis is performed in the time-window beginning from the initial non-adiabatic transition of the excited electron (~ 0.6 ps for the 1.3 eV excited electron and ~ 0.25 ps for the 2.8 eV excited electron) till the end of the simulation (2 ps).