LETTER

Direct measurement of biexcitons in monolayer WS\textsubscript{2}

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Abstract

The optical properties of atomically thin transition metal dichalcogenides are dominated by Coulomb bound quasi-particles, such as excitons, trions, and biexcitons. Due to the number and density of possible states, attributing different spectral peaks to the specific origin can be difficult. In particular, there has been much conjecture around the presence, binding energy and/or nature of biexcitons in these materials. In this work, we remove any ambiguity in identifying and separating the optically excited biexciton in monolayer WS\textsubscript{2} using two-quantum multidimensional coherent spectroscopy (2Q-MDSC), a technique that directly and selectively probes doubly-excited states, such as biexcitons. The energy difference between the unbound two-exciton state and the biexciton is the fundamental definition of biexciton binding energy and is measured to be 26 \pm 2 \text{ meV}. Furthermore, resolving the biexciton peaks in 2Q-MDSC allows us to identify that the biexciton observed here is composed of two bright excitons in opposite valleys.

1. Introduction

Coulomb correlations between photoexcited electrons and holes in atomically thin transition metal dichalcogenides (TMDCs) mediate a variety of bound electronic excitations, such as excitons \cite{1–3; 4, 5}, trions \cite{4, 5}, and biexcitons \cite{1, 4, 6}. The binding energy of these quasi-particles is greatly enhanced over those in 3D material systems because the screening of the Coulomb interaction is greatly reduced \cite{7}. The nature and binding energy of biexcitons in these materials has, however, been a topic of debate, with reported binding energies ranging from more than 60 \text{ meV} \cite{8–11} to as small as 20 \text{ meV} \cite{6, 12–19}, while others have observed that optically-induced biexciton formation is not evident in time resolved measurements \cite{20}.

Many of the early experimental observations of biexcitons in monolayer TMDCs relied on photoluminescence (PL) spectroscopy to identify peaks below the exciton energy, arising from radiative relaxation from the biexciton to the exciton state \cite{2, 4, 6, 8–12, 15, 16}. These have been combined with intensity dependent measurements to show the quadratic power dependence expected for biexcitons. There are, however, many different peaks at similar energies, including those associated with trions and dark excitons, which should grow linearly with pump fluence, as well as charged biexcitons \cite{12, 15}, defect-bound excitons \cite{21}, phonon sidebands \cite{22} and electron plasma excitations \cite{23}, which, like biexcitons, grow super-linearly with pump fluence. The ability to resolve all these peaks can be further complicated by static disorder, which leads to inhomogeneous broadening of the spectral peaks. However, recent efforts in encapsulating the monolayers in hexagonal boron nitride (h-BN) has mitigated these effects and led to narrow, resolvable peaks, which has aided the identification of biexcitons \cite{12, 24}.

In tungsten based semiconducting TMDCs, such as WS\textsubscript{2} and WSe\textsubscript{2}, the situation is further complicated by the band ordering. Specifically, the spin-orbit splitting of the conduction band results in the lowest energy exciton being a dark, spin-forbidden exciton, with the bright exciton transition 10–30 \text{ meV} higher in energy \cite{25}. It then becomes important to consider...
Multi-dimensional coherent spectroscopy (MDCS), which reveals correlations of absorption and emission energy, provides a clearer picture, and has been used to identify peaks corresponding to transitions from exciton to biexciton and charged biexciton states in monolayer MoSe$_2$ [15]. These revealed a biexciton binding energy of 20 meV, and showed the charged biexciton signature $\sim$35 meV below the exciton. In contrast, MDCS measurements on monolayer WS$_2$ saw no signatures of biexcitons [29], while in MoS$_2$ monolayers the interpretation of MDCS measurements led to conclusions that the photoinduced absorption observed is due to band gap renormalization and that there is no direct excitation of the biexciton [20].

Here, we remove any ambiguity by using two-quantum MDCS (2Q-MDCS), which selectively excites and probes doubly excited states such as biexcitons, eliminating any contributions from singly excited states, including band-gap renormalization. 2Q-MDCS has been used previously to identify and quantify the properties of biexcitons in semiconductor quantum-wells [30–32]. In this type of experiment, the energy of the biexciton (XX$^b$) and the unbound two-exciton state (XX) can be measured directly, as indicated in figure 1(e). The energy difference between these states is the fundamental definition of the biexciton binding energy ($E_b$). In contrast, all the other approaches mentioned above obtain $E_b$ indirectly, by comparing the energy of the XX$^b$ $\leftrightarrow$ X transition to that of the X $\leftrightarrow$ g transition [31]. In the 2Q-MDCS measurements reported here we identify the two-photon-optically-excited biexciton in monolayer WS$_2$ as consisting of two bright excitons from different valleys, with a binding energy of 26 $\pm$ 2 meV.

2. Experimental methods

Third-order MDCS is based on a transient four-wave mixing (FWM) experiment with the phase and amplitude of the signal measured as a function of the emission energy and the delays between the three excitation pulses [32, 33]. We use a box-CARS geometry, as depicted in figure 1(a), with each of the three incident pulses on the corners of the box and labeled $k_1$, $k_2$, $k_3$. The FWM signal is emitted in background-free directions given by conservation of momentum. We measure the signal emitted in the direction given by $-k_1 + k_2 + k_3$, which is the fourth corner of the box, and which is overlapped with a fourth and much weaker beam, referred to as the local oscillator (LO). The LO interferes with the signal in the spectrometer to give a spectral interferogram, from which we can determine both the amplitude and phase of the signal. Phase stability between each of the excitation pulses and the LO is essential and is maintained passively by ensuring all beams are incident on common optics [34, 35].
Figure 1. (a) Four beam box geometry utilized in our experiments. (b) Energy level diagram of monolayer TMDCs showing pathway to unbound (XX) and bound (XX\textsuperscript{b}) two exciton states, accessible in our experiments with polarization control over individual excitation beams. (c) In our setup, the pulse \(k_1\) is scanned in time and when it arrives before the other pulses the signal generated is a 1Q rephasing signal, which correlates the energy of the coherence excited by the first pulse, \(E_1\) (often approximated as the absorption energy) with the emission energy \(E_3\), as shown schematically in (d). When \(k_1\) arrives last, the system is driven into a 2Q coherence by \(k_2\) and \(k_3\), indicated by the black arrows in (e). This 2Q coherence is reduced to a 1Q coherence upon interaction with the third pulse after some time \(t_{2Q}\) which radiates as the signal. There are two possible radiative signal pathways, (i) and (ii), which are energetically degenerate for correlated excitons (XX), but differ by the binding energy for biexcitons (XX\textsuperscript{b}). (f) Schematic of the expected 2Q spectral peaks from XX and XX\textsuperscript{b} via the different pathways (i) and (ii) indicated in (e).

The most common type of 2D MDCS spectra is referred to as a 1Q rephasing spectrum and is acquired when the \(k_1\)-pulse arrives first. Figure 1(c) shows the relevant signal pathways in these measurements: After the first pulse, the system is in a coherent superposition of states separated by the optical photon energy (a 1Q-coherence). The second pulse, \(k_2\), converts the 1Q-coherence into a population (or low energy coherence) in either the excited or ground electronic state. The third pulse then converts this into a third-order 1Q-coherence, and corresponding macroscopic polarization, which radiates the signal. The measured spectral interferogram of the signal gives the amplitude and phase of the signal as a function of the emission energy, \(E_3\). As the delay between the first two pulses, \(t_1\), is varied, the phase of the coherent superposition excited by \(k_1\) continues to evolve, which is mapped onto the phase of the signal. The spectrally resolved signal is then Fourier transformed with respect to \(t_1\) to give the 1Q rephasing 2D spectrum, which correlates the energy of the coherence excited by the first pulse, \(E_1\) (often approximated as the absorption energy) with the emission energy \(E_3\).

In the case of biexcitons, the third pulse \(k_3\) drives the system into a third-order 1Q-coherence between the exciton and biexciton states, which radiates as the signal. In 1Q rephasing 2D spectra, biexcitons therefore appear as a peak with excitation energy \(E_1\) equal to the exciton transition energy but at an emission energy \(E_3\) below the exciton energy, by an amount given by the biexciton binding energy (figure 1(d)). Because of the polarization selection rules shown in figure 1(b), and the Pauli exclusion principle, biexcitons are typically observed with cross-circularly polarized pulse sequences [8] or linearly polarized pulses, but are not observed when all pulses are co-circularly polarized. In TMDCs, this requires an exciton in each valley as has been identified previously [8–10, 12–18].

Changing the pulse ordering so that the \(k_1\) pulse arrives last enables the acquisition of 2Q-MDCS (figure 1(e)). In this case, the first pulse still generates a 1Q coherence between the ground state and the exciton state, but the second pulse drives the transition from the singly excited state to the doubly excited state, generating a coherent superposition between the ground and doubly excited state, which we refer to as a 2Q coherence. The phase evolution of this 2Q coherence over the time interval between the second and third pulses, \(t_{2Q}\), is mapped on to the signal phase, and the subsequent Fourier transform of the signal with respect to \(t_{2Q}\) gives the energy of the doubly excited state(s). This is typically plotted on the vertical axis in the associated 2Q-MDCS spectra. The third pulse reduces the 2Q coherence back to a 1Q coherence via one of the two possible pathways, which leads to the emitted signals, as depicted in figure 1(e):
the emission in (i) is from a doubly excited state to a singly excited state while in (ii) it is from the singly excited state to the ground state. In the case of a two-exciton state with no interactions between the pair of excitons these two different pathways will cancel, leading to no signal. Where there are excitonic interactions, either pairwise or through many body effects, an asymmetry between the ground to single-exciton transition compared to the single-exciton to the two-exciton transition emerges, leading to imperfect cancellation and a measurable signal \([30, 31]\).

For biexcitons, there is an obvious asymmetry in the transition energy, which also leads to peaks from the biexciton appearing at \(E_{2Q}\) energy lower than twice the exciton energy, as indicated in figure 1(f), by the peaks labeled \(XX^b\). There are two peaks at different \(E_3\) values arising from the different energies associated with the two different signal emission pathways indicated in figure 1(e). In addition to the biexciton, another peak may appear on the diagonal line corresponding to \(E_{2Q} = 2E_X\), labeled \(XX\), which originates from a correlated two-exciton state. This is an unbound two-exciton state where many-body effects introduce an asymmetry that allows peaks in the 2Q-MDCS spectra \([30, 36]\).

We performed these 1Q- and 2Q-MDCS measurements on monolayer WS\(_2\) exfoliated from a bulk WS\(_2\) crystal and transferred to a SiO\(_2\)/Si substrate, as detailed in the supporting information (SI available online at stacks.iop.org/2DM/9/021001/mmedia) along with other sample characterizations. The laser spectrum was centered near 2 eV (\(\sim 620 \text{ nm}\)) with FWHM of 26 nm (figure S1), so that it covered the exciton energy and the energy of all other exciton complexes. Fluences were kept below 2 \(\mu\text{Jcm}^{-2}\) per pulse to ensure the contributions of signals beyond the \(\chi^{(3)}\) regime are insignificant.

### 3. Results and discussion

The 1Q rephasing 2D spectra acquired using cross- and co-circularly polarized pulse sequences are shown in figures 2(a) and (b), respectively. The cross-circular spectrum is acquired by a series of excitation pulses with alternating helicity and features two peaks: a diagonal peak (a peak for which \(E_1 = E_2\)) corresponding to excitation and emission from the exciton (X), and a cross peak redshifted from the exciton emission energy which we attribute to the neutral biexciton (\(XX^b\)). In contrast, the co-circular spectrum in figure 2(b) is acquired by a series of excitation pulses with the same helicity and shows only the X peak on the diagonal. The disappearance of the biexciton peak in a co-circular polarized excitation sequence is consistent with the optical selection rules, wherein biexcitons must consist of two excitons with opposite spin. Biexcitons made up of two excitons with the same spin is forbidden due to Pauli blocking \([30, 31, 36, 37]\). From the energy difference between the \(XX^b\) and X peaks we obtain a biexciton binding energy of \(24 \pm 4 \text{ meV}\). This spectrum is qualitatively comparable to prior 1Q-MDCS measurements in MoSe\(_2\) \([15]\), however, there remains some conjecture around the origin of such peaks in the MDCS spectra of WS\(_2\), since similar peaks can arise in the case of band gap renormalization \([20]\).

The 2Q-MDCS spectra in figures 2(c) and (d) remove any ambiguity in identifying and separating the biexciton. In both cross- and co-circular 2Q spectra there is a peak on the diagonal corresponding to unbound correlated excitons (XX) at \(E_{2Q}\) equal to twice the single exciton energy (4.18 eV), and emission energy, \(E_3\), equal to the exciton energy (2.09 eV). In the case of co-circularly polarized pulses, this is the only peak and there is no biexciton peak, as expected, due to Pauli blocking.

For the cross-circularly polarized pulse sequence (figure 2(c)), biexcitonic 2Q coherences can be excited (see SI for details of the pathways), leading to two peaks at \(E_{2Q} = 4.163 \text{ eV, 26 meV below the correlated two-exciton peak. The different } E_3\text{ values for these peaks arise from the two signal pathways shown in figure 1(e). The higher energy peak at } E_3 \sim 2.09 \text{ eV, corresponds to the single exciton to the ground state transition and arises from pathway (ii) in figure 1(e). The lower energy peak comes from pathway (i) in figure 1(e) and corresponds to the biexciton to single exciton transition, with the emission energy } E_3 \text{ corresponding to the exciton energy minus the biexciton binding energy.}

The energy difference between the correlated, unbound two-exciton state (XX) and the bound biexciton state (\(XX^b\)) is the fundamental definition of biexciton binding energy. Because 2Q-MDCS directly measures the two-exciton state energies, the biexciton binding energy can be determined reliably and directly. To do this, a vertical slice through the cross-circular 2Q 2D spectrum in figure 2(c), taken at the exciton emission energy in \(E_2\), is plotted in red in figure 3(a). The slice is fit with the sum of two Gaussians (black line), with the individual Gaussians indicated by the shaded regions corresponding to the XX and \(XX^b\) peaks. From this fit, and the splitting between the two Gaussians, we extract a biexciton binding energy in monolayer WS\(_2\) of 26 ± 2 meV, where the uncertainty comes primarily from the width of the peaks. This value is consistent with theory calculations \([14]\) which determine a binding energy of \(23.9 \pm 0.5 \text{ meV for WS}_2\), larger than for the other semiconducting TMDC monolayers.

In order to directly compare these measurements with PL, transient absorption, and 1Q-MDCS \([15]\), where the biexciton binding energy is determined as the energy difference between the \(XX^b \leftrightarrow X\) transition and the \(X \leftrightarrow g\) transition, we consider the \(E_3\) energy difference between \(XX^b_i\) and \(XX^b_j\). To quantify these energies, we take a horizontal slice through the two \(XX^b\) peaks in figure 2(c) at \(E_{2Q} = 4.163 \text{ eV (red line
Figure 2. (a) 1Q cross-circular amplitude spectrum showing a bright exciton peak (X) and the biexciton (XX<sup>b</sup>) redshifted in emission energy (E<sub>3</sub>) by the biexciton binding energy. (b) The 1Q co-circular amplitude spectrum features an exciton peak but lacks the biexciton peak because of the optical selection rules associated with the bandstructure of monolayer WS<sub>2</sub>. (c) 2Q cross-circular amplitude spectrum shows a correlated exciton (XX) peak at twice the exciton energy in E<sub>2Q</sub> and two dominant biexciton (XX<sup>b</sup>) peaks below XX by the biexciton binding energy. The two biexciton peaks are separated by the biexciton binding energy in E<sub>3</sub> and arise due to the two possible interactions with the third pulse as depicted in figure 1(e). (d) 2Q co-circular amplitude spectrum lacks the biexciton peak, consistent with the optical selection rules of monolayer TMDCs. Contours are plotted at 5% intervals.

in figure 3(b)). Three Gaussians are required to fit this slice, with peaks at 2.067, 2.077, and 2.091 eV. Taking the highest energy peak as arising from the X → g emission (XX<sup>bb</sup> (ii)) and the lowest energy peak as the XX<sup>b</sup> → X emission (XX<sup>bb</sup> (i)), gives a biexciton binding energy of 24 ± 4 meV. This is consistent with the binding energy obtained from the E<sub>2Q</sub> energies, and somewhat higher than values measured in transient absorption [6] and PL [12] for WSe<sub>2</sub> and 1Q-MDCS for MoSe<sub>2</sub> [15], which is also consistent with theory predictions [14]. Obtaining the biexciton binding energy in this manner can, however, give inaccurate values in some circumstances [31]. This arises largely because the XX<sup>b</sup> ↔ X transition depends on the overlap of the biexciton and exciton wavefunctions which can weight subsets of the biexciton and exciton states that may not reflect the precise energy of either relative to the ground state [31]. This weighting of different components may also explain the additional peak between the exciton and biexciton emission peaks in figure 3(b). This additional peak is ∼9 meV higher in energy than the XX<sup>bb</sup> (i) peak,
which is consistent with the splitting observed in the biexciton fine structure in WSe$_2$ [6]. In principle, signatures of the biexciton fine structure should also be separated in E$_{2Q}$, however, the spectral broadening of the peaks along the E$_{2Q}$ axis prevents us from being able to resolve whether there are any other distinct peaks. In these measurements the broadening arises from a combination of inhomogeneous broadening and excitonic interactions [38]. Future experiments with WS$_2$ monolayers encapsulated in h-BN may reduce these line widths and better resolve the fine-structure of the biexciton.

In addition to providing a more reliable means to confirm the direct excitation of biexcitons and quantify the biexciton binding energy, resolving the XX\textsuperscript{b} peaks in 2Q-MDCS allows us to identify the nature of the biexciton. The biexciton observed here is composed of two bright excitons from opposite valleys: a bright-bright intervalley biexciton. If bright-dark biexcitons were the dominant exciton complex then we would expect to observe XX\textsuperscript{b} signals at E$_{2Q}$ values given by twice the bright exciton energy minus the conduction band splitting (∼26–30 meV [39, 40]) minus the biexciton binding energy (∼24–26 meV); which would place it more than 50 meV below the XX peak. Despite the spectral range of our measurements extending to these lower energies, no such peak was observed. Bright-dark biexcitons have been indicated in PL experiments which measure the time integrated response of the sample [12]. At the longer timescales probed in PL, the dark exciton makes up the bulk of the excitonic population due to its favorable energy relative to the bright exciton. In contrast, MDCS measurements only directly excite the bright excitons and at the fs timescales probed, minimal relaxation to the dark exciton is expected. Furthermore, the relaxation pathways available are expected to include incoherent processes, so bright-dark biexcitons, even if they are present, are not expected to contribute to these coherent measurements except perhaps as an additional decoherence channel.

4. Conclusion

Using 2Q-MDCS we have directly observed biexcitons in monolayer WS$_2$ by spectrally separating them from the correlated unbound two-exciton state. The results presented here extend upon previous MDCS measurements of monolayer TMDCs and supports attributing signals below the exciton energy to biexciton formation instead of bandgap renormalization for pulse fluences below 2 µJ cm$^{-2}$. In addition, we experimentally resolve the biexciton binding energy in monolayer WS$_2$, (i.e. the energy difference between correlated (XX) and bound (XX\textsuperscript{b}) two-exciton states) to be 26 ± 2 meV from fits to slices of our 2Q spectrum. This value is below the intrinsic conduction band splitting in monolayer WS$_2$, confirming that the biexcitons observed here, on fs timescales, are bright-bright intervalley biexcitons.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Mak K F et al 2010 Atomically thin MoS$_2$: a new direct-gap semiconductor Phys. Rev. Lett. 105 136805
[2] Zhu B, Chen X and Cui X 2015 Exciton binding energy of monolayer WS$_2$ Sci. Rep. 5 9218
[3] Kolesnichenko P V et al 2020 Disentangling the effects of doping, strain and disorder in monolayer WS$_2$ by optical spectroscopy 2D Mater. 7 025008
[4] Plechinger G et al 2016 Trion fine structure and coupled spin–valley dynamics in monolayer tungsten disulfide Nat. Commun. 7 12715
[5] Glazov M 2020 Optical properties of charged excitons in two-dimensional semiconductors J. Chem. Phys. 153 034703
[6] Steinhoff A et al 2018 Biexciton fine structure in monolayer transition metal dichalcogenides Nat. Phys. 14 1199–204
[7] Chernikov A et al 2014 Exciton binding energy and nonhydrogenic Rydberg series in monolayer WS$_2$ Phys. Rev. Lett. 113 076802
[8] Sie E J et al 2015 Intervaly bieexcitons and many-body effects in monolayer MoS$_2$ Phys. Rev. B 92 125417
[9] Plechinger G et al 2015 Identification of excitons, trions and bieexcitons in single-layer WS$_2$ Phys. Status Solidi 9 457–61
[10] You Y et al 2015 Observation of bieexcitons in monolayer WSe$_2$ Nat. Phys. 11 477–81
[11] Shang J et al 2015 Observation of excitonic fine structure in a 2D transition-metal dichalcogenide semiconductor ACS Nano 9 647–55
[12] Chen S-Y et al 2018 Coulomb–bound four-and five-particle intervalley states in an atomically-thin semiconductor Nat. Commun. 9 3717
[13] Zhang D K, Kidd D W and Varga K 2015 Excited bieexcitons in transition metal dichalcogenides Nano Lett. 15 7002–5
[14] Kylänpää I and Komsa H–P 2015 Binding energies of exciton complexes in transition metal dichalcogenide monolayers and effect of dielectric environment Phys. Rev. B 92 205418
[15] Hao K et al 2017 Neutral and charged inter-valley bieexcitons in monolayer MoSe$_2$ Nat. Commun. 8 15552
[16] Nagler P et al 2018 Zeeman splitting and inverted polarization of bieexciton emission in monolayer WS$_2$ Phys. Rev. Lett. 121 057402
[17] Li Z et al 2018 Revealing the bieexciton and trion-exciton complexes in BN encapsulated WSe$_2$ Nat. Commun. 9 3719
[18] Ye Z et al 2018 Efficient generation of neutral and charged bieexcitons in encapsulated WSe$_2$ monolayers Nat. Commun. 9 3718
[19] Paur M et al 2019 Electroluminescence from multi-particle exciton complexes in transition metal dichalcogenide semiconductors Nat. Commun. 10 1709
[20] Wood R E et al 2020 Evidence for the dominance of carrier-induced band gap renormalization over bieexciton formation in cryogenic ultrafast experiments on MoS$_2$ monolayers J. Phys. Chem. Lett. 11 2658–66
[21] Huang J, Hoang T B and Mikkelsen M H 2016 Probing the origin of excitonic states in monolayer WSe$_2$ Sci. Rep. 6 22414
[22] Christiansen D et al 2017 Phonon sidebands in monolayer transition metal dichalcogenides Phys. Rev. Lett. 119 187402
[23] Dery H 2016 Theory of intervalley Coulomb interactions in monolayer transition metal dichalcogenides Phys. Rev. B 94 075421
[24] Vaňková D et al 2018 Singlet and triplet trions in WS$_2$ monolayer encapsulated in hexagonal boron nitride Nanotechnology 29 325705
[25] Schabley J R et al 2016 Valleytronics in 2D materials Nat. Rev. Mater. 1 16055
[26] Pandey J and Soni A 2019 Unraveling biexciton and excitonic excited states from defect bound states in monolayer MoS$_2$ Appl. Surf. Sci. 463 52–57
[27] Pogna E A A et al 2016 Photo-induced bandgap renormalization governs the ultrafast response of single-layer MoS$_2$ ACS Nano 10 1162–6
[28] Zhao J et al 2020 Dynamics of exciton energy renormalization in monolayer transition metal disulfides. Nano Research 13 1399–408
[29] Jakubczyk T et al 2018 Impact of environment on dynamics of exciton complexes in a WS$_2$ monolayer 2D Mater. 5 031007
[30] Karaïskaj D et al 2010 Two–quantum many–body coherences in two–dimensional Fourier-transform spectra of exciton resonances in semiconductor quantum wells Phys. Rev. Lett. 104 117401
[31] Stone K W et al 2009 Two-quantum 2D FT electronic spectroscopy of bieexcitons in GaAs quantum wells Science 324 1169
[32] Tollerud J O and Davis J A 2017 Coherent multi-dimensional spectroscopy: experimental considerations, direct comparisons and new capabilities Prog. Quantum Electron. 55 1–34
[33] Moody G and Cundiff S T 2017 Advances in multi-dimensional coherent spectroscopy of semiconductor nanostructures Adv. Phys. X 2 641–74
[34] Tollerud J O, Hall C R and Davis J A 2014 Isolating quantum coherence using coherent multi-dimensional spectroscopy with spectrally shaped pulses Opt. Express 22 6719–33
[35] Turner D B et al 2011 Invited Article: the coherent optical laser beam recombination technique (COLBERT) spectrometer: coherent multidimensional spectroscopy made easier Rev. Sci. Instrum. 82 081301
[36] Turner D B and Nelson K A 2010 Coherent measurements of high–order electronic correlations in quantum wells Nature 466 1089–92
[37] Tollerud J O and Davis J A 2017 Separating pathways in double–quantum optical spectroscopy reveals excitonic interactions Laser Photonics Rev. 11 1600249
[38] Tollerud J and Davis J A 2016 Two-dimensional double-quantum spectroscopy: peak shapes as a sensitive probe of carrier interactions in quantum wells J. Opt. Soc. Am. B 33 C108–14
[39] Absor M A U et al 2016 Strain–controlled spin splitting in the conduction band of monolayer WS$_2$ Phys. Rev. B 94 115131
[40] Guo S et al 2017 Large spin–orbit splitting in the conduction band of halogen (F, Cl, Br, and I) doped monolayer WS$_2$ with spin–orbit coupling Phys. Rev. B 96 245305