

The Study of Dispersive ‘*b'*’-Mode in Monolayer MoS₂ in Polarization-Resolved Resonant Raman Scattering Experiments

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We report on the study of electron–phonon interaction in monolayer MoS₂ in polarization-resolved Raman scattering experiments as a function of the excitation laser energy (1.96–2.03 eV). In complementary reflectivity contrast measurements we determined the temperature evolution of the *A* exciton resonances. We found that when excitation laser energy is tuned across the *A* exciton level the second order ‘*b'*’ mode shifts almost linearly to lower frequency with the rate equal to -78 and -70 cm⁻¹/eV at $T = 7$ and 295 K, respectively, which is about twice higher rate than those reported in the previous studies of monolayer MoS₂ but very close to the relevant rate recorded for bulk MoS₂. We interpret this effect as related to the difference of concentration of two dimensional electron gas.

DOI: [10.12693/APhysPolA.134.947](https://doi.org/10.12693/APhysPolA.134.947)

PACS/topics: transition metal dichalcogenides monolayers, exciton, phonon Raman scattering

1. Introduction

Transition metal dichalcogenides (TMDCs), such as MoS₂ have attracted a considerable attention due to the fascinating physics and the promising applications in optoelectronics and spintronics [1–3]. In monolayer MoS₂ the bottom of the conduction band and the top of the valence band are located at the binary indexed corners K^+ and K^- of the two-dimensional (2D) hexagonal Brillouin zone (BZ). The lack of inversion symmetry and strong spin–orbit coupling in monolayers of TMDCs results in valley-contrasting spin splitting of the valence and conduction bands. The confinement to a single layer and reduced dielectric screening results in very high Coulomb binding energy of excitons (*X*) of hundreds of meV [4, 5]. In the presence of excess carriers charged excitons, trions (*T*) are observed in optical spectra of TMDC monolayers [6–12].

The resonant Raman scattering (RRS) is widely used to study the electron–phonon interactions and electronic band structures in semiconductor [13]. By changing the incident photon energy different electronic states and different pairs of phonons, within the BZ, are selected in the Raman spectra [14].

The goal of presented work was to study electron–phonon interaction in RRS experiments of monolayer MoS₂. We perform the detailed studies of the RRS spectra of monolayer MoS₂ as a function of exciting laser energy and temperature $T = 7$ –300 K. In complementary RC experiments we determined the temperature evolution of the *A* exciton and trion resonances.

2. Results and discussion

The studied monolayers of MoS₂ were prepared by mechanical exfoliation of bulk crystals grown by chemical vapor transport technique. The details are described in Ref. [8]. The monolayer MoS₂ were deposited on the same Si/SiO₂ (295 nm) target substrate. The RRS measurements were performed using 610–675 nm laser lines of a DCM dye laser. The spectra were analyzed with a 0.5 m focal length spectrometer. The Peltier cooled CCD camera was used as a detector. The reflectivity contrast spectra were measured in the same setup.

We investigated the resonant Raman scattering spectra of monolayer MoS₂ mainly in the vicinity of the Raman active modes E' (in bulk E_{2g}^1) and A_1' (in bulk A_{1g}). Figure 1a presents examples of the Raman spectra at $T = 7$ K and vacuum when the incident photon energy is tuned across the *A* exciton level at 1.964 eV determined from the from the reflectivity contrast spectra presented at Fig. 1c. When the excitation energy is lower than *A* exciton energy the Raman scattering spectrum of monolayer MoS₂ is dominated by two vibrational modes: E' at 384 cm⁻¹ and A_1' at 409 cm⁻¹ (see red spectra at the bottom of Fig. 1a). The E' mode is due to in-plane vibrations of two S atoms with respect to the Mo atom and the A_1' mode results from the out of plane vibrations of S atoms in opposite directions. The broad band at ≈ 460 cm⁻¹ was in previous papers attributed to the overtone of the LA phonon at the *M* point in the Brillouin zone 2LA(*M*) [13]. However, in recent papers Carvalho et al. [15] interpreted this feature as superposition of four different second order scattering processes.

When the incident photon energy is just above the *A* exciton energy (resonant Raman scattering — RRS) an additional mode named in literature as dispersive ‘*b'*’ mode appears in the Raman spectra at 430 cm⁻¹ (see blue line in Fig. 1a) and shifts to lower frequency to A_1'

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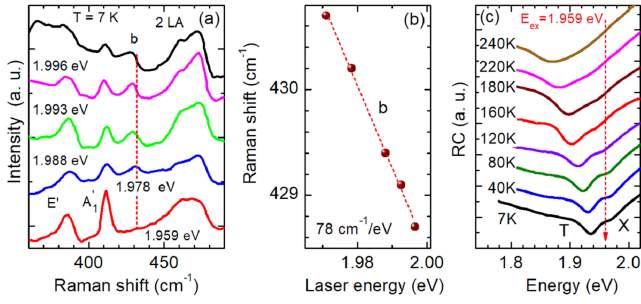


Fig. 1. (a) The Raman scattering spectra of monolayer MoS₂ recorded for various incident photon energies at $T = 7$ K. (b) The evolution of the ‘*b*’ mode as a function of the incident photon energy. (c) The temperature evolution of reflectivity contrast spectra of monolayer MoS₂.

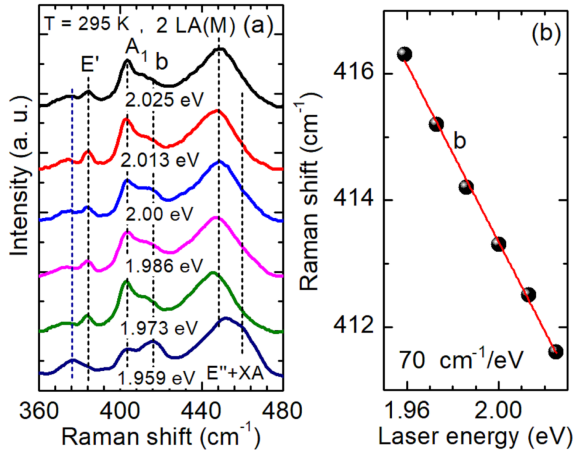


Fig. 2. (a) The Raman scattering spectra of monolayer MoS₂ recorded for various incident photon energies at $T = 7$ K and vacuum. (b) The evolution of the ‘*b*’ mode as a function of the incident photon energy.

phonon line. Figure 1b presents the dependence of the frequency shift of the ‘*b*’ mode as a function of the excitation phonon energy. The $(d\omega/dE)$ shift is almost linear and equal to $-78 \text{ cm}^{-1}/\text{eV}$. The frequencies of E' , A'_1 modes are independent on the excitation phonon energy (not shown). The dependence of the frequency shift E' , A'_1 and ‘*b*’ modes as a function of excitation energy has been obtained by a Lorentzian line-fitting procedure.

In the previous studies Sekine et al. [14] observed the ‘*b*’ mode in the RRS of bulk MoS₂ at $T = 7$ K, with a dispersive behavior near the *A* and *B* excitonic resonances and access it to excitonic polariton scattered by successive emission of a dispersive quasi-acoustic interlayer breathing phonon and a dispersionless phonon E_{1u}^2 , both along the *c* axis and at Γ point of BZ. However, the ‘*b*’ mode was also observed in RRS spectra of monolayer MoS₂ [16], which rules out this interpretation. In the RRS study of bulk MoS₂, Livneh and Spanier [17] interpreted the ‘*b*’ band as the double Ra-

man scattering involving combinations of the acoustic LA’ and TA’ phonons at *K* points of BZ. This interpretation was confirmed recently by Carvalho et al. [15] in the multiple energy excitation Raman study of monolayer and bulk MoS₂.

We performed the similar studies of the Raman scattering spectra of monolayer MoS₂ as a function of the incident phonon energy at room temperature $T = 295$ K. The results are presented in Fig. 2. As at low temperature the energy position of E' and A'_1 phonon modes are independent of excitation photon energy whereas the ‘*b*’ mode shifts almost linearly to lower frequency with the $(d\omega/dE)$ rate equal to $-70 \text{ cm}^{-1}/\text{eV}$, close to those at $T = 7$ K.

We now discuss the nature of the dispersive ‘*b*’ mode in the monolayer of MoS₂. Surprisingly, in our studies of the resonant Raman scattering spectra of monolayer MoS₂ the frequency shift of the ‘*b*’ mode as a function of the incident photon energy, equal to -78 and $-70 \text{ cm}^{-1}/\text{eV}$ at $T = 7$ and 295 K, respectively, is very close to those obtained in the similar studies of bulk crystals, equal to $\approx -80 \text{ cm}^{-1}/\text{eV}$ at $T = 7$ K [14] and almost twice higher than those recently reported by Carvalho et al. [15] for monolayer MoS₂ equal to $\approx 40 \text{ cm}^{-1}/\text{eV}$ at $T = 295$ K. The interpretation of ‘*b*’ mode in Ref. [17] as related to acoustic LA and TA phonons at *K* valleys was based on the comparison of experimental and numerical data. Carvalho et al. [15] claim that the dispersion of the numerically calculated LA and TA phonons at *K* valleys are very close to that obtained for dispersion of ‘*b*’ mode in experiment. To confirm our interpretation we performed resonant excitation polarization resolved simultaneous photoluminescence and Raman scattering measurements. Results are presented in Fig. 3a. For resonant (1.9974 eV) excitation we can distinguish in the PL spectrum two dominant, spectral lines at 1.9485 eV and 1.9119 eV, attributed to the free exciton X and trion T emission, respectively. In addition, Fig. 3b shows the comparison of helicity-resolved Raman spectra in the vicinity of the Raman active mode A'_1 , obtained by subtracting the emission in the corresponding PL spectral range, marked by dashed rectangle. It is clearly seen that the first order out-of-plane A'_1 mode is visible only in $\sigma^+\sigma^+$ configuration, whereas the ‘*b*’ mode is detected only in the spectra of opposite helicity $\sigma^+\sigma^-$. This confirms that ‘*b*’ mode is a combination of LA and TA phonons [18].

Twice higher dispersion of ‘*b*’ mode obtained in our experiments in comparison to those obtained by Carvalho et al. points out that the dispersion of ‘*b*’ mode is influenced by additional interaction. It is well known that the Raman spectra of transition metal dichalcogenides are strongly dependent on two-dimensional (2D) electrons (or holes) gas concentration [19]. With the increase of 2D electron gas concentration some Raman resonances shift to lower or higher energy, which reflects different degree of the electron-phonon interaction. In our studies we have evaluated the 2D electron gas concentration from the RC spectra as equal to $n = 1.9 \times 10^{12} \text{ cm}^{-2}$ [9].

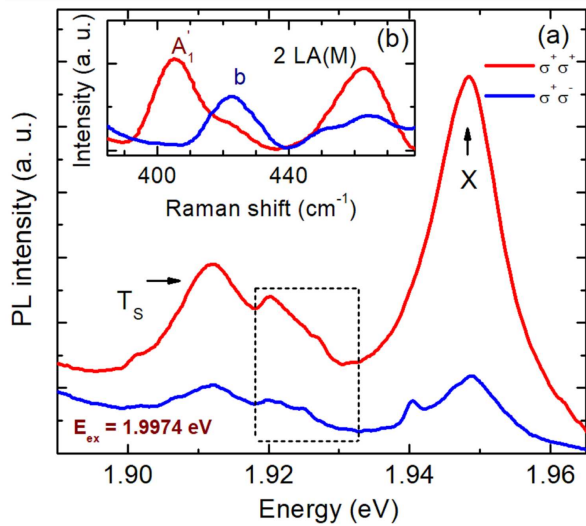


Fig. 3. (a) Helicity resolved resonant (1.9974 eV) PL spectra of monolayer MoS₂ recorded at $T = 7$ K. (b) Comparison of the helicity-resolved Raman spectra, obtained by subtracting the emission from the corresponding PL spectra in part (a).

In Ref. [15] the 2D electron gas concentration is not measured but is very likely that was strongly different than those measured in our MoS₂ monolayer. The concentration of 2D carrier gas strongly depend on native defects and methods of monolayer preparation [20]. We assume that the difference in 2D electron gas concentration in both experiments explains twice higher dispersion of 'b' mode as a function of the excitation phonon energy in our experiments. This conclusion awaits the confirmation in future theoretical and experimental study, especially in the gated monolayer MoS₂ structures where 2D electron gas concentration can be controlled.

3. Conclusion

To conclude, we present the study of resonant Raman scattering spectra of monolayer MoS₂ as a function of exciting laser frequency. In complementary reflectivity contrast (RC) experiments we determined the temperature evolution of the exciton and trion lines. We focus our studies on the dispersive, second order scattering 'b' mode. In comparison of our studies of RRS spectra of the MoS₂ monolayers with the previous studies of MoS₂ monolayers and bulk crystals we pointed out the role of mediation of the two-dimensional electron gas in the electron-phonon interaction.

Acknowledgments

This work was partly supported by the Polish Taiwanese Joint Research OSTMED PL-TWII/5/2015.

References

- [1] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, *Phys. Rev. Lett.* **105**, 136805 (2010).
- [2] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nature Nanotechnol.* **6**, 147 (2011).
- [3] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, *Nature Nanotechnol.* **7**, 699 (2012).
- [4] K. He, N. Kumar, L. Zhao, Z. Wang, K.F. Mak, H. Zhao, J. Shan, *Phys. Rev. Lett.* **113**, 026803 (2014).
- [5] A. Chernikov, T.C. Berkelbach, H.M. Hill, A. Rigosi, Y. Li, O.B. Aslan, D.R. Reichman, M.S. Hybertsen, T.F. Heinz, *Phys. Rev. Lett.* **113**, 076802 (2014).
- [6] J.S. Ross, S. Wu, H. Yu, N.J. Ghimire, A.M. Jones, G. Aivazian, J. Yan, D.G. Mandrus, D. Xiao, W. Yao, X. Xu, *Nature Commun.* **4**, 1474 (2013).
- [7] T. Godde, D. Schmidt, J. Schmutzler, M. Aßmann, J. Debus, F. Withers, E.M. Alexeev, O. Del Pozo-Zamudio, O.V. Skrypka, K.S. Novoselov, M. Bayer, A.I. Tartakovskii, *Phys. Rev. B* **94**, 165301 (2016).
- [8] J. Jadczyk, A. Delgado, L. Bryja, Y.S. Huang, P. Hawrylak, *Phys. Rev. B* **95**, 195427 (2017).
- [9] J. Jadczyk, J. Kutrowska-Girzycka, P. Kapuściński, A. Wójs, L. Bryja, *Nanotechnology* **28**, 395702 (2017).
- [10] M.R. Molas, K. Nogajewski, A.O. Slobodeniuk, J. Binder, M. Bartos, M. Potemski, *Nanoscale* **9**, 13128 (2017).
- [11] T. Smoleński, T. Kazimierzczuk, M. Goryca, M.R. Molas, K. Nogajewski, C. Faugeras, M. Potemski, P. Koszacki, *2D Mater.* **5**, 015023 (2018).
- [12] D. Van Tuan, B. Scharf, I. Žutić, H. Dery, *Phys. Rev. X* **041040**, 1 (2017).
- [13] J. Maultzsch, S. Reich, C. Thomsen, *Phys. Rev. B* **70**, 155403 (2004).
- [14] T. Sekine, K. Uchinokura, T. Nakashizu, E. Matsuura, R. Yoshizaki, *J. Phys. Soc. Jpn.* **53**, 811 (1984).
- [15] B.R. Carvalho, Y. Wang, S. Mignuzzi, D. Roy, M. Terrones, C. Fantini, V.H. Crespi, L.M. Malard, M.A. Pimenta, *Nature Commun.* **8**, 14670 (2017).
- [16] K. Gołasa, M. Grzeszczyk, P. Leszczyński, C. Faugeras, A.A.L. Nicolet, A. Wyszomolek, M. Potemski, A. Babiński, *Appl. Phys. Lett.* **104**, 092106 (2014).
- [17] T. Livneh, J.E. Spanier, *2D Mater.* **2**, 035003 (2015).
- [18] S.Y. Chen, C. Zheng, M.S. Fuhrer, J. Yan, *Nano Lett.* **15**, 2526 (2015).
- [19] B. Miller, E. Parzinger, A. Vernickel, A.W. Holleitner, U. Wurstbauer, *Appl. Phys. Lett.* **106**, 122103 (2015).
- [20] Y.-C. Lin, T. Björkman, H.-P. Komsa, P.-Y. Teng, C.-H. Yeh, F.-S. Huang, K.-H. Lin, J. Jadczyk, Y.-S. Huang, P.-W. Chiu, A.V. Krasheninnikov, K. Sue-naga, *Nature Commun.* **6**, 6736 (2015).