Influence of Polar Pressure Transmission Medium on the Pressure Coefficient of Excitonic Interband Transitions in Monolayer WSe_2 *

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(Received 26 March 2018)

The influence of the pressure transmission medium (PTM) on the excitonic interband transitions in monolayer tungsten diselenide (WSe_2) is investigated using photoluminescence (PL) spectra under hydrostatic pressure up to 5 GPa. Three kinds of PTMs, condensed argon (Ar), 1:1 n-pentane and isopentane mixture (PM), and 4:1 methanol and ethanol mixture (MEM, a PTM with polarity), are used. It is found that when either Ar or PM is used as the PTM, the PL peak of exciton related to the direct K–K interband transition shows a pressure-induced blue-shift at a rate of 32±4 or 32±1 meV/GPa, while it turns to be 50±9 meV/GPa when MEM is used as the PTM. The indirect Λ–K interband transition presents almost no shift with increasing pressure up to approximately 5 GPa when Ar and PM are used as the PTM, while it shows a red-shift at the rate of −17±7 meV/GPa by using MEM as the PTM. These results reveal that the optical interband transitions of monolayer WSe_2 are very sensitive to the polarity of the PTM. The anomalous pressure coefficient obtained using the polar PTM of MEM is ascribed to the existence of hydrogen-like bonds between hydroxyl in MEM and Se atoms under hydrostatic pressure.

PACS: 62.50.−p, 78.67.−n, 68.08.−p DOI: 10.1088/0256-307X/35/6/066201

Atomically thin two-dimensional (2D) materials including graphene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides (TMDs), have attracted tremendous attention because of their high charge carrier mobility, mechanical robustness, unique valleytronics, and optoelectronic properties.[1−5] The TMDs exhibit direct band gap transitions in the monolayer limit, with a strong photoluminescence (PL), which makes them the good candidates for future optoelectronic applications.[6−9] Electrons and holes in 2D TMDs have strong Coulomb interactions owing to the strong quantum confinement in the out-of-plane direction and a weak dielectric screening of the environment,[10,11] which can form excitons with large binding energies of several hundreds of meV.[12,13] Numerous studies on the excitonic properties, electronic band structure, and optical interband transitions related to conduction band valleys and valence band hills in 2D TMDs have been reported.[13−20] Recently, hydrostatic pressure applied by the diamond anvil cell (DAC) has been widely employed to study electronic band structures and optical transitions in 2D TMDs based on pressure-dependent PL and absorption spectra of excitons.[16−20] However, owing to larger surface-to-volume ratio in 2D TMDs, the exciton optical characters are sensitive to the surrounding conditions.[21−23] In high-pressure experiments, the pressure transmitting medium (PTM), surrounding the 2D materials, should have a huge influence on the pressure characters of the 2D materials. Recently, a quite large pressure coefficient of 49.4 meV/GPa of exciton in monolayer MoS_2 was reported,[24] and it is different from the previously reported values of the pressure coefficient.[19] In addition, quite different pressure characters of excitons in monolayer $MoSe_2$ when different PTMs of Ar and MEM were employed.[25] However, to date, the reason explaining why the PTM influences the pressure characters of monolayer and few layered TMDs in the high pressure experiments is unknown. To make this issue clear, in our work three different kinds of PTMs are chosen for the high-pressure experiments of monolayer WSe_2, such as condensed Ar, 4:1 methanol (CH_3OH) and ethanol (CH_3CH_2OH) mixture (MEM), 1:1 n-pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane ($(CH_3)_2CHCH_2CH_3$) mixture (PM). It is found that the pressure coefficients are comparable for the direct K–K and indirect Λ–K interband transitions when Ar or PM is used as the PTM. However, when the polar MEM is used as the PTM, the pressure coefficient of direct K–K interband transition becomes close to twice larger and indirect Λ–K interband transitions show an anomalous red-shift instead of insensitivity to the applied pressure. An explanation of the difference in the observed pressure coefficients is given based on the existence of hydrogen-like bonds between

*Supported by the National Key Research and Development Program of China under Grant No 2016YFA0301202, the National Natural Science Foundation of China under Grant Nos 11474275, 61674135 and 91536101, the Strategic Priority Research Program of the Chinese Academy of Sciences under Grant No XDPB0603, and the China Postdoctoral Science Foundation under Grant No 2017M622400.

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the hydroxyl in polar MEM and Se atom in monolayer WSe_2.

The monolayer WSe_2 samples were prepared by mechanical exfoliation from a bulk WSe_2 on a thinned SiO_2/Si substrate. Monolayer samples are identified by microscopic image contrast and room-temperature PL spectra, as shown in Figs. 1(a) and 1(b). A high pressure can be applied to the measured samples using a DAC device. Ar, MEM and PM were separately used as the PTM in room-temperature PL measurements under hydrostatic pressure, and the pressure-dependent ruby R_1 fluorescence line shift was used to determine pressure.[26] The PL was collected by a 20× objective (NA: 0.35) and spectrally analyzed using a 0.5 monochromator equipped with a silicon charge-coupled device at an light beam excitation of hundreds of microwatts by a continuous-wave 532 nm solid laser.

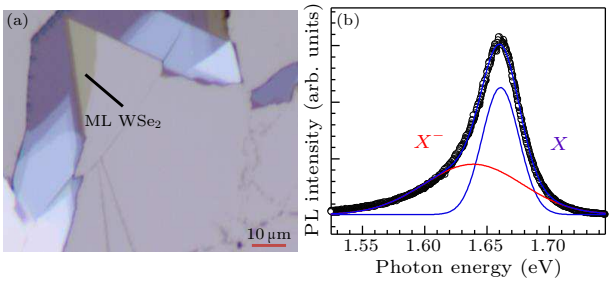


Fig. 1. (a) Optical microscopic image of the mechanically exfoliated WSe_2. (b) PL spectrum of monolayer (ML) WSe_2 under room temperature and atmospheric pressure (black circles). Two fitted peaks of X (blue line) and X^- (red line) correspond to the exciton and negatively charged exciton emissions, respectively.

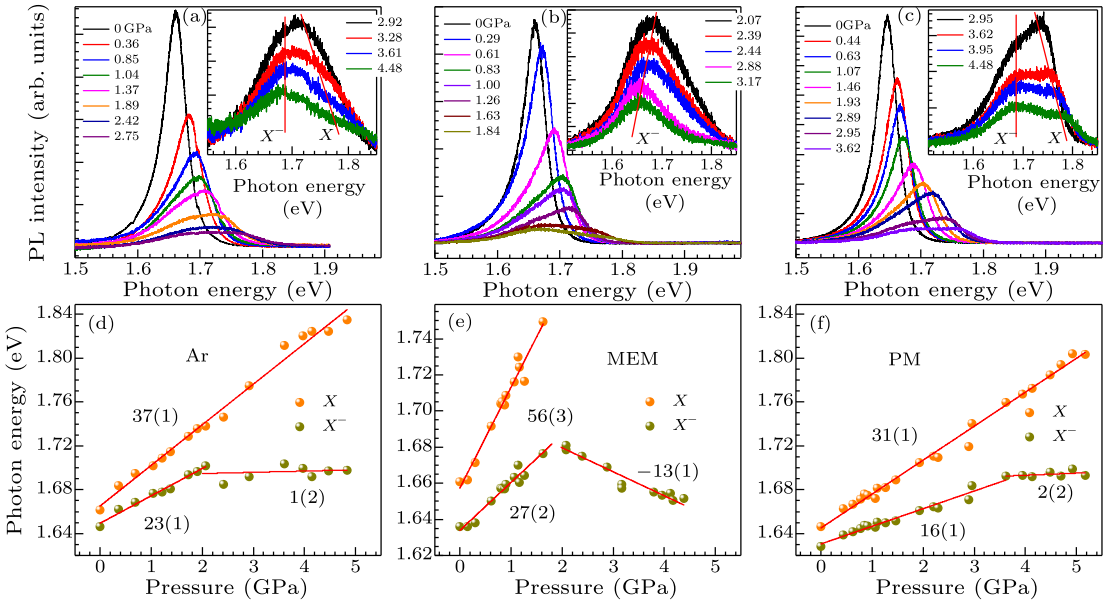
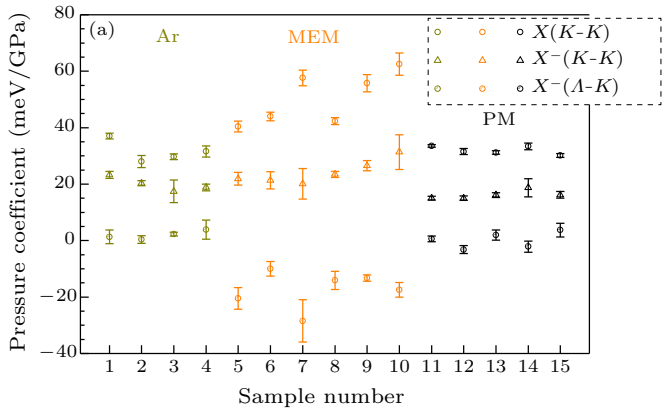


Fig. 2. (a)–(c) PL spectra under pressures when Ar, MEM and PM are used as the PTM, respectively. The insets in (a)–(c) show the PL spectra at high pressures and the red straight lines clearly show the pressure response of X and X^- emissions. (d)–(f) Photon energies of the PL peaks of X and X^- emissions as a function of pressure for the PTM of Ar, MEM and PM. Solid orange and dark yellow spheres stand for X and X^- emission peaks, respectively, and the red lines are linearly fitted to the data.



(b)

	PCs (meV/GPa)
$X(K$-$K)$(Ar)	32 ± 4
$X^-(K$-$K)$(Ar)	20 ± 3
$X^-(\Lambda$-$K)$(Ar)	2 ± 1
$X(K$-$K)$(MEM)	50 ± 9
$X^-(K$-$K)$(MEM)	24 ± 4
$X^-(\Lambda$-$K)$(MEM)	-17 ± 7
$X(K$-$K)$(PM)	32 ± 1
$X^-(K$-$K)$(PM)	16 ± 1
$X^-(\Lambda$-$K)$(PM)	0 ± 3

Fig. 3. (a) Plotted data points of pressure coefficients (PCs) of X (K–K), X^- (K–K), and X^- (Λ–K) emission peaks (open hexagons, open up triangles, open spheres, respectively) for 15 samples by using three kinds of PTM, and the corresponding average X and X^- pressure coefficients of each PTM are shown in (b).

Figure 1(b) shows a typical PL spectrum of monolayer WSe_2 sample under room temperature and atmospheric pressure.[18] The asymmetrical PL spectrum can be well fitted using two Gaussian functions. The peak on the high energy side is related to the neutral exciton X. Another peak on the lower energy side is related to the negatively charged exciton X^-.[6,7,18] They correspond to the direct K–K interband transition between the conduction band minimum (CBM) and the valence band maximum (VBM) at the K point in the Brillouin zone. Theoretical calculations and experimental measurements show that as the pressure increases, the conduction band at the K point keeps going upward and the Λ point goes slightly downward.[16,18] This leads to a K–Λ crossover of the CBM occurring at a pressure of approximately 2.25 GPa for monolayer WSe_2.[18] After the K–Λ crosses, the pressure characters of X^- emission will follow the Λ–K interband transition.[18]

The pressure characteristics of X and X^- emissions in the four monolayer WSe_2 samples denoted as samples 1–4 (see Fig. 3(a)) have been investigated using Ar as the PTM in the pressure-dependent measurements. A representative PL spectrum (sample 1) at pressure up to nearly 5 GPa is shown in Fig. 2(a). The PL peak energies of X and X^- emissions can be obtained using two Gaussian functions to fit the PL spectrum, and the peak energies of X and X^- emissions as a function of pressure are shown in Fig. 2(d). A linear fit is employed for yielding pressure coefficients of X and X^- emissions, and the fitting results are represented by the red lines in Fig. 2(d). It shows that the X peak energy undergoes a blue-shift at a rate of 37±1 meV/GPa, corresponding to the K–K interband transition, while the X^- peak energy shows firstly a blue-shift with a pressure coefficient of 23±1 meV/GPa, which is related to K–K interband transitions, and then is almost insensitive to the applied pressure with a pressure coefficient of 1±2 meV/GPa corresponding to Λ–K interband transitions. These results are consistent with the previous report.[18] Next, the polar MEM is used as the PTM, and the pressure response of the PL peak energies of X and X^- emissions in monolayer WSe_2 has been measured for six samples (denoted as samples 5–10, see Fig. 3(a)). A representative PL spectrum (from sample 9) under pressure is shown in Fig. 2(b). The PL peak energies of X and X^- emissions, obtained by using two Gaussian function's fitting, as a function of pressure are plotted in Fig. 2(e). The obtained pressure coefficients are 56±3 meV/GPa for X peak corresponding to the K–K interband transition, 27±2 and −13±1 meV/GPa for X^- peak corresponding to K–K and Λ–K interband transitions, respectively. A comparison of the pressure characters of X and X^- emissions with sample 9, as shown in Fig. 2(e), clearly reveals that when the MEM is used as the PTM, K–K interband blue-shift gives rise to a much larger positive pressure coefficient, and Λ–K interband transitions show an obvious red-shift with a negative pressure coefficient.

Normally, as ideal PTMs at room temperature, both Ar and MEM have been successfully used in many hydrostatic pressure experiments.[18–20,24–27] However, here the pressure behaviors of excitons in monolayer WSe_2 are quite different when these two different PTMs are used. It is suggested that the pressure responses of the optical transitions in monolayer WSe_2 may be quite sensitive to the polarity or the influence of particular hydrogen atoms in the PTM. Note that the pressure-induced charging effect between H atoms in MEM and Se atoms of monolayer $MoSe_2$ have been proposed to interpret the PL intensity increase of the X^- emissions.[25] Based on the composition and chemical properties of MEM, it is interesting to check, except for the polarity of hydroxyl, whether the alkyl group (hydrogen atoms connected to carbon atoms) in MEM may also affect surface bonding configuration in monolayer WSe_2. To answer this question, we choose PM as another PTM in the pressure measurements,[27] as it has no hydroxyl and is non-polar, but the hydrogen atoms in it are bonding with the carbon atoms. Five monolayer samples (denoted as samples 11–15, see Fig. 3(a)) were used to repeat the pressure measurements similar to those mentioned above. Figure 2(c) shows the PL spectra of sample 13 at pressure from 0 to 4.48 GPa. Figure 2(f) plots the PL peak energies of X and X^- emissions as a function of pressure. The pressure coefficients are 31±1 meV/GPa for X peak corresponding to the K–K interband transition, 16±1 and 2±2 meV/GPa for X^- peak corresponding to K–K and Λ–K interband transitions, respectively. These pressure coefficients are found very close to the obtained values when Ar is used as the PTM. Therefore, it is obtained that the anomalous pressure characters of X and X^- peaks when MEM is used as the PTM should be related to the influence of polarity of hydroxyl, but not to the hydrogen atoms connected to carbon atoms.

Figure 3(a) summarizes the obtained pressure coefficients of X and X^- peaks for 15 samples using three different kinds of PTM (1–4 for Ar, 5–10 for MEM, and 11–15 for PM). It can be seen that when Ar or PM is used as the PTM, both X and X^- pressure coefficient values are comparable, as presented in Fig. 3(b). Here the average values of pressure coefficients for the K–K interband transition of X peak are 32±4 and 32±1 meV/GPa, and they are 2±1 and 0± 3 meV/GPa for the Λ–K interband transitions of the X^- peak. When the polar MEM is used as the PTM, however, X peak energy shows a much faster blue-shift with an average pressure coefficient of 50±9 meV/GPa, and X^- peak energy shows an anomalous red-shift, with a pressure coefficient of −17±7 meV/GPa.

To exclude the influence of anisotropy of applied pressure on the pressure coefficients, we plot the full width at half maximum (FWHM) of the ruby R_1 peak as a function of pressure, as shown in Figs. 4(a)–4(c) for the PTMs of Ar, MEM, and PM, respectively. It is clearly shown that there is no remarkable extra broad-

ening of the ruby R_1 peak for all the three PTMs, implying that all the experiments mentioned above are under a very nice hydrostatic condition.[27]

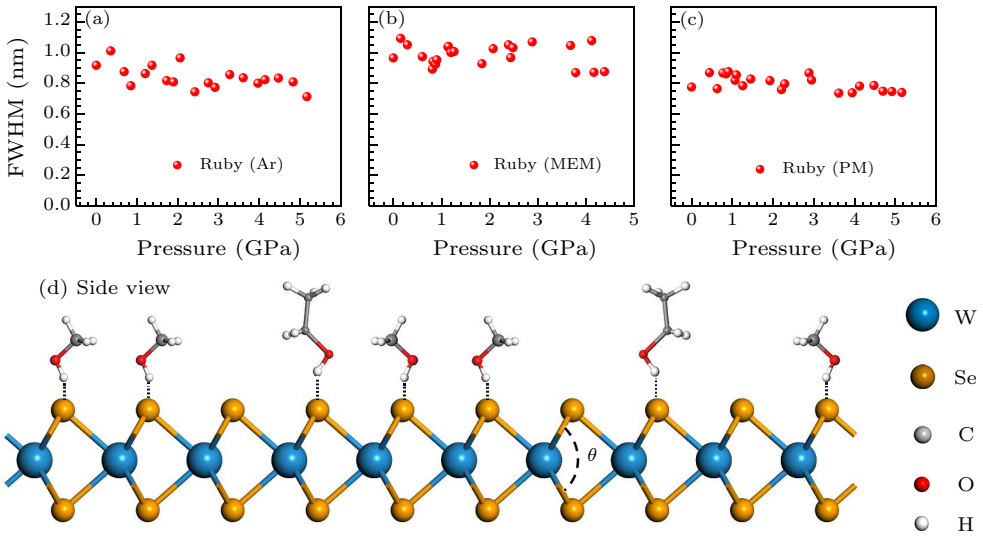


Fig. 4. (a)–(c) FWHM of ruby R_1 emission line as a function of pressure for the PTM of Ar, MEM and PM, respectively. No remarkable extra broadening is observed. (d) Schematic diagram of the lattice structure of monolayer WSe_2 under pressure in a PTM environment of MEM, where the hydrogen atoms of hydroxyl in MEM may form hydrogen-like bonds with Se atoms. The angle θ stands for the angle of Se–W–Se.

Finally, we discuss the differences in the observed pressure coefficients. For monolayer WSe_2, the electronic states near the CBM at K point are dominated by couplings of p orbitals of Se atoms and d_{z2} orbital of W atoms, while the CBM at Λ point is mainly contributed by the coupling of p orbitals of Se atoms and d_{x2-y2} and d_{xy} orbitals of W atoms.[16,17] Theoretical calculations show that the applied pressure can increase bond angle θ of Se–W–Se, as indicated in Fig. 4(d), which results in a blue-shift of the K–K interband transition and no considerable shift of the Λ–K interband transitions at a pressure of less than 5 GPa. This is due to the fact that under applied pressure the coupling between the p and d_{z2} orbitals becomes stronger while the coupling between p orbital and in-plane orbitals of d_{x2-y2} and d_{xy} becomes weaker.[16,17] These calculations are in agreement with the observed results when a non-polar PTM of Ar or PM is used. In 2D TMDs, bonding is usually considered between empty orbitals of the metal and lone pairs of ligands in transition metal complexes. In WSe_2, the W atoms provide four electrons to fill the bonding states, and the W and Se atoms can be ascribed to formal charges of $+4$ and -2, respectively.[28] As a result, the outermost layer of Se atoms has a lone pair, and it shows a weak electronegativity. However, the oxygen atom of hydroxyl has a strong electronegativity to attract electron of the hydrogen atom and to generate an empty orbit in the hydrogen atom. Therefore, the hydrogen of hydroxyl in polar MEM and Se atoms in monolayer WSe_2 have the opposite polarity, and they can easily form hydrogen-like bonds when they come in contact together, particularly under high pressure. This attractive interaction will further enlarge the bond angle θ of Se–W–Se with increasing the pressure, and will yield a large blue-shift of the K–K interband transition and an obvious red-shift of the Λ–K interband transition, as shown in Figs. 2(b) and 2(e). Furthermore, we also notice in the experiments that the pressure coefficient fluctuations in MEM are obviously larger than that in Ar or PM (see Fig. 3(a)). This should be related to the differences in the bond number and bond orientation between hydroxyl in MEM and Se atoms in WSe_2 in each pressure experiment.

In summary, we have shown that a polar PTM, such as MEM, can significantly affect the pressure-induced shift of the CBM at the K and Λ points in the Brillouin zone in monolayer WSe_2. The pressure coefficients of K–K and Λ–K interband transitions are found to be 50 ± 9 and -17 ± 7 meV/GPa, respectively, when MEM is used as the PTM. In contrast, for a non-polar PTM, such as Ar or PM used here, the corresponding pressure coefficient is 32 ± 4 or 32 ± 1 meV/GPa for direct K–K interband transitions, as well as 2 ± 1 or 0 ± 3 meV/GPa for indirect Λ–K interband transition, respectively. Such a large discrepancy can be understood by considering an existence of hydrogen-like bonds between the hydroxyl in polar MEM and Se atoms in monolayer WSe_2.

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