Monolayer (ML) transition metal dichalcogenides (TMDs) are material representatives of a broader class of atomically thin direct-gap semiconductors [1,2], pivotal for the realization of van der Waals heterostructures and devices with novel functionality [3,5]. They feature strong optical transitions promoted by excitons [6–9] and, paired with valley-selective excitation [10], manipulation [11–15] and detection [16–19] schemes, represent viable resources for opto-valleytronic applications [20–22]. While optical transitions of lowest-energy excitons in molybdenum-based MoSe₂, MoS₂ or MoTe₂ MLs is spin-allowed, the exciton ground state of ML tungsten dichalcogenides WSe₂ and WS₂ is spin-forbidden [23,24]. This striking difference stems from a reversed energetic order of momentum-dark excitons as well as their charged counterparts provide a powerful platform for spin-valley and microcavity physics in two-dimensional materials. The corresponding spectral signatures, however, are insufficient to explain the main characteristic peaks observed in the photoluminescence spectra of ML TMDs on the basis of momentum-direct excitons alone. Here, we show that the notion of momentum-indirect excitons is important for the understanding of the versatile photoluminescence features. Taking into account phonon-assisted radiative recombination pathways for electrons and holes from dissimilar valleys, we interpret unidentified peaks in the emission spectra as acoustic and optical phonon sidebands of momentum-dark excitons. Our approach will facilitate the interpretation of optical, valley and spin phenomena in TMDs arising from bright and dark exciton manifolds.

Identifying optical signatures of momentum-dark excitons in transition metal dichalcogenide monolayers

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Transition metal dichalcogenide (TMD) monolayers (MLs) exhibit rich photoluminescence spectra associated with interband optical transitions of direct-gap semiconductors. Upon absorption of photons, direct excitons with zero center-of-mass momentum are formed by photo-excited electrons in the conduction band and the respective unoccupied states in the valence band of the same valley. Different spin configurations of such momentum-direct excitons as well as their charged counterparts provide a powerful platform for spin-valley and microcavity physics in two-dimensional materials. The corresponding spectral signatures, however, are insufficient to explain the main characteristic peaks observed in the photoluminescence spectra of ML TMDs on the basis of momentum-direct excitons alone. Here, we show that the notion of momentum-indirect excitons is important for the understanding of the versatile photoluminescence features. Taking into account phonon-assisted radiative recombination pathways for electrons and holes from dissimilar valleys, we interpret unidentified peaks in the emission spectra as acoustic and optical phonon sidebands of momentum-dark excitons. Our approach will facilitate the interpretation of optical, valley and spin phenomena in TMDs arising from bright and dark exciton manifolds.

Monolayer (ML) transition metal dichalcogenides (TMDs) are material representatives of a broader class of atomically thin direct-gap semiconductors [1,2], pivotal for the realization of van der Waals heterostructures and devices with novel functionality [3,5]. They feature strong optical transitions promoted by excitons [6–9] and, paired with valley-selective excitation [10], manipulation [11–15] and detection [16–19] schemes, represent viable resources for opto-valleytronic applications [20–22]. While optical transitions of lowest-energy excitons in molybdenum-based MoSe₂, MoS₂ or MoTe₂ MLs is spin-allowed, the exciton ground state of ML tungsten dichalcogenides WSe₂ and WS₂ is spin-forbidden [23,24]. This striking difference stems from a reversed energetic order of momentum-dark excitons as well as their charged counterparts provide a powerful platform for spin-valley and microcavity physics in two-dimensional materials. The corresponding spectral signatures, however, are insufficient to explain the main characteristic peaks observed in the photoluminescence spectra of ML TMDs on the basis of momentum-direct excitons alone. Here, we show that the notion of momentum-indirect excitons is important for the understanding of the versatile photoluminescence features. Taking into account phonon-assisted radiative recombination pathways for electrons and holes from dissimilar valleys, we interpret unidentified peaks in the emission spectra as acoustic and optical phonon sidebands of momentum-dark excitons. Our approach will facilitate the interpretation of optical, valley and spin phenomena in TMDs arising from bright and dark exciton manifolds.

While early photoluminescence (PL) spectroscopy studies have established elementary signatures of bright excitons in neutral [6,8] and charged TMD MLs [36–38], the emission from spin-forbidden excitons has been identified only recently [23,26–30]. The observations of lowest-lying momentum-bright yet spin-forbidden states in tungsten dichalcogenide MLs explain some of the differences between the rich structure in the PL spectra of tungsten-based MLs and the rather simple one- or two-peak PL of ML molybdenum dichalcogenides [39]. Some of the main PL peaks that can be more intense than the bright exciton, however, have escaped unambiguous assignment and are thus commonly attributed to defect-localized excitons. Moreover, unequivocal deconvolution of individual PL contributions from neutral and charged excitons has been compromised by the lack of control over the charge doping level in most samples and impeded further by the conspiracy of similar energy scales of optical phonons [40,41] and trion binding energies [19,37,42]. Here, we propose a unifying explanation for unidentified PL features in the spectra of TMD MLs by expanding the realm of momentum-direct excitons with their momentum-indirect counterparts. This analysis benefits from the greatly improved optical quality of TMD MLs encapsulated in hBN [29,39,43–45] in charge tunable structures.

Signatures of direct and indirect excitons in the emission spectra. First we describe our approach to decompose the optical spectra of ML TMDs involving momentum-dark exciton contributions. Subsequently, we demonstrate how this simple approach can be applied to reproduce the most prominent spectral features observed in PL. The basic understanding of the optical phenomena in TMD MLs derives from the single-particle band structure shown schematically in Fig. 1. The conduction band (CB) and valence band (VB) feature spin-polarized sub-bands with energy splittings ∆SO at K and K’ points of the first Brillouin zone. The VB spin-orbit splitting of a few hundred of meV as estimated from first-principles calculations [31,33,53] and determined experimentally [46,47] is contrasted by a much smaller CB splitting ∆SO on the order of a few tens of meV [31,33,35]. In addition to the K and K’ valleys, the CB of TMD MLs exhibits local minima at six non-equivalent Q-pockets related pairwise by time-reversal symmetry [48,49]. Depending on the specific material and the details of calculations, the Q-valley band-edges can be as far as ∆KQ ≈ 160 meV above the CB minimum as in MoSe₂, or in the range of ∼ 0–80 meV in tungsten-based MLs [35,40,50].
With this single-picture view in mind we interpret the rich PL spectra of TMD MLs by including indirect transitions associated with electrons and holes in dissimilar valleys \[51\]–\[53\], as initially proposed by Dery and Song for combinations of electrons in K with empty VB states in K’ in tungsten-based MLs \[51\]. To this end we construct excitons by forming an empty state in the upper valence sub-band at the K valley and the Coulomb-correlated electron at the K’ or, alternatively, at one of the Q-points. Note that the hole state is formally associated with the time-reversal of the unoccupied state in the valence band \[9\]. Neglecting the upper sub-band at the Q-points due to sizable spin-orbit splittings of the order of 100 meV \[25\] and omitting electron-hole exchange for simplicity (energy scale of a few meV), we obtain the exciton spectrum shown schematically in Fig. 1b. Two zero-momentum configurations with both electron and hole at K correspond to the well studied spin-allowed and spin-forbidden exciton (X and D) \[26,28,30,53,56\].

In addition to direct excitons, also excitons with finite center-of-mass momenta can be constructed from electrons in valleys other than the unoccupied state in K. They do not recombine directly via photon emission but require the assistance of acoustic or optical phonons. We label these momentum-dark excitons with capital letters denoting the electron valley with the subscript l (u) for spin-like (spin-unlike) configurations of the electron and hole spins (in electron spin notation). By neglecting electron-hole exchange we obtain two pairs of degenerate states with electrons and holes in K (D and K₁, as well as X and K₃'), and degenerate spin-like and spin-unlike Q-excitons with electrons in six inequivalent Q-pockets. The energetic ordering in Fig. 1c corresponds to tungsten-based MLs. In the presence of time-reversal symmetry, all states have their counterparts with the unoccupied state at the K’-valley and reversed spin orientation.

As the manifold of momentum-dark excitons, shown encaged in Fig. 1c, has no dipolar radiative pathways due to momentum conservation constraints, the states do not appear directly in PL or reflection spectroscopy. However, in analogy to indirect band-gap bulk semiconductors such as silicon \[57\] or hexagonal boron nitride (hBN) \[58\], finite-momentum excitons can decay radiatively via simultaneous emission of phonons. Such decay channels, indicated schematically in Fig. 1c by colored arrows and enabled by acoustic and optical phonons as well as higher order combinations of multi-phonon processes, will give rise to phonon replicas of momentum-dark excitons in the PL emission. Once the energy positions of all states are determined from spectral decomposition, the splittings \(\Delta_{XD}\) and \(\Delta_{XQ}\) are obtained as indicated in Fig. 1c.

Analysis on monolayer MoSe₂ emission. First, we apply our analysis to ML MoSe₂ encapsulated in hBN with active doping control. The cryogenic PL spectrum shown in Fig. 2 features two bright PL peaks, commonly attributed to the emission from neutral and charged excitons. In high signal-to-noise differential reflectivity measurements in our gated structure, however, no trion signature was detected in addition to the solitary resonance of the neutral exciton (see Supplementary Information) in contrast to doped samples \[59\]. We
therefore argue that the intense PL peak ~ 30 meV below X could also be interpreted as an optical phonon sideband of the momentum-dark exciton state $K_u'$ that we set resonant with the bright exciton by neglecting electron-hole exchange. The respective acoustic sidebands would then contribute weak yet finite PL in between the two peaks.

To obtain a model fit of the neutral ML MoSe$_2$ spectrum in the framework of this analysis shown by the red solid line in Fig. 2 we modeled the ZPLs of resonant momentum-bright and momentum-dark states X and $K_u'$ by homogeneously broadened Lorentzians with the same full-width at half-maximum linewidth $\gamma_X$. Moreover, we restricted the phonon replicas of $K_u'$ to first-order processes. By taking the corresponding phonon modes calculated in Ref. [40] (recapitulated in Table S1 of the Supplementary Information for convenience) with explicit phonon energies of 16.6, and 19.9 meV for the TA and LA acoustic phonons, and 35.5, 37.4, and 25.6 meV for TO($E'$), LO($E'$) and $A_1$ optical phonons available for the scattering of the electron from the $K'$ into the K-valley, we allowed the fitting procedure to determine the best-fit energy position indicated by the dashed line and linewidth $\gamma_X = 2.3$ meV for the ZPL of X and thus of $K_u'$.

Remarkably, the correspondence between the spectrum and the model fit in Fig. 2 was obtained with vanishing contributions from TO and LO phonons, and thus the lower-energy peak can be ascribed entirely to the $A_1$ optical sideband of $K'$. Our analysis of ML MoSe$_2$ PL from a more disordered sample (see Supplementary Information) indicates that both TO and LO phonons as well as higher-order phonon processes can be activated in the presence of disorder [40]. For phonon replicas to be as intense in emission as the bright exciton emission in the PL of neutral ML MoSe$_2$, long-lived population of dark states without efficient decay channels must be present. Such population can be provided by the reservoir of momentum-dark $K'$ excitons, or by momentum-dark $Q$ states if the value of 28 meV [40] instead of the much higher prediction of 137 meV [55] is anticipated for the splitting $\Delta_{KQ}$ in ML MoSe$_2$.

Analysis of monolayer WSe$_2$ emission. The analysis of the simple MoSe$_2$ emission has served as an illustration of the possible involvement of phonon-assisted recombination of momentum-dark excitons. In the next step we apply our decomposition analysis to ML WSe$_2$ with a rich spectrum of unidentified peaks [19] as in Fig. 3 recorded on ML WSe$_2$ encapsulated in hBN and tuned to the point of charge neutrality [61]. It features narrow spectral lines characteristic of high-quality MLs with PL close to the homogeneous limit [60, 39, 44] and we assume a negligible contribution from trions, again based on the absence of a trion resonance in high signal-to-noise reflectivity. As discussed previously, the PL signatures of ML WSe$_2$ in Fig. 3 differ significantly from the PL of ML MoSe$_2$ in Fig. 2 because of the reversed ordering of spin-polarized sub-bands in tungsten and molybdenum based dichalcogenides. To model the PL spectrum of WSe$_2$, one has to include the spin-forbidden exciton state D red-shifted...
by 40 meV from the ZPL of the bright state X in this specific sample [30, 61]. In order to obtain the best model fit shown as the red solid line in Fig. 3, we allowed not only the phonon energies to vary around the values given for ML WSe$_2$ in Ref. [40] but also the energies and linewidths of the Lorentzian ZPLs of D, K$'$$'_l$, K$'$$'_u$, and X states. Assuming similar timescales for phonon-assisted decay and transform limited broadening of momentum-dark states, a joint linewidth $\gamma_M$ was used for both states. The best-fit model spectrum of Fig. 3a with up to third-order processes was obtained with $\gamma_X = 5.0$ meV and comparable linewidths of $\sim 2.5$ meV for both spin-forbidden and momentum-dark states at the respective energy positions of the ZPLs indicated by the dashed lines. The overall correspondence between the measured spectrum and the model is again compelling. It interprets the bright-most peak in between the bright and dark exciton ZPLs as the model and the model is again compelling. It interprets the bright-most peak in between the bright and dark exciton ZPLs as the model.

**Analysis of monolayer WS$_2$ emission.** The analogous spectral decomposition was also carried out for ML WS$_2$ sandwiched in hBN without means of field-effect charge control. The best fit to the PL spectrum of Fig. 3b was obtained according to the refined fitting procedure used for ML WSe$_2$ in Fig. 3a with a fixed bright-dark splitting of 55 meV derived from experiment [30] and similar values for the linewidths of momentum-bound and dark excitons in the range of 4–5 meV. It is worth pointing out the main similarities and differences in the PL spectra for the two tungsten-based MLs. For the WS$_2$ spectrum, only second-order processes were required since the absolute energies are larger as compared to WSe$_2$ [40]. Moreover, the phonon modes exhibit larger splittings (see Supplementary Information, Table S1). The LA-TA splitting at the K point of WS$_2$, for example, exceeds the value in WSe$_2$ by $\sim 4$ meV. More significantly, the optical phonon energies differ by $\sim 15$ meV and up to $\sim 20$ meV at the $\Gamma$ and K points, respectively.

Among the similar PL signatures is the weak peak below D and the intense peak between X and D with fine structure due to the specific optical phonon spectrum of WS$_2$. Akin to WSe$_2$, the former and the latter are assigned to acoustic and optical replicas of momentum-dark states K$'$$'_l$ and K$'$$'_u$, respectively. Surprisingly, best fit suggests an exchange splitting of $\Delta(K'_{l}-X) = 11.4$ meV in contrast to 2.7 meV for WSe$_2$ in Fig. 3a. The fit to WS$_2$ PL requires a significant upshift of the state K$'$$'_l$ in order to optimally accommodate the optical phonon sidebands into the intense and complexly structured PL peak between X and D. This could be an artefact of the non-quantified contribution from trions in this sample, or indicate that the set of involved momentum-dark excitons could be expanded by the Q-exciton manifold as will be discussed in the next section.

**Role of Q-momentum excitons in monolayer WSe$_2$ and WS$_2$ emission.** For WSe$_2$ MLs the Q-momentum excitons can play an important role, since the Q-valley is in close proximity to the lowest CB minimum at K according to single-particle calculations [35, 40, 50]. Excitonic corrections have been predicted to reduce the energy level of Q-excitons well below the energy of the lowest spin-forbidden state D both in WSe$_2$ and WS$_2$ MLs [54, 55, 62]. This, however, is in contradiction to the analysis developed so far that explains the lowest-energy PL peak in terms of acoustic replicas of the momentum-dark reservoir K$'$$'_l$. Any deeper momentum-dark state should exhibit large population with pronounced PL phonon sidebands as in the case of bilayer WSe$_2$ with momentum-indirect band gap [63]. The only two remaining scenarios for the energy position of the Q-exciton level is in between D and X or above X (apart from placing it in resonance with K$'$$'_l$ or K$'$$'_u$ with trivial implications).

The analysis of best fits shown in Fig. 4 suggests that the first scenario is better suited to model the spectrum of ML WSe$_2$. Before proceeding, we note that second- and higher-order phonon-assisted processes were restricted to combina-
tions of multiple phonons with total phonon momentum of $Q$ or $K$ depending on the respective initial valley of the electron (see Supplementary Information for details). For example, the scattering of the electron from the $Q$-valley into the $K$-valley and subsequent emission of an optical phonon would involve an LA or TA phonon at the $Q$-point and a zero-momentum optical phonon at the $K$-point of the first Brillouin zone. With this approach to the best-fit, the energy position of the $Q_1$ state in Fig. [3] is identified at $\Delta_{QQ} \approx 19$ meV below the bright exciton with marginal variations in other fit parameters as compared to Fig. [3]. The corresponding energy level hierarchy would assign the bright-most PL peak now to acoustic phonon replicas of the $Q$-exciton manifold with contributions to the lowest-energy peak via optical sidebands.

In the case of ML WS$_2$ in Fig. [5], on the other hand, the second scenario performed better. It adds an explanation to the first weak PL peak below $X$ as an acoustic sideband of $Q_1$ with its respective optical sidebands merging into the most intense PL peak between $X$ and $D$. Moreover, this configuration reduced the conspicuously large exchange splitting between $X$ and $K'_0$ found in the fit of Fig. [3], and is at least qualitatively in line with theoretical calculations that predict a small separation between $Q$- and $K$-excitons in WS$_2$ rather than in WSe$_2$ MLs [62].

Overall, within the suggested approach we find good qualitative and satisfactory quantitative description of the spectra. Its quantitative validity is limited by the assumption of identical linewidths for all momentum-dark excitons which is not necessarily the case since different phonon-assisted pathways determine the effective lifetimes of momentum-dark excitons. Moreover, as opposed to the inclusion of both in-plane and out-of-plane optical phonon modes, we discarded the out-of-plane acoustic phonon mode $Z_A$. The experimental precision limited by the spectral broadening even in best samples [30, 39, 44] currently provides an upper bound of a few meV on these effects.

Even with the current uncertainty in the values of exchange interaction and the energetic splittings between the valleys, our model highlights the importance of the role played by momentum-dark excitons in elementary optical response of ML TMDs. The conclusions are fully in line with the interpretation of cryogenic spectra from bilayer WSe$_2$ [63] and MoSe$_2$-WSe$_2$ heterobilayers [54]. Based on our findings, further experimental work and more precise theoretical calculations of the single-particle band structure and phonon modes will finally consolidate a quantitative understanding of excitons in TMD MLs. Placed into a broader perspective of prevalent puzzles in TMD spectroscopy [55], our analysis provides sufficient guidelines for new interpretations.

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SUPPLEMENTARY INFORMATION

Experimental setup

Cryogenic confocal PL spectroscopy studies were performed at 3.1 K in a closed-cycle cryostat (attocube systems, attoDRY1000) or a helium dewar at 4.2 K. The samples were positioned with piezo-steppers and scanners (attocube systems, ANP101 series and ANSxy100/hr) into the diffraction limited spot of a low-temperature apochromatic objective with a numerical aperture of 0.82 (attocube systems, LTAPO/VISIR/0.82) and a spot size of 0.6 µm. A He-Ne laser at 632 nm, a continuous wave green laser at 532 nm or a supercontinuum laser (NKT Photonics, SuperK EXW-12) operated at 532 nm with a spectral width of 6 nm were used to excite the PL. A monochromator (PI, Acton SP-2558) equipped with a nitrogen-cooled silicon CCD (PI, Spec10:100BR/LN) was used to detect PL with a spectral resolution of 0.4 meV.

Gated samples

We have fabricated van der Waals heterostructures by mechanical exfoliation from commercially available bulk crystals and very high quality hBN crystals [66]. A first layer of hBN was mechanically exfoliated and transferred onto a SiO₂ (90 nm)/Si substrate using PDMS stamping [67]. The deposition of the subsequent ML and the second hBN capping layer was obtained by repeating this procedure to complete the full stack. We also transferred a thin graphite flake between the top surface of the ML and a Au pre-patterned electrode. Carrier concentration was varied by applying a bias between this electrode and the p-doped Si substrate (back gate).

Photoluminescence and differential reflectivity

The charge doping level of ML MoSe₂ and WSe₂ was controlled with field-effect devices described above and monitored with differential reflectivity (DR). The PL and reflectivity spectra of ML MoSe₂ at the charge neutrality point are shown in Fig. S1a and b, respectively as in [61]. The reflectivity spectrum shows no signature of trion absorption. The respective PL and DR spectra of ML WSe₂ at the charge neutrality point are shown in Fig. S2a and b, respectively. As for ML MoSe₂, the DR spectrum shows no signature of trion absorption.

We also applied our analysis to ML MoSe₂ encapsulated in hBN without active doping control. As in Fig. 2 of the main text, the PL spectrum in Fig. S3 features two bright PL peaks. In addition, the PL exhibits an extended red wing with some structure commonly ascribed to localized excitons in potentials of unintentional disorder. Here, we assume that the intensive PL peak ~ 30 meV below X is not related to trions but is instead composed of optical phonon sidebands of the momentum-dark exciton state K₁' resonant with the bright exciton in the absence of electron-hole exchange.

Figure S1: a, Photoluminescence spectrum of monolayer MoSe₂ adopted from Fig. 2 of the main text. b, Corresponding reflectivity at V_g = +10 V. Note the absence of trion-related features.

Figure S2: a, Photoluminescence spectrum of monolayer WSe₂ adopted from Fig. 3a of the main text. b, Corresponding differential reflectivity. Note the absence of trion-related features.
Figure S3: Spectral decomposition of cryogenic photoluminescence from monolayer MoSe$_2$ without active control of charge doping. a. Basic model fit (red solid line) with first-order phonon replicas of momentum-dark $K'_u$ excitons resonant with the bright exciton state X in the absence of electron-hole exchange. The best-fit energy position indicated by the dashed line was obtained with $\gamma_{X}$ as fit parameter and $\gamma_{M}$ set identical to $\gamma_{X}$. The green and orange arrows indicate phonon sidebands of momentum-dark excitons associated with acoustic and optical phonons with respective energies taken from Ref. [40]. b. Refined model fit (red solid line) with variable energy positions and linewidths of X and $K'_u$ states and up to fourth order phonon replicas with variable phonon energies bound by $\pm 2 \text{meV}$ around the values of Ref. [40]. Free (fixed) fit parameters are given in the legends in black (grey).

The model fit to the ML MoSe$_2$ spectrum of Fig. S3a was obtained with ZPLs of momentum-bright and momentum-dark excitons modeled by homogeneously broadened Lorentzians at the same energy and with the same full-width at half-maximum linewidth $\gamma_{X}$. Analogous to Fig. 2 of the main text, first-order scattering processes by acoustic and optical phonons with energies from Ref. [40] yield the two peaks as the main PL features with $\gamma_{X} = 5.9 \text{meV}$ and best-fit energy positions indicated by the dashed lines.

To improve the fit up to the striking correspondence with the spectrum in Fig. S3b, we allowed the phonon energies to vary by $\pm 2 \text{meV}$ around their theoretical values. Such small variation of phonon energies account for sample-to-sample variations in the dielectric environment or strain and are well within the range of quantitative observations with Raman spectroscopy [68]. Moreover, we included phonon processes of up to fourth order (the cut-off to the model spectrum around 1.48 eV is because processes beyond fourth order were truncated), and allowed the energy positions and the linewidths to vary for both X and $K'_u$ states. Remarkably, all intricate features of the PL spectrum are well reproduced by the model fit without significant changes to the ZPL energies and linewidths, and with higher-order phonon processes improving the correspondence between the fit and the intricate spectral details of the extended red tail of the PL spectrum. The bright peak below X is interpreted as composed of optical phonon sidebands of the momentum-dark state $K'_u$ that also gives rise to broad lower-energy PL peaks via its higher-order phonon replicas. In contrast, the emission from disorder-localized excitons [69], characterized by narrow spectral features in Fig. S3b, is not captured by the present model.

| Model | MoSe$_2$ | WS$_2$ | WSe$_2$ |
|-------|----------|--------|---------|
| Mode  | $\Gamma$ | $K$ | $Q$ | $\Gamma$ | $K$ | $Q$ | $\Gamma$ | $K$ | $Q$ |
| TA    | 0  | 16.6 | 13.3 | 0  | 17.4 | 15.9 | 0  | 15.6 | 11.6 |
| LA    | 0  | 19.9 | 16.9 | 0  | 23.6 | 19.5 | 0  | 18.0 | 14.3 |
| TO(E')| 36.1| 35.5 | 36.4 | 44.4| 43.8 | 45.3 | 30.5| 26.7 | 27.3 |
| LO(E')| 36.6| 37.4 | 37.5 | 44.2| 43.2 | 42.3 | 30.8| 31.5 | 32.5 |
| $A_{1}$| 30.3| 25.6 | 27.1 | 51.8| 48.0 | 50.0 | 30.8| 31.0 | 30.4 |

TABLE S1: Phonon mode energies at the high-symmetry points of the first Brillouin zone for monolayer MoSe$_2$, WS$_2$, and WSe$_2$ used in the model fits. Higher order scattering processes with phonon energies equal to the energy of LO(E') within 1 meV (listed in the table in grey) were discarded from our analysis for simplicity. All energies are given in meV and reproduced from Ref. [40].

Group theory analysis

The symmetry of the Q-point is $C_s$ with only two symmetry operations: identity and horizontal plane reflection. There are two irreducible (vector) representations of this group, namely $A'$ (invariant) and $A''$ (z-coordinate, i.e. normal to the reflection plane). The intersection of the two symmetry groups $C_s$ (Q-point) and $C_{3h}$ (K-point) is $C_s$. The conduction band both at the Q- and K-points corresponds to the $A'$ representation and, hence, transitions are possible via phonons with the same symmetry $A'$ (these modes are symmetric under $z \rightarrow -z$). All phonon modes in question indeed correspond to this representation: acoustic $E'$ at the $\Gamma$-point corresponds to $A'$ at the Q-point, optical $E'$ at the $\Gamma$-point corresponds to $A'$ at the Q-point, and optical $A_{1}$ at the $\Gamma$-point corresponds to $A'$ at the Q-point. Combinations of these phonons are also allowed (provided that momentum conservation is fulfilled). With account for spin-orbit interaction all other phonons (asymmetric for $z \rightarrow -z$) are also active in $K$ to $Q$ transitions. In order to account for spin-orbit effects we need to also consider the spinor representations $\Gamma_{4}$ (spin-up, $\uparrow$) and $\Gamma_{4}$ (spin-down, $\downarrow$): $\Gamma_{4} = A' \uparrow = A'' \downarrow$, $\Gamma_{4} = A'' \uparrow = A' \downarrow$. Thus, spin-up and spin-down states can be mixed with Bloch functions of different orbital symmetry and odd in $z \rightarrow -z$ phonon modes can enable spin-flip transfer between K and Q valleys.

Transitions between the K- and K'-points can be consid-
ered analogously. To that end, we note that both elements of the wavevector group $C_{3h}$ leave the K and $K'$ valleys intact. The orbital Bloch functions of the conduction bands belong to the $E'(1)$ ($\sim x + iy$) and $E'(2)$ ($\sim x - iy$) irreducible representations of the $C_{3h}$ point group. The transitions between the conduction band states are enabled by phonon modes with $E'$ symmetry. In contrast, the orbital Bloch functions of the valence band transform according to the $A'$ (invariant) irreducible representation. Thus, hole intervalley scattering is provided by the fully symmetric $A'$ modes.

In the following we briefly address the activation of the spin-unlike $K'_u$ excitons. In accordance with the symmetry analysis these states form basis irreducible representations $E''(1)$ and $E''(2)$ of the $C_{3h}$ point symmetry group transforming as $(x \pm iy)z$. Formally, these states can be transferred to the optically active ones by phonons with $A''$ symmetry (transforming like $z$) or by $E''$ phonons. Moreover, the interaction with $E'$ phonons converts these excitons into $z$-polarized states. If the mirror symmetry is distorted, the $z \to -z$ operation (together with $S_3$ mirror rotation) should be excluded from the $C_{3h}$ point symmetry group and the representations $E''$ (odd in $z \to -z$) and $E'$ (even at $z \to -z$) cannot be formally distinguished. Hence, in experiments involving different dielectric environments at the top and the bottom of TMD MLs, $A'$ and $E''$ phonons may enable activation of spin-unlike $K'_u$ excitons.