Few-layered materials have dramatically different properties from their bulk phase. Their tunable optoelectronic characteristics are largely governed by the interactions between the vertically stacked layers, and are affected by the number and orientation of the layers. The vibrations corresponding to these interlayer interactions, known as shear modes, manifest as low frequency Raman peaks very close to the laser Rayleigh line, which are not detected by traditional Raman spectroscopy. Using low frequency/THz-Raman® however, the shear modes have been easily measured for transition metal Dichalcogenide (TMD) materials, enabling clear, unambiguous measurement of both the number and orientation of layers.

**THE ONDAX THz-RAMAN® SOLUTION**

Ondax THz-Raman® systems extend the range of traditional Raman spectroscopy to the THz/low frequency Raman regime, where lattice modes that correlate to material structure are found and inter-layer modes can be clearly and quickly observed. While conventional Raman spectra might hint at similar information, the spectra are often indirect and not easily verified using ab-initio simulations. In this example, a sample of MoSe$_2$ with a distribution of two different relative orientations of the two layers was studied (Figure 1). The Raman spectral data presented here were collected with excitation at 532 nm using an Ondax TR-MICRO-532 THz-Raman® system connected to a single-stage spectrometer with a spectral resolution of 1.5 cm$^{-1}$. Normalized THz-Raman® spectra of the two orientations of MoSe$_2$ are shown in Figure 2.

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**Fig. 1 Generalized chemical structure of TMDs, showing the metal (grey) and chalcogenide (yellow) atoms, adapted from S. Mouri, K. Matsuda et al., Nano Lett. 13, (2013) 5944 (Top). Optical Micrographs (100x) of two layer MoSe$_2$ substrates. Red dot indicates the approximate location of the Raman measurement (Bottom).†**

**Fig. 2 Normalized THz-Raman® spectra of two-layer MoSe$_2$ materials showing the corresponding shift and change in magnitude of the peak corresponding to the bulk mode at 242 cm$^{-1}$ (Left) and the shear mode peak at 18 cm$^{-1}$ (Right)**

†The MoSe$_2$ sample was synthesized and characterized at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory (X. Li, A.A. Puretzky; see ACS Nano 9, 6333-6342 (2015) for details).
THz-Raman® Analysis

The Raman spectra in Figure 2 illustrate that regardless of orientation, both the two-layer MoSe$_2$ materials show an out-of-plane bulk mode as a peak at 242 cm$^{-1}$ in the Raman spectrum. The shear modes at 18 cm$^{-1}$ are not present for single layer MoSe$_2$. The opposing two-layer MoSe$_2$ case has a shear mode peak at 18.9 cm$^{-1}$ as determined by a center of mass analysis. When the MoSe$_2$ layers are oriented to be concentric, the peak undergoes a bathochromic shift to 18.4 cm$^{-1}$ and a large change in the intensity of the peak. This demonstrates that THz-Raman® spectroscopy provides direct information about the number and orientation of the layers in 2D materials.

While atomic force and scanning tunneling microscopies can be used determine the exact atomic registration between different layers, they are slow techniques and require expensive instrumentation and off-line analysis. For rapid prototyping of two dimensional materials, THz-Raman® provides a fast, non-destructive and cost-effective solution.

Ondax’s patented THz-Raman® spectroscopy systems extend the range of traditional Raman spectroscopy into the THz/low-frequency regime, enabling simultaneous analysis of both molecular structure and chemical composition for advanced materials characterization. All THz-Raman® systems are compact, robust, plug-and-play platforms that deliver incredible speed, throughput and ease of use, all at an extremely affordable price. With a broad selection of excitation wavelengths from 488 nm to 1064 nm, optional polarization control and a wide variety of sample interfaces, there is a THz-Raman® solution for any application.

Direct measurement of inter-layer vibrations in few-layered materials
Works with small traces of materials.

Quantitative analysis number of layers.

Direct correlation of orientation with peaks positions and magnitude.

Sensitivity to defects and dopants in the 2D material structure.

Simultaneous chemical and structural analysis.

Directly calculate THz-Raman® spectra using ab-initio calculations.

850 E. Duarte Rd. Monrovia, CA 91016
626.357.9600 (Tel)
626.513.7494 (Sales Fax)

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