Investigation of energy transitions in MoS$_2$
by photoreflectance spectroscopy method

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Abstract. Photoreflectance spectroscopy was used to study the energy spectra of natural molybdenum disulfide samples at various temperatures. Measurements using Fourier transform infrared spectrometer make it possible to observe a fine structure in the photoreflectance spectra which appears due to transitions involving excited excitonic states. The K-exciton binding energy obtained from our experiments is about 90 meV. In addition, an optical transition involving the excited state from the H-point of the Brillouin zone was observed, and the corresponding H-exciton binding energy was found to be 77 meV.

1. Introduction
Molybdenum disulfide is a layered semiconductor compound with strong covalent bonds within the plane, and weak van-der-Waals bonds between the triple-layers (S-Mo-S). Today MoS$_2$ is one of the most studied graphene-like materials, however it did not lose its relevance for research [1]. It is also a good model object, which can be used for refinement of experimental techniques intended for further characterization of less studied layered semiconductors. In this work, we apply the photoreflectance (PR) spectroscopy method to probe the weak features of MoS$_2$ band structure.

2. Experiment
The current study has been conducted on natural MoS$_2$ crystals obtained from “2D Semiconductors” (USA). PR spectroscopy is an optical method that provides information about the main transitions in the energy spectrum of a semiconductor material. The measurements were carried out using both the classical grating spectrometer (figure 1 (a)) according to the “dark configuration” (where photomodulated reflectance of the monochromatic probe beam was recorded from the sample placed in the dark), and using the setup based on the Fourier transform infrared (FTIR) spectrometer [2].

![Figure 1. The photoreflectance spectra (ΔR/R) of natural MoS$_2$ measured at 80 K using the grating spectrometer (a) and the Fourier transform infrared (FTIR) spectrometer (b).](image-url)
In the latter case (figure 1 (b)), the measurements were carried out according to the “bright configuration” (a probe beam of “white” light from the Michelson interferometer was reflected from the sample). In both cases, a modulated highly stable violet (405 nm) semiconductor laser was used as the source of the second (modulating) beam. Typically, the PR spectra consist of derivative-like features, from which the values of the transition energies can be obtained using the transformation method described by Hosea in [3]. Examples of the transformation of our PR spectra are shown in figure 2 (a, b). It can be seen that only four spectral features were recorded with the help of the grating spectrometer (figure 2 (a)).

![Figure 2(a, b). The transformed (by the method from [3]) PR spectra from figure 1(a, b) with the energy transitions marked by arrows.](image)

Note that the FTIR-based setup [2] proved to be a powerful tool not only in IR, but also in the visible spectral range. A total of seven spectral features, including very weak ones, have been observed quite clearly in each of the PR measurements at various temperatures: 80, 120 and 160 K. At higher temperatures, only three spectral features were observed: E₁, E₂ and E₆. Since the PR spectra measured with the FTIR setup are more informative, we will consider them further.

### 3. Results and Discussions

To interpret the transitions observed in the PR spectra, we have considered two approaches, described in refs. [4] and [5]. Both hypotheses identify E₁ as the first ground state exciton (A) at the K-point (figure 3) of the Brillouin zone [6]. This state has a spin-orbit split valence band (figure 4), which is also exhibited in the spectrum as a B transition (the E₆ peak in figure 2(a, b)). However, the two hypotheses considered provide a different interpretation of the remaining extrema.

According to the first model [4], features with energies from E₂ to E₄ could be related to the excited states of the K-exciton. The exciton energy levels were estimated according to the well-known expression: \( A_n = E_g - E_b/n^2 \). When choosing the corresponding values of the band gap (\( E_g \)) and the binding energy of the exciton (\( E_b \)), the obtained values are the following: 1.930 eV, 1.972 eV, 1.980 eV and 1.982 eV. This could be sufficient to describe the first two of the observed extrema (see the table 1), but not the third and the fourth one. This model is not at all suitable for interpretation the E₅ energy peak. Its remoteness from the E₆ feature suggests that the E₅ maximum does not apply to the excited states of the K-exciton and the nature of its appearance is different. The PR spectrum measured at 300 K also confirmed the inapplicability of the first model. The temperature increase lead to the disappearing of the excited states (E₃ – E₅) that were exhibited at 80-160 K, whereas the E₂ feature amplitude was comparable with the E₁ peak.
Figure 3. The Brillouin zone of bulk MoS$_2$ with several points of high symmetry indicated.

Figure 4. Schematic excitonic energy diagram and transitions around the K- and H-point of the Brillouin zone.

The other model, which has been put forward by Saigal and Ghosh [5], is able to explain the large amplitude of E$_2$ and the existence of the E$_5$ feature. The authors describe the E$_2$ energy peak as the exciton ground state transition, but at the H-point of the Brillouin zone instead of the K-point (figure 4). Our observed difference between the transition energies at K- and H-points of the valence band ($\Delta E$) is equal to 42 meV, whereas the spin-orbit splitting is $\Delta E_{b} = 209$ meV and $\Delta E_{b}^{*} = 191$ meV for K- and H-points, respectively. The obtained values are close to the data that were published in [5], but the E$_5$ peak was not resolved in their PR spectra. We assume that this peak corresponds to the first excited state of the H-point exciton. This makes it possible to obtain the H-exciton binding energy ($E_{b}^{*}$) from our PR spectrum, which is found to be 77 meV.

So, the E$_3$ and E$_4$ energy transitions are the excited states A$_2$ and A$_3$ of the K-point exciton. The binding energy value calculated from the PR spectrum was obtained as follows: $E_{b} = \frac{4}{9}[A_2 - A] \approx 90.7$ meV, and $E_{b} = \frac{9}{8}[A_3 - A] \approx 90$ meV.

Table 1. Experimental values of the energy transitions (T = 80K) and their interpretation.

|   | E$_1$ | E$_2$ | E$_3$ | E$_4$ | E$_5$ | E$_6$ | E$_7$ |
|---|------|------|------|------|------|------|------|
| Energy, eV | 1.930 | 1.972 | 1.998 | 2.010 | 2.029 | 2.139 | 2.163 |
| Interpretation | A | A* | A$_2$ | A$_3$ | A$_2$* | B | B* |

In the work [7], the authors estimated from the absorption spectrum simulation that the K-exciton binding energy should be $84 \pm 8$ meV. It can be seen that our experimental results fall within the predicted range.

4. Conclusions
As a result, we were able to describe the E$_5$ feature in the PR spectrum of MoS$_2$ for the first time, which corresponded to the transition to the excited level of the H-exciton ground state (E$_2$). Its presence in the PR spectrum confirms an existence of the optical transitions at the H-point of the Brillouin zone. This fact enabled us to experimentally determine the H-exciton binding energy, which turned out to be 77 meV. In addition, we observed two excited states of the K-exciton (E$_3$ and E$_4$). They were well described by the expression for the excitonic series and allowed us to refine the binding energy of the K-exciton, which was about 90 meV.
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References
[1] Robert C, Semina M A, Cadiz F, Manca M, Courtade E, Taniguchi T, Watanabe K, Cai H, Tongay S, Lassagne B, Renucci P, Amand T, Marie X, Glazov M M, Urbaszek B 2018 Phys. Rev. Mat. 2 011001(R)
[2] Komkov O S, Firsov D D, Lvova T V, Sedova I V, Semenov A N, Solov’ev V A, Ivanov S V 2016 Physics of the Solid State 58 2394
[3] Hosea T J C 1995 Phys. Stat. Sol. (b) 189, 531
[4] Evans B, Young P 1965 Proc. R. Soc. Lond. A 284 402
[5] Saigal N, Ghosh S 2015 Appl. Phys. Lett. 106 182103
[6] Kasowski R V 1973 Phys. Rev. Let. 30 1175
[7] Saigal N, Sugunakar V, Ghosh S 2016 Appl. Phys. Lett. 108 132105