Supporting Information

Composition-Dependent Raman Modes of $Mo_{1-x}W_xS_2$ Monolayer Alloys

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1. Detailed MREI model analysis of $Mo_{1-x}W_xS_2$ monolayer alloys

According to isodisplacement and randomness assumptions, for out-of-plane A'_1 Raman active mode of the mixed $Mo_{1-x}W_xS_2$ monolayer alloys, Mo and W atoms remain stationary. The top-layer and bottom-layer S atoms vibrate in opposite phases, but with the same amplitude. The S-S interaction can be ignored. The equation of motion for the S atoms can be written as

$$m_s\ddot{\mu}_s = -(1-x)F_1\mu_s - xF_2\mu_s, \quad (1)$$

where m_s and μ_s are mass and displacement of the S atoms. The terms F_1 and F_2 are force constants representing interactions between S-Mo, S-W along the vertical direction (see Figure 5a), respectively. These force constants depend on lattice parameters and therefore on W composition *x*. Here, the functional dependence of the force constants is assumed to be linear with composition *x*

$$\frac{F_1}{F_{10}} = \frac{F_2}{F_{20}} = 1 - \theta_1 x \quad (2)$$

where F_{10} and F_{20} are the limiting values of force constants F_1 and F_2, respectively, as x→0. The parameter θ_1 take into account the variation of force constants. In the long-wavelength limit, given $\ddot{\mu}_s = Ae^{i\omega t}$ in equation（1）, ω^2 can be given by

$$\omega^2 = \frac{(1-x)F_1 + xF_2}{m_s} \quad (3)$$

Since the MREI-model must be at least valid at *x*=0 and *x*=1, applying boundary conditions to equation (3) gives

at *x*=0

$$\omega = \left(\frac{1}{m_s}F_{10}\right)^{1/2} = \omega(MoS_2), \quad (4)$$

at *x*=1

$$\omega = \left[\frac{1}{m_s}F_{20}(1-\theta_1)\right]^{1/2} = \omega(WS_2) \quad (5)$$

Equations (4) and (5) are the A'_1 mode frequencies of end samples MoS_2 and WS_2. The solution of equation (3) can be written as

$$\omega^2 = \frac{(1-x)(1-\theta_1 x)F_{10} + x(1-\theta_1 x)F_{20}}{m_s} \tag{6}$$

The equation (6) was used to fit the experimental data points of A'_1 mode frequencies using least squares fitting in Figure 3a.

For in-plane Raman active E′ mode of the $Mo_{1-x}W_xS_2$ monolayer alloys, the S atoms vibrate like a rigid unit in the same phase and with identical amplitude. The Mo and W atoms vibrate in the phase opposite to S atom sheets. Here, the functional dependence of the force constants is assumed to be nonlinear with composition *x*, which is different from the linear assumption as reported in previous MREI-model applications.

$$\frac{F_3}{F_{30}} = \frac{F_4}{F_{40}} = \frac{F_5}{F_{50}} = 1 - \theta_2 x - \theta_3 x^2 \tag{7}$$

The equations of motion for the three type of atoms (Mo, W and S) are written as

$$m_s \ddot{\mu}_s = -(1-x)F_3(\mu_s - \mu_{Mo}) - xF_4(\mu_s - \mu_W) \tag{8}$$

$$m_{Mo} \ddot{\mu}_{Mo} = -2F_3(\mu_{Mo} - \mu_s) - xF_5(\mu_{Mo} - \mu_W) \tag{9}$$

$$m_W \ddot{\mu}_W = -2F_4(\mu_W - \mu_s) - (1-x)F_5(\mu_W - \mu_{Mo}) \tag{10}$$

where m_s, m_{Mo} and m_W are the mass of S, Mo and W atoms, respectively. μ_s, μ_{Mo} and μ_W are the displacement of S, Mo and W atoms, respectively.The terms F_3, F_4 and F_5 are force constants representing interactions between S-Mo, S-W and Mo-W along the horizontal direction(as shown in Figure 4a), respectively. The parameters θ_2 and θ_3 take into account the variation of force constants. F_{30}, F_{40} and F_{50} are the limiting values of force constants F_3, F_4 and F_5, respectively. First we define $U_1 = \mu_s - \mu_{Mo}$, $U_2 = \mu_s - \mu_W$

(8)-(9), (8)-(10) give

$$\ddot{U}_1 = -R_1 U_1 - R_{12} U_2 \tag{11}$$

$$\ddot{U}_2 = -R_{21} U_1 - R_2 U_2 \tag{12}$$

where

$$R_1 = \frac{(1-x)F_3}{m_s} + \frac{2F_3}{m_{Mo}} + \frac{xF_5}{m_{Mo}}$$

$$R_2 = \frac{xF_4}{m_s} + \frac{2F_4}{m_W} + \frac{(1-x)F_5}{m_W}$$

$$R_{12} = \frac{xF_4}{m_S} - \frac{xF_5}{m_{Mo}}$$

$$R_{21} = \frac{(1-x)F_3}{m_S} - \frac{(1-x)F_5}{m_W}$$

We define $U_1 = u_1 e^{i\omega t}$, $U_2 = u_2 e^{i\omega t}$ and substitute them into equations(11) and (12), then we obtain

$$-\omega^2 u_1 = -R_1 u_1 - R_{12} u_2$$

$$-\omega^2 u_2 = -R_{21} u_1 - R_2 u_2$$

The eigen frequencies are determined by the following equation

$$\begin{vmatrix} -\omega^2 + R_1 & R_{12} \\ R_{21} & -\omega^2 + R_2 \end{vmatrix} = 0 \tag{13}$$

ω^2 can be written as

$$\omega^2 = \frac{R_1 + R_2 \pm \sqrt{(R_1 - R_2)^2 + 4R_{12}R_{21}}}{2} \tag{14}$$

Finally, we substitute R_1, R_2, R_{12} and R_{21} defined in equation (11) and (12) into equation (14), ω^2can be given as

$$\omega^2 = \frac{1}{2}\left\{\frac{(1-x)\left(1-\theta_2 x-\theta_3 x^2\right)F_{30}}{m_s}+\frac{2\left(1-\theta_2 x-\theta_3 x^2\right)F_{30}}{m_{Mo}}+\frac{x(1-\theta_2 x-\theta_3 x^2)F_{50}}{m_{Mo}}+\right.$$

(15)

The equation (15) was used to fit our experimental data of MoS_2-like and WS_2-like E′ mode frequencies using least squares fitting (Figure 4b). Finally, substituting the fitted parameters into equation (6) and (15), we get

$$\omega_{A_1'}^2 = 256.4x^2 + 12862.6x + 161311.0, \quad (16)$$

$$\omega_{MoS_2-like\,E'}^2 = 3196.88x^3 - 15858.4x^2 + 10830.9x + 1329(\quad (17)$$

$$\omega_{WS_2-like\,E'}^2 = 3196.88x^3 - 15858.4x^2 + 10830.9x + 1329(\quad (18)$$

2. MREI-model calculation of E′ mode based on linear dependence of force constants as composition (this gives a poor fitting of WS_2-like E′)

Similarly, if the functional dependence of force constants on composition x is assumed to be linear, for in-plane Raman active E′ mode of the mixed $Mo_{1-x}W_xS_2$ monolayer alloys, we define

$$\frac{F_3}{F_{30}} = \frac{F_4}{F_{40}} = \frac{F_5}{F_{50}} = 1-\theta_4 x \quad (19)$$

The equations of motion for the three types of atoms (Mo, W and S) are written as

$$m_s\ddot{\mu}_s = -(1-x)F_3(\mu_s-\mu_{Mo}) - xF_4(\mu_s-\mu_W) \quad (20)$$

$$m_{Mo}\ddot{\mu}_{Mo} = -2F_3(\mu_{Mo}-\mu_s) - xF_5(\mu_{Mo}-\mu_W) \quad (21)$$

$$m_W\ddot{\mu}_W = -2F_4(\mu_W - \mu_s) - (1-x)F_5(\mu_W - \mu_{Mo}) \quad (22)$$

Finally, ω^2 can be given as

$$\omega^2 = \frac{1}{2}\left\{\frac{(1-x)(1-\theta_4 x)F_{30}}{m_s} + \frac{2(1-\theta_4 x)F_{30}}{m_{Mo}} + \frac{x(1-\theta_4 x)F_{50}}{m_{Mo}} + \frac{x(1-\theta_4 x)F_{40}}{m_s} + \frac{2(1\right.$$

(23)

The equation (23) was used to fit our experimental data of MoS_2-like and WS_2-like E' mode frequencies using least squares fitting (Figure S1). Substituting the calculated parameters into equation (23), we can get

$$\omega^2_{MoS_2-like\,E'} = -18800.7x^2 + 16953.9x + 131438.0 + 50(10. \quad (24)$$

$$\omega^2_{WS_2-like\,E'} = -18800.7x^2 + 16953.9x + 131438.0 - 50(10.(\quad (25)$$

The MREI-model calculation matches well with the variation of MoS_2-like E' frequency, but does not match well with WS_2-like E' mode (Figure S1).

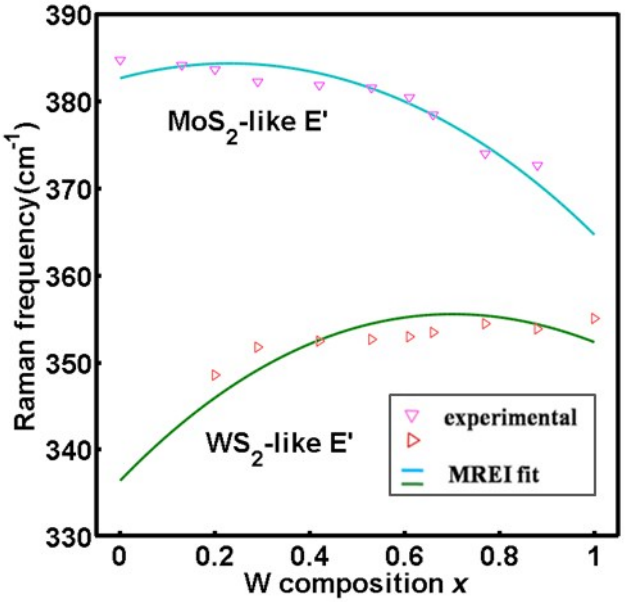

Figure S1. Composition-dependent Raman frequencies of E′ modes as calculated using MREI model based on linear dependence of force constants as composition. The solid lines are the fits of MREI model and the scattered points are the experimental data from Figure 3a.

Table S1. EDX characterization results of $Mo_{1-x}W_xS_2$ single crystals.

$Mo_{1-x}W_xS_2$ samples	**nominal growth W content *x***	**EDX of W content *x***
MoS_2	0	0
$Mo_{0.87}W_{0.13}S_2$	0.1	0.13
$Mo_{0.80}W_{0.20}S_2$	0.2	0.20
$Mo_{0.71}W_{0.29}S_2$	0.3	0.29

$Mo_{0.58}W_{0.42}S_2$	0.4	0.42
$Mo_{0.47}W_{0.53}S_2$	0.5	0.53
$Mo_{0.39}W_{0.61}S_2$	0.6	0.61
$Mo_{0.34}W_{0.66}S_2$	0.7	0.66
$Mo_{0.23}W_{0.77}S_2$	0.8	0.77
$Mo_{0.12}W_{0.88}S_2$	0.9	0.88
WS_2	1	1