The role of electron-phonon interactions on the coherence lifetime of monolayer transition metal dichalcogenides

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Abstract. We investigate the excitonic dephasing of transition metal dichalcogenides, namely MoS₂, MoSe₂, and WSe₂ atomic monolayer thick and bulk crystals, in order to understand the factors that determine the optical coherence in these materials. Coherent nonlinear optical spectroscopy, temperature dependent absorption combined with theoretical calculations of the phonon spectra, reveal the important role electron-phonon interactions play in dephasing process. The temperature dependence of the electronic band gap and the excitonic linewidth combined with 'ab initio' calculations of the phonon energies and the phonon density of state reveal strong interaction with the E' and E" phonon modes.

1. Introduction

Transition metal dichalcogenides (TMDs) have recently received a lot of attention and have been suggested for numerous electronic and optoelectronic applications. Therefore, understanding the fundamental many-body interactions and how these interactions influence the optical properties of these materials is crucially important [1]. As bulk materials TMDs are indirect band semiconductors with rather poor optical properties. However, when reduced to atomic monolayer they transition to direct band gap materials leading to greatly enhanced emission [2]. When photon absorption occurs electrons are excited from the valence band to the conduction band. The Coulomb interaction between the positively charged hole and the electron leads to a new quasi-particle, namely the exciton. Excitons are of importance for the optical properties of semiconductors, therefore understanding their properties, such as coherence loss or dephasing can be key for many optoelectronic devices. Many-body effects play a crucial role in determining the optical coherence and lifetime of excitons through electron-phonon interactions and exciton-exciton scattering [3]. Recent experimental studies have measured the radiative recombination lifetime of excitons in WSe₂ to be exceedingly short and therefore limit the coherence time [4]. Strong exciton-exciton scattering or excitation induced dephasing was thought to be a limiting
factor in monolayer MoSe\textsubscript{2} as well \cite{5}. Finally, theoretical studies have attributed the dephasing mechanism to phonon assisted scattering of excitons to a lower lower lying dark state \cite{6}.

2. Experiment

The optical excitation in the four-wave mixing (FWM) experiments was provided by a laser oscillator, within the tuning range of the Ti:Sapphire crystal, whereas outside the oscillator spectral range, an optical parametric oscillator was used. In the three pulse FWM, three pulses are incident on the sample with wavevectors $-\vec{k}_a$, $\vec{k}_b$, and $\vec{k}_c$. The nonlinear interaction gives rise to a signal in the direction $-\vec{k}_a + \vec{k}_b + \vec{k}_c$. The phase conjugate pulse $-\vec{k}_a$ and the second pulse $\vec{k}_b$ are separated by the time delay $\tau$ whereas pulse $k_b$ and the third pulse $k_c$ are separated by the population time $T$. By varying the time delay $\tau$ and monitoring the time-integrated FWM intensity, the dephasing time of excitons can be measured.

3. Results and discussion

The strength of electron-phonon interactions often determines the optical properties of materials and can be a limiting factor for many applications. While the inhomogeneous linewidth of excitons is determined by material imperfections and can be reduced by improving the material quality, the homogeneous linewidth is often limited by the fundamental interactions taking place, which place limitations on the material system. The excitonic coherence is a direct measure of the homogeneous linewidth, therefore processes leading to dephasing can be the limiting factor \cite{3}.

Figure 1. (a) The four phase-stabilized linearly polarized beams obtained from the multi-dimensional optical nonlinear spectrometer (MONSTR) instrument are focused on the sample, which is held in the cryostat at 5 K. The FWM signal can be measured as a function of the time delays $\tau$ and $T$ using a detector, which integrates over the time delay $t$. The sequence of the laser pulses used in the experiments, where A$^*$ corresponds to the phase conjugated pulse. The time delay $\tau$ corresponds to the time between the pulses A$^*$ and B, $T$ is the time delay between the pulses B and C, and $t$ is the evolution of the echo in ‘real time’. (b-d) Time-integrated FWM of atomic monolayers (a) MoS\textsubscript{2} (b) MoSe\textsubscript{2} and (c) WSe\textsubscript{2}. The black symbols are the experimental data whereas the red line is the single exponential fit. (e) Temperature dependence of the homogeneous linewidth for atomic monolayer MoS\textsubscript{2}. Squares are the measured values whereas the red line is the linear fit. (f) Excitation density dependence of the homogeneous linewidth for atomic monolayer MoS\textsubscript{2}. Squares are the measured values whereas the red line is the linear fit.
We start by discussing the FWM measurements shown in Fig. 1. The dephasing time $T_2$ provides the homogeneous linewidth and was measured for atomic monolayers of MoS$_2$, WSe$_2$, and MoSe$_2$ to be 200 fs ($\sim$6.58 meV), 279 fs ($\sim$4.72 meV), and 394 fs ($\sim$3.34 meV) respectively, showing a rapid decay for all the materials. The temperature dependence of the homogeneous linewidth for atomic monolayer MoS$_2$ is shown in Fig. 1 (e) and the homogeneous linewidth $\gamma$ increases very rapidly with temperature. At temperatures higher than 40 K it exceeds our ability to measure it. The scattering rate of excitons with acoustic phonons at low temperature is described by a linear relationship $\gamma = \gamma^* + aT$, where $\gamma^*$ is the temperature independent broadening originating from other sources. The linear fit leads to an acoustic phonon scattering coefficient $a \sim 45 \, \mu eV/K$, which is large and indicates strong electron-phonon interactions. Furthermore, the excitation density dependence of the homogeneous linewidth $\gamma$ is shown in Fig. 1 (f) and exhibits some excitation induced dephasing [3]. However, at the limit of ‘zero’ excitation power the residual homogeneous linewidth independent of excitation density is $\sim$4.5 meV.

![Figure 2](image-url) (a) Electronic band gap shift, temperature broadening of the direct excitons, and calculated phonon density of states for atomic monolayer MoS$_2$ (a-c), MoSe$_2$ (d-f), and WSe$_2$ (g-i), respectively. The blue arrows indicate the phonon energies used in the fittings.

In order to obtain a quantitative understanding of the electron-phonon interactions in TMDs we measure the energy shift of the electronic band gap with temperature for both bulk and atomic monolayer samples. Temperature dependent absorption spectra of the excitons provide the energy shift of the band gap with temperature and also the temperature broadening of the excitonic resonance. These effects are in large part a result of electron-phonon interactions [7]. The energy shift of the exciton resonance with temperature for bulk MoS$_2$, MoSe$_2$, and WSe$_2$ have been discussed elsewhere [1]. The fitting procedure was performed using,

$$E_g = E_0 - E_1 \left[2\exp\left(\frac{\Theta}{kT}\right) - 1\right]^{-1} + 1$$  \hspace{1cm} (1)

where $E_0$ and $E_1$ are fitting parameters, whereas $\Theta$ is either a dominant phonon or an average phonon energy. The absorption spectra of the excitons in TMDs at low temperature are predominantly inhomogeneously broadened. However, as the temperature rises, the phonon scattering leads to observable broadening. The linewidths of the exciton absorption spectra as a function of temperature for bulk MoSe$_2$ and WSe$_2$ were also discussed elsewhere [1]. The theoretical fit was performed according to
\[ \gamma = \gamma_I + \frac{b}{\exp(\Theta/kT) - 1} \] (2)

where \( \gamma_I \) is the temperature independent inhomogeneous broadening. Both the energy shift and broadening of the excitonic resonance can be fitted simultaneously by using a phonon energy \( \Theta = 22.1 \text{ meV}, 16.3 \text{ meV and } 15.5 \text{ meV for MoS}_2, \text{WSe}_2, \text{and MoSe}_2, \) respectively.

Electronic band gap shift and temperature broadening of the excitons for atomic monolayer MoS\(_2\) (a-b), MoSe\(_2\) (d-e), and WSe\(_2\) (g-h) are shown in Fig. 2. In order to be able to identify the phonon energies and gain a deeper understanding of the dephasing mechanism we performed ‘ab initio’ calculations of the phonon spectra and phonon DOS for bulk and atomic monolayer TMDs [1]. The phonon DOS for monolayer MoS\(_2\), MoSe\(_2\) and WSe\(_2\), are shown in Fig. 2 (e), (f), and (i), respectively, where the blue arrows marks the energies of the \( \Theta \) phonons obtain from the fitting of the experimental data. The calculations also reveal two phonon modes at these energies corresponding to the \( \text{E}' \) and \( \text{E}'' \) representation. The calculated phonon energies are 23.3 (\( \text{E}' \)) meV and 23.5 (\( \text{E}'' \)) meV for MoS\(_2\), 12.6 (\( \text{E}' \)) and 15.8 (\( \text{E}'' \)) for WSe\(_2\), and 15.8 meV (\( \text{E}' \)) and 17.7 meV (\( \text{E}'' \)) for MoSe\(_2\). These energies are very close to the observed phonon energies.

However, the two modes are energetically very close which makes it difficult to distinguish them experimentally.

In conclusion, we provide a detailed description of the electron-phonon interactions and their possible role on the dephasing mechanism of direct excitons in atomic monolayer TMDs. The temperature dependence and excitation density dependence of the dephasing in atomic monolayers indicate that the electron-phonon interactions to play an important role in the rapid dephasing, and as a result, the large residual homogeneous linewidths in this material system. Calculations of the phonon energies and phonon DOS determined these phonon energies as the \( \text{E}' \) and \( \text{E}'' \) phonon modes, which could facilitate the rapid dephasing observed in TMDs. The large residual homogeneous linewidth at low excitation densities and low temperature observed experimentally for MoS\(_2\) is well in agreement with the efficient exciton relaxation in WS\(_2\) through phonon emission at all temperatures, reported in the theoretical studies [6].

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