

# **Appendices**

## Appendix I

### Physical properties of selected TMDCs (WS<sub>2</sub>)

Material	WS <sub>2</sub>	MoS <sub>2</sub>
<b>Molar mass</b>	247.98 g/mol	160.07 g/mol
<b>Density</b>	7.5 g/cm <sup>3</sup> (25 °C)	5.06 g/cm <sup>3</sup>
<b>Solubility in water</b>	Slightly soluble	Insoluble
<b>Melting point</b>	1250 °C	1185 °C
<b>Crystal structure</b>	Hexagonal	Hexagonal
<b>Lattice parameters (at 300 K)</b>	a=b= 3.15 Å and c=12.27 Å (2H)	a = b= 3.16 Å (2H), 3.163 Å (3R), c = 12.295 Å (2H), 1.837 (3R) Å
<b>Appearance</b>	Blue-grey powder	Black powder
<b>Band gap (at 300 K)</b>	1.4 eV for bulk form (indirect) 1.9 eV for monolayer form (direct)	1.2 eV for bulk form (indirect) 1.8 eV for monolayer form (direct)

## Appendix II

### Stokes, anti-Stokes and Rayleigh Scattering

When photons from an excitation source collide with a molecule, the molecule is excited and jumps to a short lived virtual state. However within a very short time it relaxes back to the lowest vibrational state by emitting photons. Most of the emitted photons have the same energy ( $h\nu_0$ ) as the incident photons. Such type of elastic scattering is called Rayleigh scattering. Few photons are emitted with energy ( $h\nu_0 - h\nu_m$ ) less than that of the incident photons ( $h\nu_0$ ). In this case, the scattering is called as Stokes scattering. Very few photons are scattered with energy greater ( $h\nu_0 + h\nu_m$ ) than that of the incident photon. This scattering type is called anti-Stokes scattering. The energy diagrams of Stokes, Rayleigh, and anti-Stokes Raman scattering is shown in the figure below.

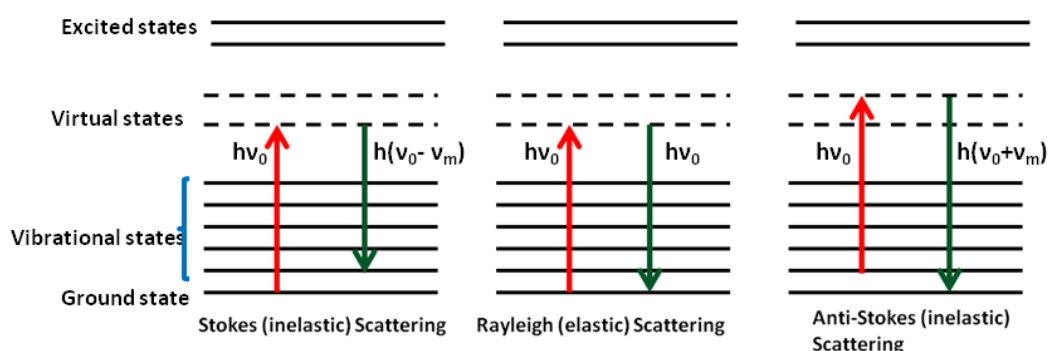


Figure 1: Energy diagrams of Stokes, Rayleigh, and anti-Stokes Raman scattering.

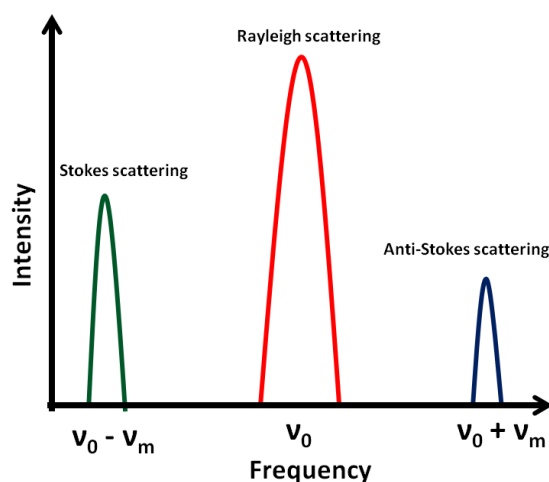


Figure 2: Raman spectrum showing Stokes, Rayleigh and Anti-Stokes lines

### Appendix III

#### Working of a tribometer:

The method of study adopted for the measurement of tribological properties of WS<sub>2</sub>/PVA nanocomposites is the Ball on three plate method. In contrast, the tribological behavior was assessed by a Twinedrive™ Rheometer (Anton Paar, MCR 702). A schematic diagram of the set up used for the measurement is shown in Fig.3. In this set up, a ball of steel of diameter 12.7 mm is pressed with a normal force ( $F= 10$  N) against three plates that are mounted on a movable stage. The ball is made to rotate with an increasing sliding speed while the plates are kept stationary at rest. This generates three sliding point contacts. The value of coefficient of friction is measured against the sliding/rotational velocity.

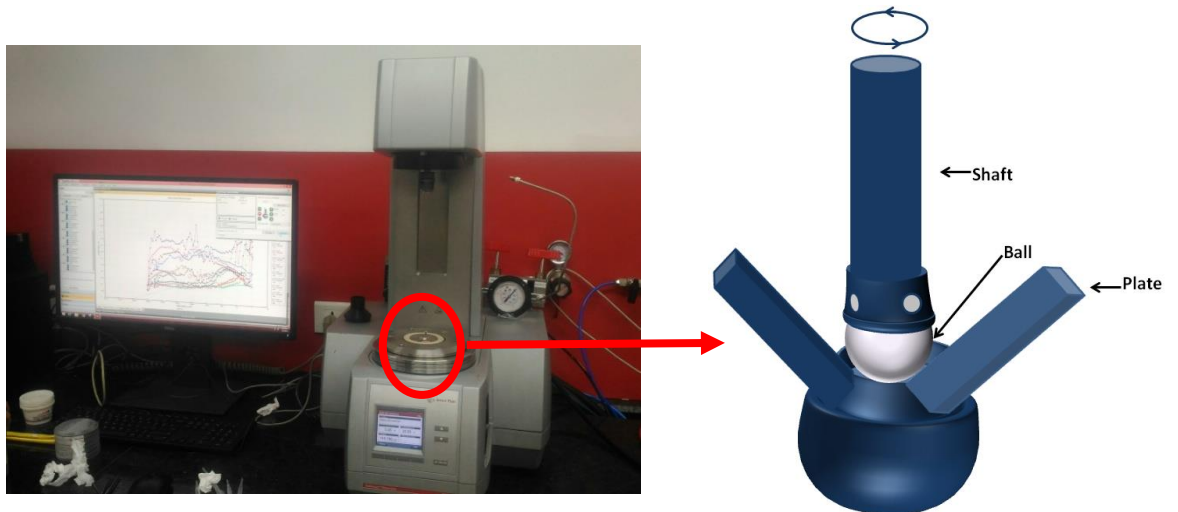


Figure 3: Ball on three plates arrangement (Twinedrive™ Rheometer, Anton Paar MCR-702) performed at Anton Paar Pvt. Limited Headquarter at Gurugram, Haryana, India.

## Appendix IV

### SRIM calculation

Using the SRIM calculation the values of  $S_e$  and  $S_n$  have been calculated for  $TiS_2$ ,  $MoS_2$  and  $WS_2$ , using Oxygen and Xenon as the energetic ions. The respective plots are given below:

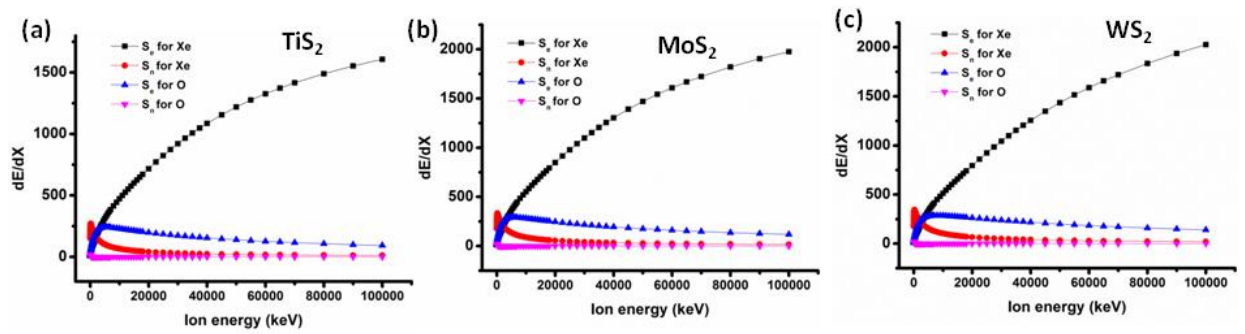


Figure 4: The  $S_e$  and  $S_n$  values vs ion energy curves for (a)  $TiS_2$ , (b)  $MoS_2$  and (c)  $WS_2$

## Appendix V

### TRIM calculations

TRIM simulation of the trajectories, ion range and lateral distribution of 80 keV  $\text{Xe}^+$  ions in  $\text{WS}_2$  material are shown in Fig. 4, The ions are found to penetrate well inside the material as shown in Fig.4(a) The energetic ions do not follow the straight path due to elastic collisions but forms a collision cascade as a result of successive recoil process..

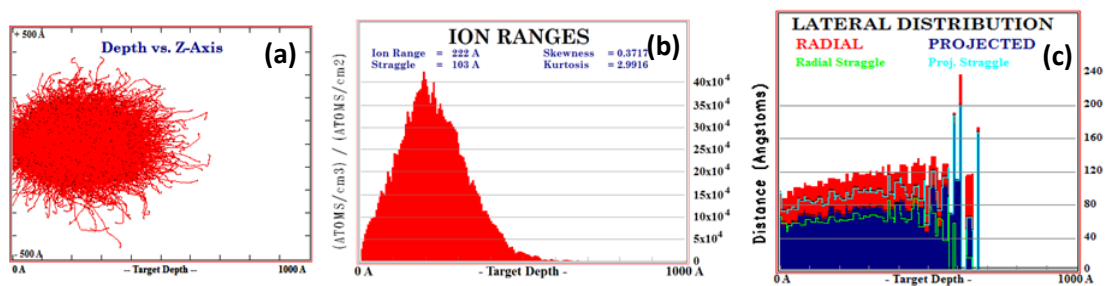


Figure 5: TRIM calculations (a) depth profile of 80 keV  $\text{Xe}^+$  ions in  $\text{WS}_2$ , (b) ion range along the target depth, and (c) lateral distribution of ions inside the target.

## Appendix VI

### Franck Condon principle:

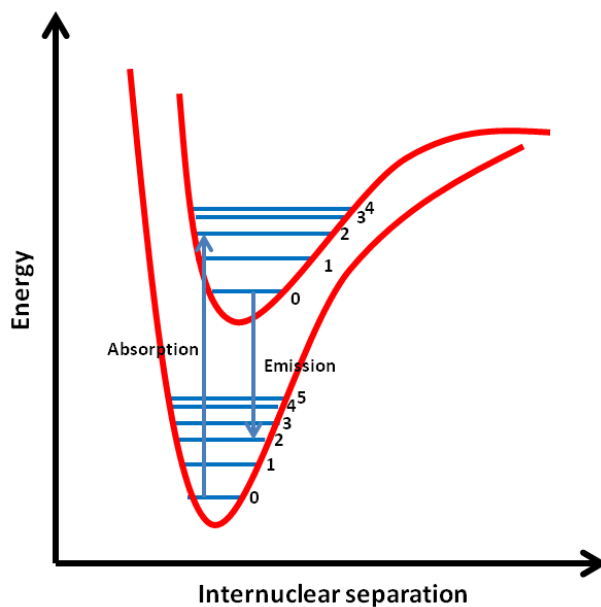


Figure 6: Potential energy curves for the ground state and an excited state of a diatomic molecule

According to Franck Condon principle, the transition between different vibrational states should be represented by vertical lines. This is due to the fact that electrons move much faster than the nuclei of molecules. This means the intermolecular distance of a vibrating molecule does not change appreciably during the transition between two electronic states, thus allowing the transition to be represented by vertical line.

As shown in figure, a transition is shown from the lowest vibrational level of the ground electronic state of the molecule to an excited vibrational level of an upper electronic state. The molecule then may lose vibrational energy through collision with other molecules and reach the lowest vibrational level of the excited state. This process is often more rapid than the spontaneous emission of radiation. So when the molecule finally reemits radiation, it is from the lowest vibrational level of the excited state. Thus the fluorescence radiation is of lower frequency than the absorbed radiation.

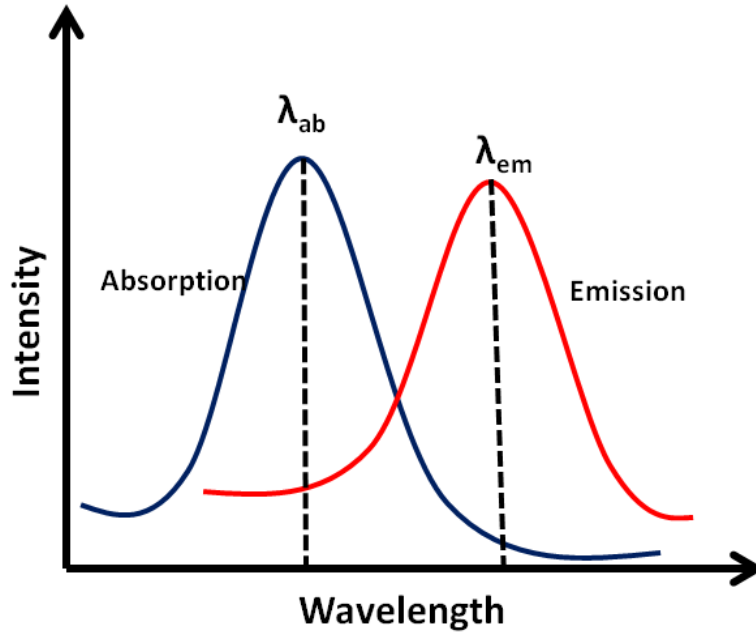


Figure 7: Schematic representation of absorption and emission spectra

The experimental observation that the fluorescence wavelength is longer than the excitation wavelength can be described by Stokes shift which is given by,

$$\Delta = \frac{hc}{\lambda_{ab}} - \frac{hc}{\lambda_{em}} = 2S_p \hbar\omega_{LO},$$

where,  $\lambda_{ab}$  and  $\lambda_{em}$  characterize the associated wavelengths of absorption and emission maxima; respectively. Also,  $\hbar$  is the reduced Planck's constant,  $\omega_{LO}$  is the longitudinal optical (LO) phonon frequency and  $S_p$  is the electron-phonon (e-ph) coupling constant.

$S_p > 1$  for strong e-ph interaction

$S_p < 1$  for weak e-ph interaction