Theoretical Investigation of Strain and Doping on the Raman Spectra of Monolayer MoS$_2$

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Two-dimensional heterostructures are generally extremely sensitive to perturbations due to the large surface–volume ratio. A widely used non-destructive experimental technique to characterize these perturbations is the Raman spectroscopy. However, vibrational frequencies of monolayer MoS$_2$ is proven to be non-sensitive to perturbations such as strain and doping. In order to characterize the effect of these perturbations to the spectra we compute the frequencies and Raman intensities of monolayer MoS$_2$ on the *ab initio* level. In agreement with previous experimental works, we show that the frequencies of the Raman active peaks (A'_1 and E') are rather non-sensitive to strain or doping. On the other hand, we demonstrate that the intensity ratio depends strongly on the strain — thus it can be used as a supplementary method to characterize strain in the samples.

1. Introduction

Transition metal dichalcogenides are one of the largest family of novel two dimensional (2D) materials with miscellaneous properties for example there are semiconductors, insulators, topological insulators, etc. One of the most promising member of this family is the MoS$_2$[1] which inherits an indirect band gap in the bulk[2] evolving to a direct band gap in the monolayer.[3] Furthermore recent works showed that large area single crystal monolayer MoS$_2$ can be exfoliated[4] or grown on substrates[5,6] which makes it a great candidate for future application in the industry.

Monolayers are usually extremely sensitive to the perturbations due to the large surface-volume ratio. In order to fabricate devices from such a material one needs a reliable method to characterize the typical perturbations like the strain or the doping in the sample. Raman spectroscopy is a widely applied, non-destructive method to characterize electronic and vibrational properties of 2D materials. A remarkable example is the graphene where the shift of vibrational frequencies due to strain can be described fairly well with the Grüneisen parameters[7] and doping can be determined by measuring the integrated intensity ratio of the 2D and the G peak[8] However it has been shown both

theoretically and experimentally that the vibrational frequencies of MoS$_2$ are rather non-sensitive to these perturbations.[9–11]

On the other hand previous studies were mostly focusing on the frequencies of the Raman peaks, but we are not aware of results discussing the relative intensities of the two Raman active peaks (A'_1 and E'). In this study we report calculations of the Raman spectra of monolayer MoS$_2$ with applied strain and doping on the *ab initio* level using the Placzek approximation. We show that in agreement with previous works the frequencies of the peaks are not sensitive to these perturbations. However our results concluded that even significant amount of electron doping cannot change the integrated intensity ratio, although it can slightly perturb the frequencies. On the contrary we demonstrate that even small amount of strain ($\varepsilon < 1\%$) can change the intensity ratio of the two peaks drastically. In this way we demonstrate that this intensity ratio can be used to distinguish and quantify these perturbations.

2. Methods

The structure of monolayer MoS$_2$ is hexagonal — similarly to graphene — but instead of a single atomic layer it consists of three strongly bound atomic layers. One Mo atomic layer at the A site and two S layers at the B site placed out of plane symmetrically compared to the Mo layer as shown in **Figure 1**.

The Raman spectra were calculated based on the Placzek approximation:

$$I(\omega) = \sum_v \frac{\omega_s^4}{\omega_v} \sum_{\rho,\sigma} \left| \frac{\partial \alpha_{\rho\sigma}(\omega_l)}{\partial Q_v} \right|^2 \delta(\omega - \omega_v)(n(\omega_v) + 1), \qquad (1)$$

where $\omega_l, \omega_s, \omega_v$ are the frequencies of the laser, the scattered light and the vibrational modes, $\alpha_{\rho\sigma}(\omega_l)$ is the frequency dependent polarizability tensor, Q_v are the normal modes, $\delta(x)$ is a normalized Lorentzian function with a full width at half maximum value of $10\,\text{cm}^{-1}$ and $n(\omega_v)$ is the Bose-Einstein distribution at room temperature. Polarization of the incident and reflected light were averaged in the plane of the MoS$_2$ in parallel and perpendicular cases (xx, xy, yx, yy). Calculations were performed on the *ab initio* level as implemented in the Vienna *ab initio* simulation package (VASP)[12,13] using the projector-augmented wave method (PAW) and the Perdew–Burke–Ernzerhof type GGA fuctionals.[14]

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/pssb.201700184.
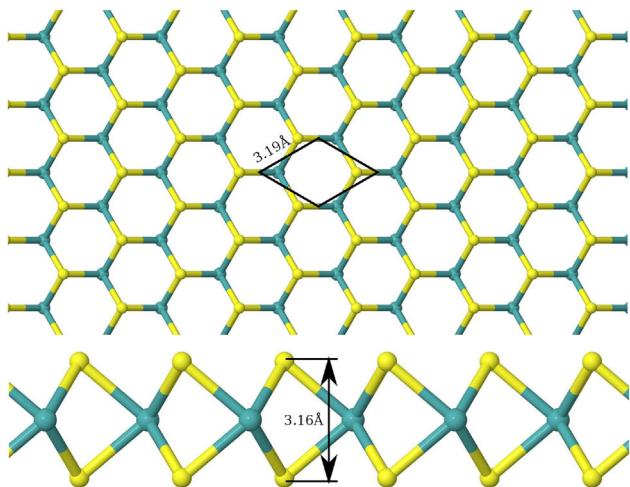
Figure 1. Structure of monolayer MoS$_2$: top and side view.

Technical details of structural optimization: a k-point grid of $30 \times 30 \times 1$ Γ-centered Monkhorst-Pack set[15] was applied with a 700 eV plane wave energy cutoff, the geometry was relaxed until all atomic forces fell below 0.003 eV Å^{-1}. Vibrational frequencies were calculated in the frozen phonon approximation in a 5×5 supercell with the same cutoff and a $6 \times 6 \times 1$ Γ-centered Monkhorst–Pack set and 0.015 Å displacement of atoms.

The matrix elements of the frequency dependent polarizability tensor were also calculated on the *ab initio* level with the same parameters applied to the structural optimization, using the built in LOPTICS switch of VASP.[16] The atoms were shifted manually according to the normal modes in both positive and negative directions and the derivative was calculated numerically. The maximum shift of the atoms was chosen to be 0.015 Å in order to avoid anharmonic effects. During the calculation of the polarizability the number of bands were chosen to be three times the number of electrons in order to acquire the frequency-dependent polarizability more accurately.

Strain was applied by stretching the lattice vectors in the given directions: parallel to the Mo—S bond in the uniaxial case and uniformly in the biaxial case, then we relaxed the atoms in the unit cell. Electron doping was applied by adding extra electrons to a unit cell hence our former calculation suggested that electrons may be transferred from the substrate to the monolayer due to the interlayer interaction.[17] For all strain and doping configuration the rest of the calculation was carried out similarly to the unperturbed case.

3. Results

The symmetries of monolayer MoS$_2$ structure corresponds to the D_{3h} point group. The irreducible decomposition of the representation of the lattice (omitting translations) is the following:

$$\Gamma_{\text{vib}} = A_1' \bigoplus E' \bigoplus A_2'' \bigoplus E'',$$

from these representations only A_1' is not Raman active. However, in experiments only two peaks are observed as the mode corresponding to E'' irreducible representation changes the (xz, yz) matrix elements of the polarizability tensor. Thus in usual Raman setups (with perpendicular incident and scattered light), where polarization of the incoming and the scattered light are in the xy plane, this peak is undetectable. Therefore we will also neglect the frequency change of this peak as we average the polarizability tensor in the xy plane (parallel to the MoS$_2$ layer).

Thus the Raman spectrum of monolayer MoS$_2$ consists two major peaks: a double degenerated peak around 375 cm^{-1} which corresponds to an in-plane vibration with E' symmetry and a non-degenerated peak around 400 cm^{-1} corresponding to an out-of-plane vibration with A_1' symmetry as shown in **Figure 2**.

By adding extra electrons to the system the symmetries of the system are preserved. In **Figure 3** we present the simulated Raman spectra for the monolayer with electron doping of 1.1×10^{13}, 2.2×10^{13}, and 3.3×10^{13} cm^{-2} (equivalent of 0.01, 0.02, and 0.03 extra electrons per unit cell). It can be seen that the frequency of the E' peak is not sensitive to doping, but the position of the A_1' peak shifts if doping is applied. However the shift of this peak is extremely small, also the difference in the integrated intensity ratio of the peaks shows to be non-sensitive to doping as well. Although in previous experimental works it was shown that doping can strongly affect the intensity of the A_1' peak, [18,19] but the integrated intensity ratio is rather non-sensitive as for higher (lower) intensity the peak sharpens (broadens), hence the integrated intensity ratio will be rather non-sensitive. In our approximation the change in the linewidth (or in the FWHM of the Lorentzian) due to doping or strain were
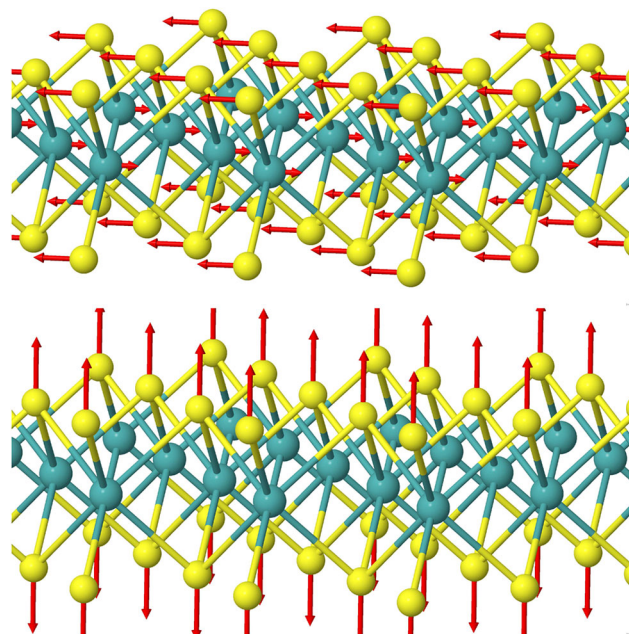
Figure 2. Raman active vibrations of monolayer MoS$_2$: the doubly degenerate in-plane E' mode (top) and the out-of-plane A_1' mode (bottom).
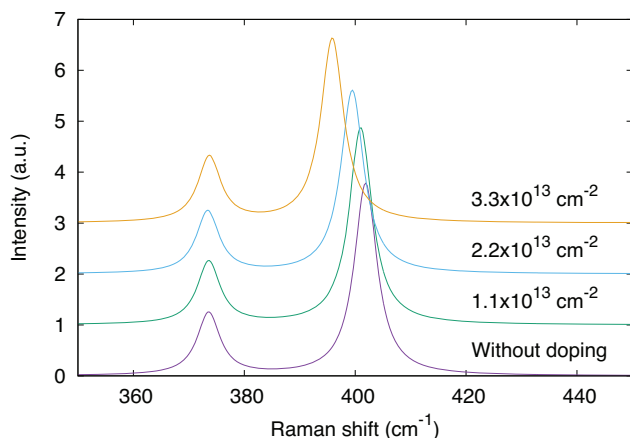
Figure 3. Effect of electron doping to the Raman spectra.

excluded, thus this effect is not visible in the calculated Raman spectra.

If uniaxial strain is applied the D_{3h} point group of the free lattice breaks down to the C_{2v} group, thus the degeneracy of the E' peak is lifted. Therefore the peak in the spectra splits into two different peaks but in order to measure the strain the peaks must be fitted which can introduce a large error in the measurements especially for small strains ($\varepsilon < 1\%$). Hence if the splitting is smaller than the error of the fitting (as the peak positions are rather non-sensitive for strain) thus one need significant amount of strain in the sample to measure it accurately.

In the left panel of **Figure 4** we present the simulated Raman spectra of monolayer MoS_2 with both compressing and stretching uniaxial strain calculated with laser energy of 2.33 eV (532 nm). It is clearly visible that the double degeneracy of the E' is lifted, moreover the intensity of the splitted peaks are not equal, the peak which is more affected by the strain is always more intensive. The summed intensity of the splitted peak clearly shows a dependence of strain as an even function of applied strain (compared to the unstrained intensity). The position of the other Raman active peak (A_1') is well known to be non-sensitive to strain on the other hand from our calculations it

is evident that the intensity of the peak changes with the applied strain. Moreover the change of the intensity can be described with a odd function of applied strain (compared to the unstrained intensity) with a negative slope. The combination of this two effects makes the relative intensity of the two peaks a great way to measure strain as illustrated in the right panel of Figure 4, thus the relative difference compared to the unstrained case can reach up to 10%–30% for 1–2 and 50%–110% for −1 to −2% of uniaxial strain which can make the intensity ratio a more accurate measure of strain than the frequencies.

Biaxial or hydrostatic strain unlike uniaxial does not lower the symmetry thus the degeneracy of the E' peak is preserved, hence the shift of the E' peak can be determined more accurately. In the left panel of **Figure 5** we present the calculated Raman spectra and it is evident that the shift of the peak positions are much larger compared to the uniaxial case. However the intensities are following similar trends as we saw in the case of uniaxial strain: the E' peak intensity is an even function of strain, while the A_1' intensity is an odd function of strain (compared to the unstrained intensities respectively). Therefore the intensity ratio of the peaks once again shows larger relative dependence on the amount of strain than the frequency of the peaks as shown in the right panel of Figure 5, which clearly indicates that measuring the intensity ratio of the peaks can give more accurate information from strain than the peak shifts.

Although the frequency shift of the two Raman active peaks due to both uniaxial and biaxial strain were studied by former experimental works,[9–11] the integrated intensity ratio was not examined in those articles. However the measured Raman spectra in these experiments shows similar trends as our presented results, such as the increasing intensity of the E' peak and the lowering intensity of the A_1' peak when extensive strain is applied. This clearly suggest that our prediction could be observed, therefore it could be used as a supplementary method to characterize strain in the given monolayer samples.

In both cases as shown in the right panels of both Figure 4 and Figure 5 the frequency shift of the A_1' and E' peak caused by strain is around only 1.23 cm^{-1} × ε and 3.67 cm^{-1} × ε, respectively, which is in the range of fitting error especially in the case of low strain. Hence the Grüneisen parameters are
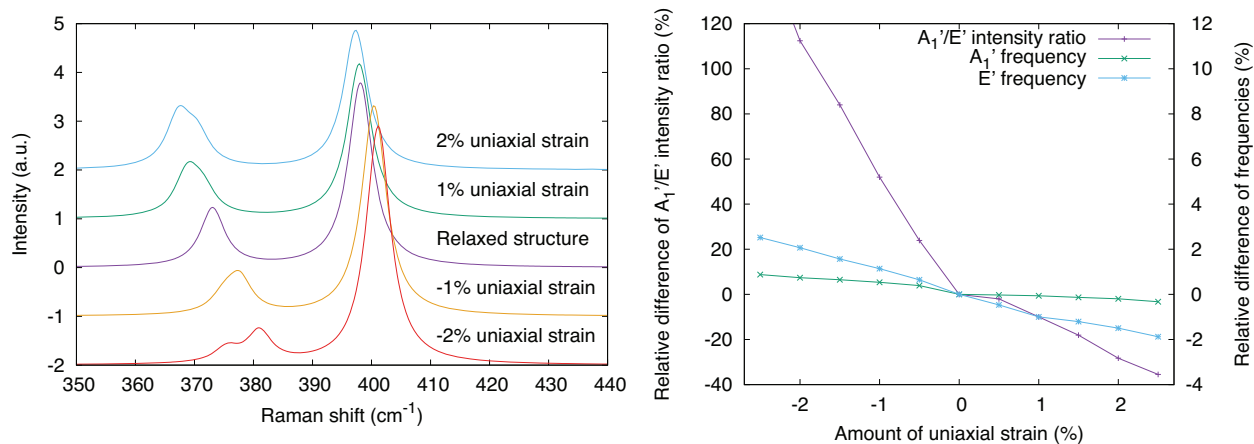
Figure 4. Effect of uniaxial strain: Raman spectra of strained structures (left) and the effect to the relative intensity and the positions of the peaks (right).
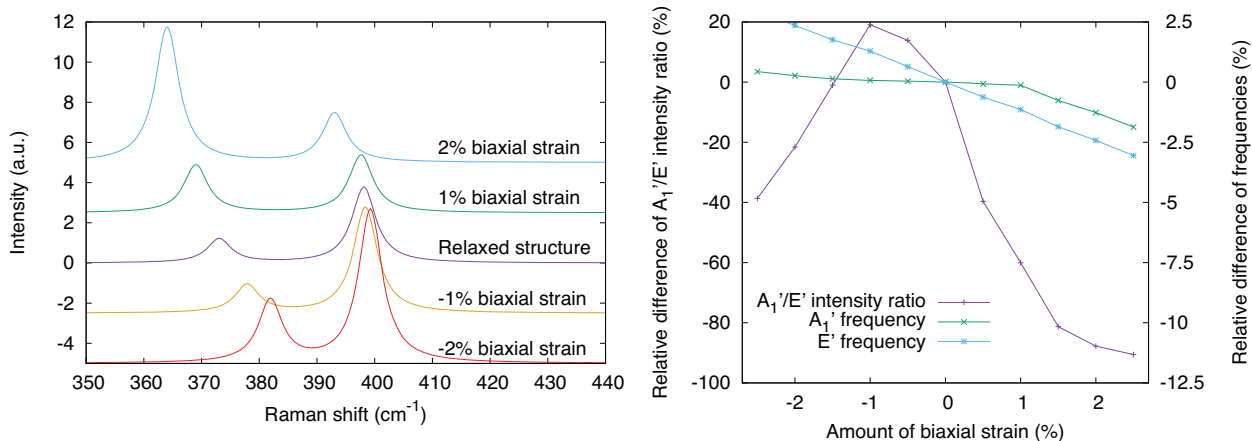
Figure 5. Effect of biaxial strain: Raman spectra of strained structures (left) and the effect to the relative intensity and the positions of the peaks (right).

positive for both peaks which indicates that the thermal expansion should be positive. For some two dimensional crystals it has been shown that on low enough temperatures the thermal expansion can be negative (e.g., graphene or boron-nitride).[20,21] But for MoX_2 monolayers it has been concluded from first principles calculations that the thermal expansion coefficients are positive.[22,23]

However the change of intensity ratio is much larger than the change of positions as for small amount of extending strain the ratio drops by $10\% \times \varepsilon$ for uniaxial and $70\% \times \varepsilon$ for biaxial strain. Furthermore the intensity ratio is a single valued function of applied strain between -1 and 1.5% which means that only one strain value corresponds to one intensity ratio. The width of the E' peak in the Raman spectra can be used to distinguish between different strain configurations. Hence, measuring the intensity ratio of the two Raman active peaks can be a more accurate method of measuring strain in monolayer MoS_2, rather than measuring peak positions by the fitting of the peaks.

4. Conclusions

In this work we presented a supplementary method to characterize and measure strain in monolayer MoS_2 using Raman spectroscopy. We demonstrated that especially for small amount of strain, measuring the intensity ratio of the two Raman active peaks can be a more accurate method because the intensity ratio shows a much greater dependence on strain compared to the peak positions. Furthermore, this method is free from any fitting method, therefore the errors of fitting the spectra are eliminated. By using this method one can retain invaluable information about the strain configuration in the samples which is essential for future applications.

Conflict of Interest

The authors declare no conflict of interest.

[1] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, *Phys. Rev. Lett.* **2010**, *105*, 136805.

[2] A. Jason, K. EllisMelissa, J. Lucero, *Appl. Phys. Lett.* **2011**, *99*, 261908.

[3] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C. Y. Chim, G. Galli, F. Wang, *Nano Lett.* **2010**, *10*, 1271.

[4] G. Z. Magda, J. Petö, G. Dobrik, C. Hwang, L. P. Biró, L. Tapasztó, *Sci. Rep.* **2015**, *5*, 14714.

[5] K. K. Liu, W. Zhang, Y. H. Lee, Y. C. Lin, M. T. Chang, C. Y. Su, C. S. Chang, H. Li, Y. Shi, H. Zhang, C. S. Lai, L. J. Li, *Nano Lett.* **2012**, *12*, 1538.

[6] Y. Zhan, Z. Liu, S. Najmaei, P. M. Ajayan, J. Lou, *Small* **2012**, *8*, 966.

[7] T. Mohiuddin, A. Lombardo, R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D. Basko, C. Galiotis, N. Marzari, K. Novoselov, A. Geim, A. Ferrari, *Phys. Rev. B* **2009**, *79*, 205433.

[8] C. Casiraghi, S. Pisana, K. S. Novoselov, A. K. Geim, A. C. Ferrari, *Appl. Phys. Lett.* **2007**, *91*, 233108.

[9] C. Rice, R. J. Young, R. Zan, U. Bangert, D. Wolverson, T. Georgiou, R. Jalil, K. S. Novoselov, *Phys. Rev. B* **2013**, *87*, 081307.

[10] Y. Wang, C. Cong, C. Qiu, T. Yu Raman, *Small* **2013**, *9*, 2857.

[11] D. Lloyd, X. Liu, J. W. Christopher, L. Cantley, A. Wadehra, B. L. Kim, B. B. Goldberg, A. K. Swan, J. S. Bunch, *Nano Lett.* **2016**, *16*, 5836.

[12] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558.

[13] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169.

[14] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.

[15] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188.

[16] M. Gajdos, K. Hummer, G. Kresse, J. Furthmüller, F. Bechstedt, *Phys. Rev. B* **2006**, *73*, 045112.

[17] G. Kukucska, G. Z. Magda, G. Dobrik, J. Pető, G. Piszter, J. Koltai, L. Tapasztó, to be submitted.

[18] B. Chakraborty, A. Bera, D. V. S. Muthu, S. Bhowmick, U. V. Waghmare, A. K. Sood, *Phys. Rev. B* **2012**, *85*, 161403.

[19] M. Yamamoto, T. L. Einstein, M. S. Fuhrer, W. G. Cullen, *J. Phys. Chem. C* **2013**, *117*, 25643.

[20] W. Paszkowicz, J. B. Pelka, M. Knapp, T. Szyszko, S. Podsiadlo, *Appl. Phys. A* **2002**, *75*, 431.

[21] D. Yoon, Y. W. Son, H. Cheong, *Nano Lett.* **2011**, *11*, 3227.

[22] C. Sevik, *Phys. Rev. B* **2014**, *89*, 035422.

[23] K. H. Michel, S. Costamagna, F. M. Peeters, *Phys. Status Solidi B* **2015**, *252*, 2433.