## Energy gap determination from photoacoustic spectroscopy measurements

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Photoacoustic spectroscopy (PAS) is a powerful technique to investigate the basic physical properties of semiconducting materials, e.g., thermal diffusivity, heat capacity, electron-trapping sites, energy gap, and so on. Moreover, PAS is a method that allows obtaining an optical absorption based on a sound wave emitted by a semiconducting sample. That sound wave is formed due to a periodic heat generation in the sample, which subsequently causes pressure changes in a surrounding gas detected by an acoustic transducer [1]. This method does not require any special sample preparation and allows examining materials even in powdered form, which is not possible for other absorption-like methods. However, so far, no in-depth studies comprehensively approach such issues as how sample size and thickness influence the photoacoustic signal. Here we address the questions mentioned above. All the experiments were carried out on molybdenum disulfide ( $MoS_2$ ) since its properties are well-known, and it is easy to exfoliate  $MoS_2$  crystal to obtain thinner samples.

In the first step, we investigated how the thickness of  $MoS_2$  influenced the photoacoustic signal. Surprisingly when the sample is thinner, more signal is generated during PAS measurements (see Fig. 1a). Moreover, it is clearly visible in Fig. 1a that the energy gap determined from the knee method (see gray lines) is blue-shifted, going from the thick to thin samples. For the thickest  $MoS_2$  crystals, we observed that the obtained energy is close to the indirect band gap at 1.2 eV, while for the thinnest  $MoS_2$ , the energy is around the lowest direct optical transition (~1.8 eV). The second issue on which we focused is the sample size. In Fig. 1b, we showed photoacoustic amplitude for different sample sizes. All values of the PAS signal were taken at 1.9 eV (saturation area). It can be seen that signal slowly increases when reducing the sample size and then starts to drop quicker, following a linear trend as shown by a straight cyan line (inset of Fig. 1b). As mentioned, below certain sample size signal decreases, which is expected since the less light is absorbed and the signal from smaller volume is generated. In our studies, we will provide a tentative explanation for observed behavior.

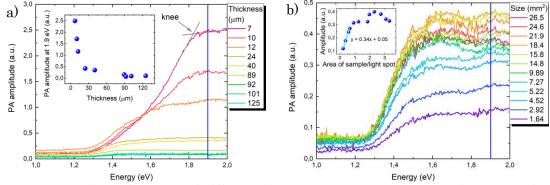


Figure 1. (a) PAS signal for  $MoS_2$  of different thicknesses. Inset shows PA amplitude taken from 1.9 eV (blue line), gray lines shows knee, and (b) PAS signal for a samples of various size. Inset shows PA amplitude against area of sample/light spot taken at 1.9 eV (blue line). The Cyan line in inset represents linear fit.

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