K-point longitudinal acoustic phonons are responsible for ultrafast intervalley scattering in monolayer MoSe₂

Phonon-mediated intervalley scattering is a central process in photoexcited carrier dynamics of valleytronic materials. In transition metal dichalcogenides (TMDs), a prototypical family of valleytronic materials, it has been reported that the degree of valley polarization exhibits ultrafast decays in picosecond time scale due to intervalley carrier-phonon scattering. In such scattering processes, zone-edge acoustic phonons play a definitive role in transferring photoexcited carriers from one valley to another; acoustic phonons at the K-point scatter carriers from K to K’ valleys (or K’ to K valleys) and those at the M point scatter carriers from Q to K’ valleys (or Q’ to K valleys) due to the momentum conservation (see Fig. 1a). While numerous optical experiments have been performed to probe zone-edge acoustic phonons by using resonant Raman scattering, photoluminescence excitation, and coherent phonon generation, the phonon momentum have often remained largely unidentified because the frequencies of phonon modes at the zone-edge are nearly degenerate.
K and M points TMDs are nearly degenerate (see Table 1). For instance, the LA phonon frequencies at the M and K points in Mo-, W-, and Re-based TMDs (MoS₂ and MoSe₂) and the ZA phonon frequencies at the M and K points of W-based TMDs (WS₂ and WSe₂) are nearly degenerated (frequency differences <0.1 THz = 0.4 meV), which are hardly resolved with the phonon frequencies obtained by typical linear spectroscopies.

**Results**

**Coherent phonon measurement**

Here, we report on unambiguous determination of the phonon mode that dominates intervalley scattering in MoSe₂: the K-point LA phonon. This conclusion was obtained through phonon-symmetry analysis and first-principles calculations, combined with nonlinear coherent phonon (CP) measurement, whose principle is schematically shown in Fig. 1b. The transmission modulations induced by CPs were monitored in the time domain, which was Fourier transformed to generate a CP spectrum (see Fig. 1c). On the basis of comparison with the calculated phonon dispersions of monolayer MoSe₂ in Fig. 1d, we assign the observed CP peaks at 4.65 and 7.37 THz to the first-order LA mode and the optical A₁(Γ) mode, respectively.

### Table 1 | Phonon frequencies of acoustic branches (LA, ZA, and TA) at the M and K points in several transition metal dichalcogenides

| Material | ω(M) (THz) | ω(K) (THz) | ω(K)−ω(M) (THz) |
|----------|------------|------------|------------------|
| MoSe₂    |            |            |                  |
| LA       | 4.76       | 4.79       | 0.04             |
| ZA       | 3.95       | 4.03       | 0.08             |
| TA       | 3.21       | 3.63       | 0.42             |
| WSe₂     |            |            |                  |
| LA       | 3.84       | 4.22       | 0.38             |
| ZA       | 3.62       | 3.69       | 0.06             |
| TA       | 2.91       | 2.93       | 0.0              |
| MoS₂     |            |            |                  |
| LA       | 7.05       | 7.05       | 0.00             |
| ZA       | 5.16       | 5.40       | 0.24             |
| TA       | 4.67       | 5.51       | 0.85             |
| WS₂      |            |            |                  |
| LA       | 5.32       | 5.52       | 0.20             |
| ZA       | 4.28       | 4.29       | 0.02             |
| TA       | 3.90       | 4.44       | 0.54             |

ω(M) and ω(K) denote the phonon frequencies at the M and K points and ω(K)−ω(M) are their frequency differences, in THz. Frequency differences lower than the frequency resolution of conventional femtosecond pump-probe measurements (typically, 0.1 THz = 0.4 meV) are marked in bold.

**Phonon displacements and symmetry**

To clarify the nonlinear optical response and zone-edge LA phonon mode, we first...
Figure 2 | Lattice deformations of the $A_1^\prime (\Gamma)$, LA(K), and LA(M) modes in monolayer MoSe$_2$ and their optical modulations (e.g., differential transmittance $\Delta T/T_0$) associated coherent phonon (CP) spectra. a Asymmetric atomic lattice deformations of the $A_1^\prime (\Gamma)$ and LA(K) modes. Q(t) represents the atomic displacements oscillating over time. The + and − signs of Q(t) denote the directions of vibrations. Lattice deformations of the $A_1^\prime (\Gamma)$ and LA(K) modes are asymmetric because the atomic structures with +Q and −Q displacements are not identical. b Symmetric lattice deformations of the LA(M) mode. In contrast with the asymmetric $A_1^\prime (\Gamma)$ and LA(K) modes, the lattice deformations of +Q and −Q displacements of the LA(M) mode superimposed after the lattice translation are identical. c Lattice oscillations of the asymmetric $A_1^\prime (\Gamma)$ and LA(K) modes, with derived optical responses and CP spectra. As +Q and −Q displacements yield asymmetric atomic structures, nonlinear optical modulations with respect to the phonon frequency $\omega$ can be recorded as higher-order CP signals. d Lattice oscillation of the symmetric LA(M) mode, the derived optical response and CP spectrum exhibiting only even orders of the phonon frequency, due to the even function behavior of the optical response.

(a) $A_1^\prime (\Gamma)$: Asymmetric
(b) LA(M): Symmetric
(c) LA(K): Asymmetric
(d) LA(M): Symmetric

Theoretical exploration of the lattice deformations and optical modulations of monolayer MoSe$_2$ using density-functional theory. Figure 2a, b shows the lattice deformations and derived optical responses of the $A_1^\prime (\Gamma)$ (Valence) and LA(K) modes, with atomic displacements of the phonon modes calculated by density-functional theory (see Methods). As all monolayer TMDCs have the same type of atomic structure, the same description can be generally applied to other TMDCs. Figure 2a, b shows the lattice deformations and displaced atomic structures induced by the phonon modes, with Q(t) denoting the degree of atomic displacements at time t, which oscillates with the phonon frequency. We illustrate the displaced atomic structures of monolayer MoSe$_2$ with lattice deformations of Q(t) = +Q and −Q, where + and − signs denote directions of the phonon vibrations. While all phonon modes deform the lattice structure from the equilibrium structure, we found a significant difference between lattice deformations in the LA(M) mode and both the $A_1^\prime (\Gamma)$ and LA(K) modes. +Q and −Q displacements induced by the $A_1^\prime (\Gamma)$ and LA(K) modes result in different atomic deformations, as shown in Fig. 2a, but those of the LA(M) mode can be superimposed after the lattice translation shown in Fig. 2b. Thus, +Q and −Q displacements induced by the $A_1^\prime (\Gamma)$ and LA(K) modes are asymmetric, but those of the LA(M) modes always induce symmetric atomic structures.

The optical modulations induced by the coherent phonon generation of asymmetric and symmetric lattice deformations of the $A_1^\prime (\Gamma)$, LA(K), and LA(M) modes and associated CP spectra are shown in Fig. 2c, d. Deformations of the atomic structure of monolayer MoSe$_2$ by cosinusoidal lattice oscillations induced by coherent phonon vibrations are illustrated in the left-lower panels in Fig. 2c, d. As the asymmetric lattice deformations of the $A_1^\prime (\Gamma)$ and LA(K) modes differ, the differential transmittance $\Delta T/T_0$ at the +Q and −Q displacements should have different values, as shown in Fig. 2c. The time evolution of $\Delta T/T_0$ is expected to oscillate with the phonon frequency $\omega$. However, its shape is not a perfect cosinusoidal wave, leading to induction of the higher orders of $\omega$ such as 2$\omega$, 3$\omega$, 4$\omega$, and so on, as obtained by Fourier transformation. By contrast, linear behavior of the differential transmittance $\Delta T/T_0$ can derive a perfect cosinusoidal optical modula-

Period $= 2\pi/\omega$

Even function

$\Delta T(Q)/T_0 = Q(t) = \cos(\omega t + \phi)$ (where $\phi$ is a phase shift), yielding only first-order CP signals at the phonon frequency $\omega$. This indicates that the nonlinear optical modulation of LA(K) modes is responsible for single and higher-order CP signals. On the other hand, because LA(M) phonons deform the atomic structure in the same crystallographic structure at both the +Q and −Q displacements, the differential transmittance $\Delta T(Q)/T_0$ should be an even function, i.e., $\Delta T(Q)/T_0 = a_0 + a_2 Q^2 + a_4 Q^4 + a_6 Q^6 ...$, the odd-order coefficients (for example $a_1$ and $a_3$) must be zero for the LA(M) mode due to the even function behavior of $\Delta T(Q)/T_0$. If an atomic displacement $Q(t) = \sin(\omega t + \phi)$ is plugged into the $\Delta T(Q)/T_0$, the differential transmittance exhibits only even orders of the phonon frequency $\omega$ (see Methods for details). This indicates that the LA(M) mode is not responsible for...
the odd-order LA signals, our experimental CP spectrum is therefore attributable to dominant generation of LA(K) phonons, which are responsible for phonon-mediated ultrafast intervalley carrier scattering in monolayer MoSe$_2$\cite{20,23}. In turn, the striking difference between the LA(K) and A$\,\_1'(\Gamma)$ modes observed in the CP spectrum is attributable to the linear and nonlinear behavior of the differential transmittance $\Delta T(Q) / T_0$. Seeking numerical details of the differential transmittance associated with the CP spectra, we next explicitly evaluate the differential transmittance induced by the A$\,\_1'(\Gamma)$, LA(K) and LA(M) coherent phonons from the absorption spectra calculations using density-functional theory.

**Phonon-mediated optical modulation**

Figure 3 presents the transmittance spectra, the differential transmittance $\Delta T(Q) / T_0$ and simulated CP spectra of the A$\,\_1'(\Gamma)$, LA(K), and LA(M) modes calculated by linear-response time-dependent density-functional theory (LR-TDDFT) using the HSE06 functional including spin-orbit coupling (SOC). We here quantify the degree of atomic displacements $Q$ by introducing a generalized atomic displacement $Q^2 = \sum m_i d_i^2$ evaluated for the MoSe$_2$ formula unit (three atoms), where $m_i$ and $d_i$ are the mass and displacement of the $i$-th atom in atomic mass units (amu) and angstroms (Å), respectively. The calculated transmittance with the atomic...
displacement of each phonon mode is shown in the left panels of Fig. 3. The A-exciton position of the calculated transmittance spectrum is calibrated to the experimental value. The asymmetric $\Gamma_3'(\Gamma)$ and LA(K) modes modulate each transmittance spectrum with $+Q$ and $-Q$ displacements shown in Fig. 3a, b (magenta and blue lines, respectively), while the transmittance spectra associated with $+Q$ displacement of the LA(M) phonon are the same (Fig. 3c). These numerical results corroborate our findings derived from the asymmetric and symmetric behaviors of the $\Gamma_3'(\Gamma)$, LA(K), and LA(M) modes previously explained and illustrated in Fig. 2. Using the calculated transmittance spectra, the differential transmittance is obtained by the overlap integration of the experimental laser spectrum and calculated transmittance (see Methods). The calculated differential transmittance $\Delta T(Q)/T_0$ is shown in the middle panels of Fig. 3. Differences in behavior of $\Delta T(Q)/T_0$ among the three phonon modes can be clearly seen. The $\Delta T(Q)/T_0$ of the $\Gamma_3'(\Gamma)$ mode responds almost linearly with respect to the displacement $Q$ (in Fig. 3a), whereas the LA(K) mode exhibits a highly nonlinear modulation on $\Delta T(Q)/T_0$ (in Fig. 3b). The LA(M) mode exhibits the symmetric $\Delta T(Q)/T_0$ due to an even function of the displacement $Q$ (in Fig. 3c). We note that the $\Gamma_3'(\Gamma)$ mode reduces and increases the band gap of monolayer MoSe$_2$ with $+Q$ and $-Q$ displacements, respectively, whereas both LA(K) and LA(M) modes with $+Q$ and $-Q$ displacements only reduce the band gap.

By comparing the calculated $\Delta T(Q)/T_0$ in Fig. 3 to the experimentally determined differential transmittance in Fig. 1c, the range of the displacement $Q$ of each phonon can be approximately estimated. The gray shading in the $\Delta T(Q)/T_0$ spectra presented in middle panels of Fig. 3 show the experimental range of the differential transmittance, $\Delta T(Q)/T_0$, with maximum and minimum values of around $1 \times 10^{-3}$. This corresponds to $Q$ values of the $\Gamma_3'(\Gamma)$, LA(K) and LA(M) modes of 0.05, 0.2, and 0.15 amu$^{1/2}$Å, respectively. We set these maximum displacements, $Q_0$, as the amplitudes of cosinusoidal lattice motions of the phonon modes, as shown in the right-upper panels in Fig. 3a–c. Evolutions with time of the differential transmittance $\Delta t/dT(t)/T_0$ are then readily obtained from the calculated $\Delta T(Q)/T_0$ by inserting $Q(t) = Q_0 \cos \omega t$ as the time-dependent displacement $Q$. Simulated CP spectra of the $\Gamma_3'(\Gamma)$, LA(K) and LA(M) modes are obtained from Fourier transformations of $\Delta T(Q)/T_0$, as shown in the right-bottom panels of Fig. 3a–c. The simulated CP spectra explain the experimental CP spectra well, as follows. The first-order peak dominates the CP spectrum of the $\Gamma_3'(\Gamma)$ mode because its atomic motion monotonically increases and decreases the band gap of monolayer MoSe$_2$. The higher-order CP signals of LA phonons originate from nonlinear behavior of the optical modulation induced by LA(K) phonons. Activation of the LA(M) mode in the CP spectrum is strictly limited to its even orders due to the symmetric lattice deformations of the $+Q$ and $-Q$ displacements. Thus, our numerical simulations resolve the acoustic momentum of LA phonons through the nonlinear and higher-order optical responses of monolayer MoSe$_2$ induced by the LA(K) mode.

We present a quantitative comparison of the experimental and simulated spectra in Fig. 4. To include the fast decay of the experimental $\Delta T(t)/T_0$, the single exponential decay of 2 ps has been imposed on the simulated $\Delta T(t)/T_0$ modulated by the LA(K) mode. The simulated $\Delta T(t)/T_0$ spectrum obtained with the combination of the LA(K) and $\Gamma_3'(\Gamma)$ modes quantitatively reproduces the experimental $\Delta T(t)/T_0$ spectrum, as shown in the bottom panels of Fig. 4a. Here, amplitudes $Q_0$ of the $\Gamma_3'(\Gamma)$ and LA(K) modes are set to 0.003 and 0.2 amu$^{1/2}$Å, whose atomic displacements of the $\Gamma_3'(\Gamma)$ and LA(K) modes are presented in Table 2. The large atomic displacements of the LA(K) mode compared to that of the $\Gamma_3'(\Gamma)$ mode indicates that intervalley scattering process would dominantly occur compared to the impulsive stimulated Raman scattering (ISR) in monolayer MoSe$_2$. We showcase the simulated Fourier-transformed CP spectrum compared to the experimental CP spectrum in Fig. 4b, which reproduces overall characteristics of the experimental CP spectrum. The simulated spectrum comes from a combination of $\Gamma_3'(\Gamma)$ mode and LA(K) mode having a rapid damping of 2 ps, which could result in asymmetric shapes of Fourier signals. Some marginal inconsistencies remain e.g., relative intensity of the 3LA(K) mode and small variation of the 2LA(K) and 4LA(K) frequencies, which might be attributed to transient phonon frequency chirping through light-induced lattice strain.

Discussion

Finally, we briefly discuss the generation mechanism of the LA(K) phonon in monolayer MoSe$_2$ observed in our experiment. It has been previously reported that K-point phonon generations in TMDs can involve multiple acoustic phonon branches. For instance, the LA(K) phonon has been widely detected in several TMDs. In contrast, the coherent ZA(K) phonon generation has been reported for monolayer MoSe$_2$ when the spin-flip intervalley scattering occurs in between lowest energy K-point valleys with opposite spins, resulting in variations of 2LA(K) and 4LA(K) modes.
in the generation of the flexure (out-of-plane) ZA(K) phonons. Because our laser spectrum (cf. gray shadings in Fig. 3) spreads over a wide excitation energy range which includes high energy excitations over the lowest energy valleys, intervalley carrier-phonon scatterings are not limited to the spin-flip intervalley scattering as in Ref. 20 but includes spin-conserved intervalley scatterings. The predominant occurrence of spin-conserved intervalley scatterings over the spin-flip intervalley scatterings then leads to the generation of the in-plane LA(K) phonons in our experiment rather than the flexural ZA(K) phonons as in Ref. 20. This demonstrates that, since the generation mechanism of zone-corner acoustic phonons is intimately related to the carrier excitation energy and spin relaxation, the nonlinear optical response should present an essential clue for exploring the valley depolarization process of TMDs.

In summary, we demonstrate higher-order optical responses of coherent phonon generation in monolayer MoSe2 that identifies the momentum of the LA phonon. The symmetric analysis of lattice deformations of coherent phonons decodes the higher-order optical response of zone-edge acoustic coherent phonons, and the higher-order coherent LA signals can be attributed to LA(K) phonons. Our first-principles calculations enable quantitative analysis of coherent phonon generation of the A′(Γ) and LA(K) modes, revealing that acoustic LA(K) phonon generation via intervalley scattering dominates over generation of the A′(Γ) mode through ISRS processes. Our work unveils hidden physics of the higher-order optical responses of monolayer MoSe2, thus facilitating deterministic descriptions of ultrafast phonon-mediated carrier scattering processes in a wide range of valleytronics.

Methods
Experimental setup and sample
Coherent phonon experiments with a degenerate pump-probe configuration were performed using a sub-10-fs Ti:sapphire laser (VEN-TEON PulseONE) with 7.5 fs pulse duration, 90 MHz repetition rate and 300 mW output power. The spectrum of the laser ranges from 650 nm (1.91 eV) to 1050 nm (1.18 eV) (see gray shadings in Fig. 3). The laser output was divided into pump (100 mW) and probe (5 mW) beams, both of which were simultaneously focused on the sample at approximately a normal incidence using a parabolic mirror with 50 mm focal length. The diameter of the focus at the sample was 20 μm. An optical shaker with a 15 ps scanning range running at 20 Hz was used in the pump beam path, and changes in transmitted probe pulses were detected using a Si photodiode. After subtraction of the intensity of the reference probe pulses, the signal was amplified with a SR560 transimpedance current amplifier. The amplified signal was collected with an ana-to-digital converter and analyzed with the position signal sent from the optical shaker. All the measurements were performed at room temperature.

The sample consisted of monolayer MoSe2 crystals grown by the chemical vapor deposition technique on a sapphire substrate. The triangular single crystals of monolayer MoSe2 with the typical size of 200 μm were confirmed by optical microscopy. We implemented the in-situ microscope at the sample position of the setup for coherent phonon experiment and confirmed that the pump and probe beams are oriented on the monolayer region of the sample. The reported waveforms were repeatedly observed during the experiments, indicating that no degradation of the sample occurred during the experiments. The absorption peak of the A-exciton resonance was observed around 1.6 eV in our sample, which was confirmed by a conventional transmission spectrometer.

First-principles calculations
We calculated electronic and vibrational properties of monolayer MoSe2 using density-functional theory (DFT) with the projector augmented wave (PAW) method, implemented in the Vienna ab initio simulation package (VASP). The kinetic energy cut-off of plane waves was set to 350 eV and a Γ-centered 2 × 2 × 1 Monkhorst-Pack k-point grid was used for the primitive cell. For supercell calculations, Γ-centered 2 × 2 × 1 and 6 × 6 × 1 Monkhorst-Pack k-point grids were employed for 6 × 6 × 1 and √3 × √3 × 1 supercells, respectively. The phonon dispersion of monolayer MoSe2 and atomic displacements of the A′(Γ), LA(K), and LA(M) modes were calculated using the Phonopy package. Force constants used in the phonon dispersion calculation were generated with DFT calculations of displaced 6 × 6 × 1 supercells of the monolayer MoSe2 primitive cell using the PBEsol functional. Optical properties of monolayer MoSe2 with and without atomic displacements of the phonon modes were obtained from the optical calculations of linear-response time-dependent density-functional theory (LR-TDDFT) with the HSE06 kernel including the spin-orbit coupling (SOC) effect as implemented in the VASP package. Transmittance spectra of monolayer MoSe2 were extracted using VASPkit code from the real and imaginary dielectric functions of the LR-TDDFT results.

Simulation of optical modulation and coherent phonon spectra
Integrated transmittance with a generalized atomic displacements Q are evaluated for monolayer MoSe2 as $T(Q) = |\tilde{T}(Q)e^{i\phi}|^2$ (where ϵ = ϵ(Q) − ϵ(Q) + ϵ(Q)), where ϵ is the excitation energy, $\tilde{T}(Q)e^{i\phi}$ is the calculated transmittance spectra of monolayer MoSe2 using LR-TDDFT with generalized atomic displacement Q, and ϵ(Q) is the experimental lager spectrum used in the pump-probe experiment. The generalized atomic displacements are estimated as $Q^2 = \sum_{ij} m_i d_j^2$, where $m_i$ and $d_j$ are the mass and displacement of the i-th atom in atomic mass units (amu) and angstroms (Å), respectively. A constant 0.1 eV downshift was applied to the excitation energy of the calculated transmittance $\tilde{T}(Q)e^{i\phi}$ to adjust the A-exciton energy to the experimental value. The differential transmittance $\Delta T(Q)/T_0(Q)$ was calculated for various Q values with atomic displacements of A′(Γ), LA(K), and LA(M) modes as $\Delta T(Q) = |T(Q) − T_0(Q)|/T_0(Q)$, where $|T(Q) − T_0(Q)|$ are integrated transmittance spectra with generalized atomic displacements Q and T0 = 0. The time-dependent differential transmittance $\Delta T(Q)/T_0(Q)$ was obtained by giving a cosinusoidal oscillation $\omega(t) = Q cos(\omega t)$ into the $\Delta T(Q)$Q. For actual calculations of $\Delta T(Q)/T_0(Q)$, the differential transmittance $\Delta T(Q)/T_0(Q)$ of each phonon mode was expanded into a polynomial of Q up to 6th order by numerical fitting. Finally, a simulated coherent phonon spectrum of each phonon mode was obtained by Fourier transformation of $\Delta T(Q)/T_0(Q)$. Odd-order regulation of coherent phonon signals of the LA(M) mode
The differential transmittance $\Delta T(Q)/T_0$ of the LA(M) mode is an even function which satisfies $\Delta T(Q)/T_0 = -\Delta T(-Q)/T_0$. Accordingly, the polynomial expansion of $\Delta T(Q)/T_0$ with respect to Q can be written as $\Delta T(Q)/T_0 = a_0 + a_2 Q^2 + a_4 Q^4 + \ldots$ (without odd orders of Q) where $a_n$ is the nth-order coefficient. By giving $Q = Q cos(\omega t)$ to $\Delta T(Q)/T_0$, the time-dependent differential transmittance is $\Delta T(t)/T_0 = a_0 + a_2 cos(\omega t) + a_4 cos(\omega t) + \ldots$. By adopting double angle identities of the cosine function $\cos(\omega t) = [1 + \cos(\omega t)]/2$ to $\cos(\omega t)$ terms, $\Delta T(t)/T_0$ can be reformulated into $\Delta T(t)/T_0 = b_0 + b_2 cos(2\omega t) + b_4 cos(4\omega t) + \ldots$ (where $b_n$ is the nth coefficient) when Fourier transform coefficients [the coherent phonon spectrum of the LA(M) mode] only have even orders of the phonon frequency ω, such as 2ω, 4ω, 6ω... excluding odd orders.

Data availability
All relevant data are available from the authors upon reasonable request.
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Author contributions

S.B., J.K., J.T. and I.K. conceived and coordinated this project. S.B., K.S. and H.R. performed the sub-10-fs pump-probe setup and performed the experiments. Y.S., X.Z., R.V., P.A. and J.K. synthesized monolayer MoSe2 and ω-H, M.K. and T.N. characterized the samples. S.B., J.T., J.K and I.K. wrote this paper with the other, anonymous, reviewer(s) for their contribution to the peer review.

Competing interests

The authors declare no competing interests.

Additional information

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