Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Surface morphology and adlayer structure of Se on Rh(111)

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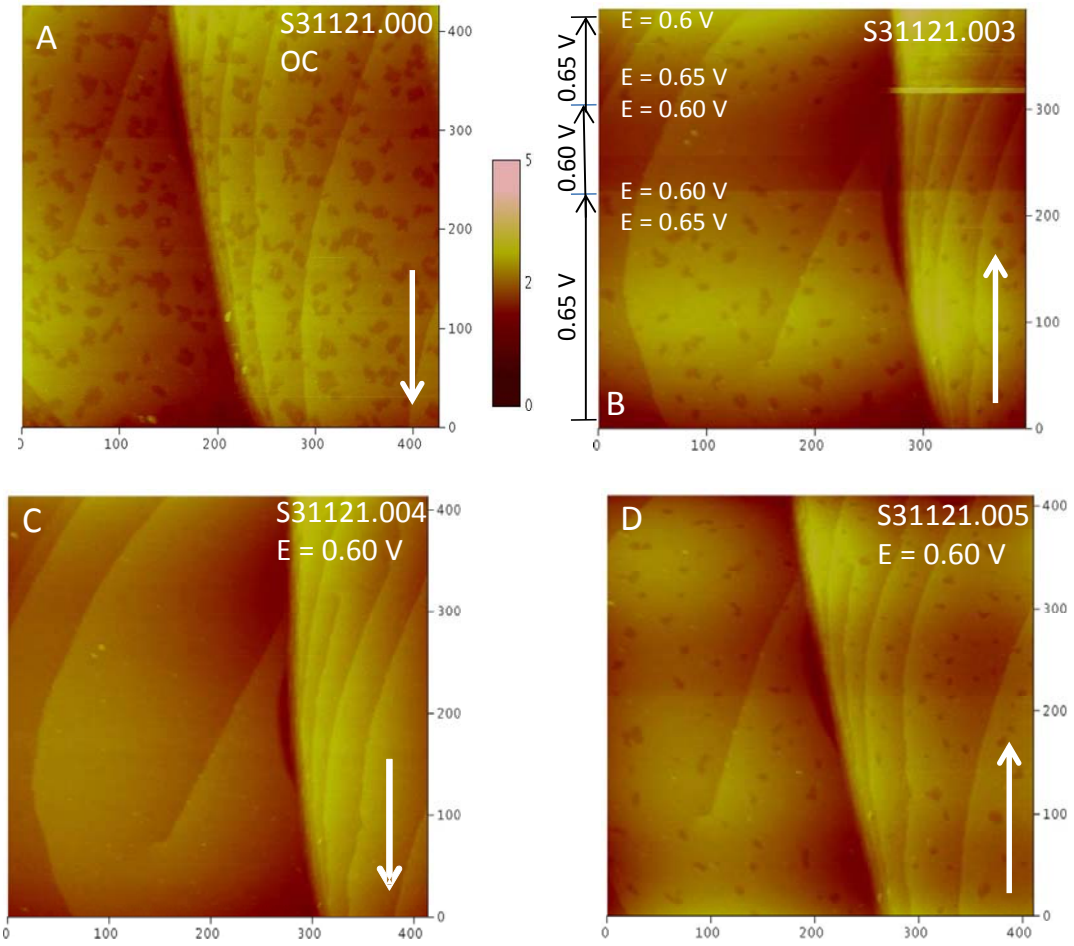
1) Potential dependence of Se islands on Rh(111)

Partial coverage of Rh(111) with Se appeared as patches of atomically smooth islands are shown in STM images. These patches of islands merge at a more negative potential ~ 0.5 V and given rise to a smooth surface.



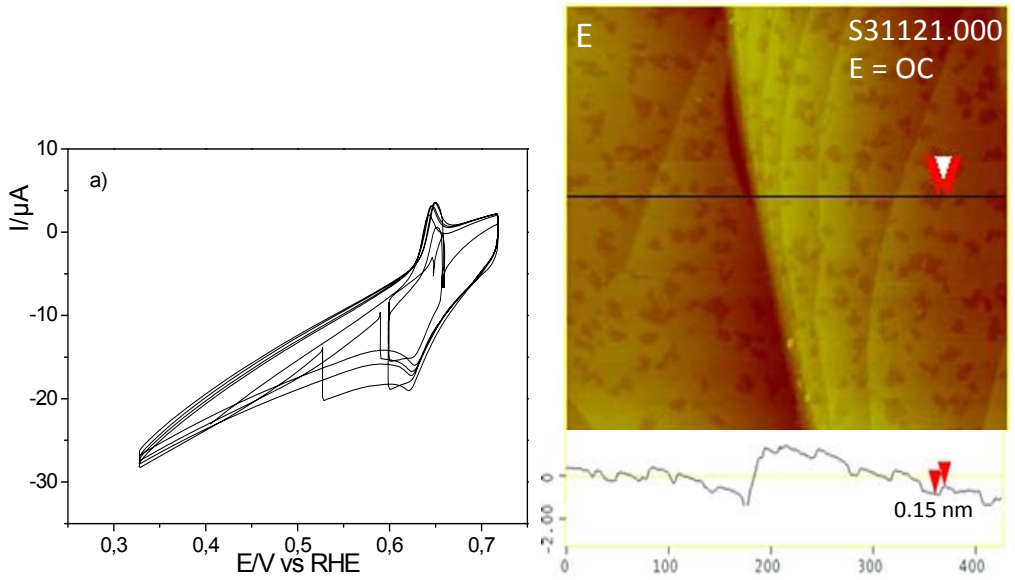


Fig. S1: STM images for Se modified Rh(111) in 0.1 M $HClO_4$ (ϑ =0.25). (A) Deposited Se covered most of the Rh(111) surface with a height of 0.15 nm (B-D) the electrode potential switched from 0.65V to 0.60 V caused Se dispersion on whole surface and Rh(111) patches appeared again at 0.65 V. (E) Se modified Rh(111) STM image at open circuit with cross section showing the height of Se deposits. Sample bias of 40 mV, set point = 0.7 nA & scan rate of 4 Hz. Arrows indicate scan direction. a) CV for Se modified Rh(111) (——) in the STM cell, sweep rate 50 mV/s is also shown.

2) Correcting the distortion of the STM images

The observed lattice is distorted by drift (mainly thermal drift) and missing or incomplete calibration of the scanner. Drift can be corrected for by comparing images in upward and downward directions. Calibration factors can be obtained by comparison of the image with that of a known structure.

A) Drift calculation for atomically resolved images

Thermal drift is a usual problem in scanning probe microscopic techniques, especially when acquiring atomically resolved images in liquid and under potential control. The following calculations are performed to determine drift, and to correct the observed lattice vectors from drift.

The observed distorted lattice be represented by the vectors shown in fig. S1a. Vector **a'** (and similarly **b'**) have to be corrected for the thermal drift which is given by

$\vec{\upsilon} = (\upsilon_x, \upsilon_y)$ times the time Δt corresponding to the time needed by the tip for scanning in the slow scan direction(y) from bottom of vector **a'** to its end point (fig. S1b and c). This time is obtained from the length of vector a' in y-direction divided by the scan

velocity C_y.

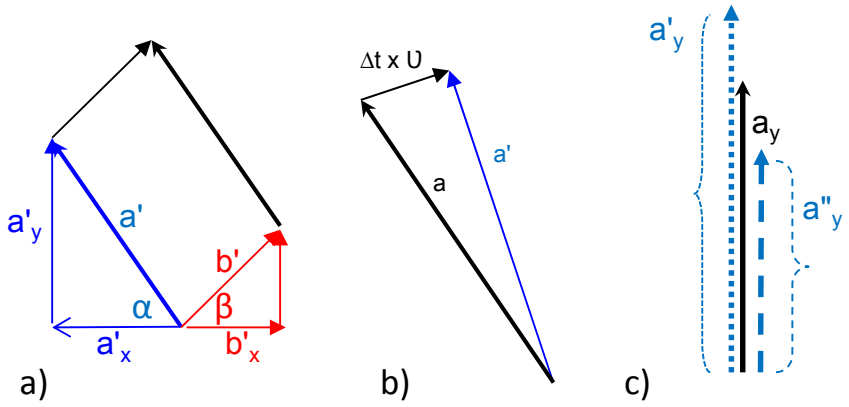


Fig. S2: a) lattice vectors, b) actual and drifted vector, c) atomic vectors in consecutive scans. **a'**$_y$ and **a''**$_y$ are apparent lattice vectors along scan 'up' and scan 'down'; respectively.

We therefore have;

$$\vec{a} + \vec{\upsilon} \cdot a'_y / C'_y = \vec{a'} \qquad \text{eq. S1}$$

and after rearrangement

$$\vec{a} = \vec{a'} - \vec{\upsilon} \cdot a'_y / C'_y \qquad \text{eq. S2}$$

Similarly, for the downword direction we have;

$$\vec{a} - \vec{\upsilon} \cdot a''_y / C'_y = \vec{a''} \qquad \text{eq. S3}$$

and

$$\vec{a} = \vec{a''} + \vec{\upsilon} \cdot a''_y / C'_y \qquad \text{eq. S4}$$

Similar relations hold for vector **b'**.

By comparing eq. S2 with eq. S4, the drift velocity is calculated

$$\vec{a'} - \vec{\upsilon} \cdot a'_y / C'_y = \vec{a''} + \vec{\upsilon} \cdot a''_y / C'_y \qquad \text{eq. S5}$$

$$\vec{\upsilon} \cdot (a'_y + a''_y) / C'_y = (\vec{a'} - \vec{a''}) \qquad \text{eq.S6}$$

$$\vec{\upsilon} = (\vec{a'} - \vec{a''}) \cdot C'_y / (a'_y + a''_y) \qquad \text{eq. S7}$$

Similarly, from vector **B**:

$$\vec{\upsilon} = (\vec{b'} - \vec{b''}) \cdot C'_y / (b'_y + b''_y) \qquad \text{eq. S8}$$

From the filtered STM images for sulfate on Rh(111) (fig. S3) we get:

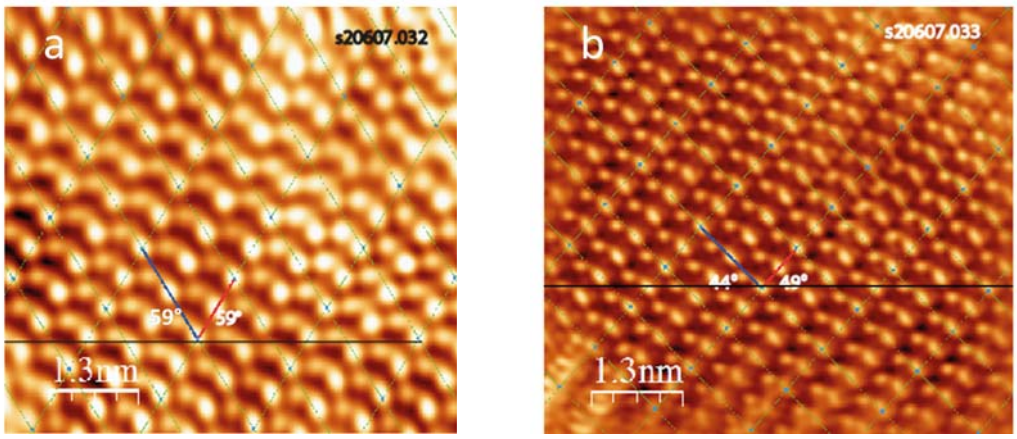


Fig. S3. Filtered consecutive STM images of sulfate a) in upward direction, b) in downward direction. Shown are the doubled vectors.

$|\mathbf{a'}| = 0.760$ nm, $|\mathbf{b'}| = 0.505$ nm, $\alpha = 59°$ and $\beta = 59°$

This leads to:

$\mathbf{a'_y} = \text{Sin}59° \times |\mathbf{a'}| = 0.652$ nm, and $\mathbf{a'_x} = -\text{Cos}59° \times |\mathbf{a'}| = -0.392$ nm

Thus $\mathbf{a' = (a'_x, a'_y) = (-0.392, 0.652)}$

Similarly,

$b'_y = \text{Sin}59° \times |b'| = 0.433$ nm, $b'_x = \text{Cos}59° \times |b'| = 0.260$ nm

Thus $\mathbf{b' = (b'_x, b'_y) = (0.260, 0.433)}$

Similarly for the downward direction:

$|\mathbf{a''}| = 0.603$ nm, $|\mathbf{b''}| = 0.372$ nm, $\alpha = 44°$ and $\beta = 49°$

$\mathbf{a''_y} = \text{Sin}44° \times |\mathbf{a''}| = 0.419$ nm, $\mathbf{a''_x} = -\text{Cos}44° \times |\mathbf{a''}| = -0.433$ nm

Thus $\mathbf{a'' = (a''_x, a''_y) = (-0.433, 0.419)}$

Similarly,

$b''_y = \text{Sin}49° \times |b''| = 0.281$ nm, $b''_x = \text{Cos}49° \times |b''| = 0.244$ nm

Thus $\mathbf{b'' = (b''_x, b''_y) = (0.244, 0.281)}$

The Scan velocity (C'_y) along Y-dir in our case as per fig. S2 is 0.745 nm/s.

Accordingly, the drift velocities for vectors a and b were calculated based on eq. S7 and eq. S8:

From Vectors a' and a''

$\vec{\upsilon} = (0.017,\ 0.097)$

From Vector b' and b''

$\vec{\upsilon} = (0.01,\ 0.095)$

which are in good agreement with each other.

Then the components of vector a and b using eq. S2 and eq. S4 are

Vector a = (a_x, a_y) = (-0.417, 0.510) and Vector b = (b_x, b_y) = (0.250, 0.341)

$$L_{ab} = \begin{pmatrix} a_x & a_y \\ b_x & b_y \end{pmatrix} = \begin{pmatrix} -0.417 & 0.510 \\ 0.282 & 0.341 \end{pmatrix}$$

The length and angles are:

$$\left|\vec{a}\right| = \sqrt{a_x^{\,2} + a_y^{\,2}} = 0.658 \qquad \left|\vec{b}\right| = \sqrt{b_x^{\,2} + b_y^{\,2}} = 0.423$$

The drift corrected angles α and β are

$$\theta_\alpha = \tan^{-1}(a_y / a_x) = 50.7^\circ \qquad \theta_\beta = \tan^{-1}(b_y / b_x) = 53.7^\circ$$

Therefore angle between vector **a** and **b** is = 180-50.7-53.7 = **75.6°**

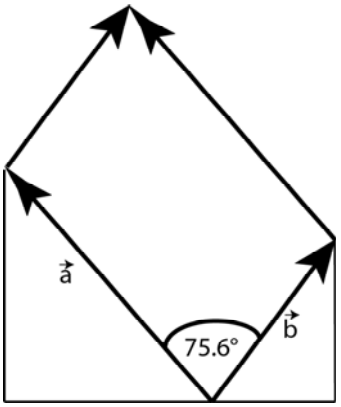


Fig. S4: Drift corrected lattice vector for SO_4^{2-} adlayer based on experimentally observed lattice.

B) Calibration of the scanner using the SO_4^{2-} adlayer

The azimuthal orientation of the √3x√7 lattice model was chosen such that best coincidence with the experiment was achieved as shown in fig. S4.
The actual (theoretical) sulfate adlayer lattice (with respect to the drawn substrate lattice) is given by

$$L_{AB} = \begin{pmatrix} A_x & A_y \\ B_x & B_y \end{pmatrix}$$

with the length:

$$\left|\vec{A}\right| = 0.709 \qquad \left|\vec{B}\right| = 0.464$$

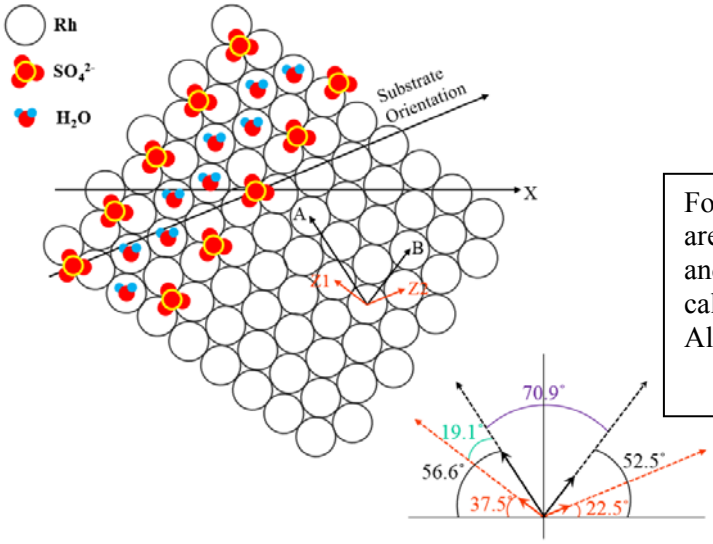
The experimental and actual lattices are related by $L_{AB} = M_{cal} \cdot L_{ab}$, eq. S9

which leads to:

$$M_{cal} = L_{AB} \cdot L_{ab}^{\,-1}$$

$$M_{cal} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} = \begin{pmatrix} A_x & A_y \\ B_x & B_y \end{pmatrix} \begin{pmatrix} b_y & -a_y \\ -b_x & a_x \end{pmatrix} \cdot 1/\left(a_x b_y - a_y b_x\right)$$

where, M_{cal} is the calibration matrix.



For the matrix elements, lower case letters are for actual measurements (experiment) and Capital Letters for theoretical or calibrated ones.
All are in nm.

Fig. S5: Sulfate adlatice model on Rh(111)

Vector A

$A_y = Sin56.6° \times |A| = 0.592$

$A_x = -Cos56.6° \times |A| = -0.390$

A (A_x, A_y) = **(-0.390, 0.592)**

Vector B

$B_y = Sin52.5° \times |B| = 0.282$

$B_x = Cos52.5° \times |B| = 0.368$

A_2 (A_{2x}, A_{2y}) = (0.282, 0.368)

$$L_{AB} = \begin{pmatrix} A_x & A_y \\ B_x & B_y \end{pmatrix} = \begin{pmatrix} -0.390 & 0.592 \\ 0.282 & 0.368 \end{pmatrix}$$

By substituting the values of vector **A** and **B** to determine transpose of vector L_{AB}

$$L_{ab}^{-1} = 1/(-0.270)\begin{pmatrix} 0.341 & -0.510 \\ -0.250 & -0.417 \end{pmatrix} = \begin{pmatrix} -1.263 & 1.890 \\ 0.929 & 1.547 \end{pmatrix}$$

Evaluation of calibration matrix M_{cal} using the eq. S9

$$\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} = \begin{pmatrix} 1.043 & 0.178 \\ -0.015 & 1.103 \end{pmatrix}$$

C) Selenium adlayer lattice determination

Filtered STM images for Se adlayers on Rh(111) fig. S6 was used in a similar way like that of sulfate adlayer.

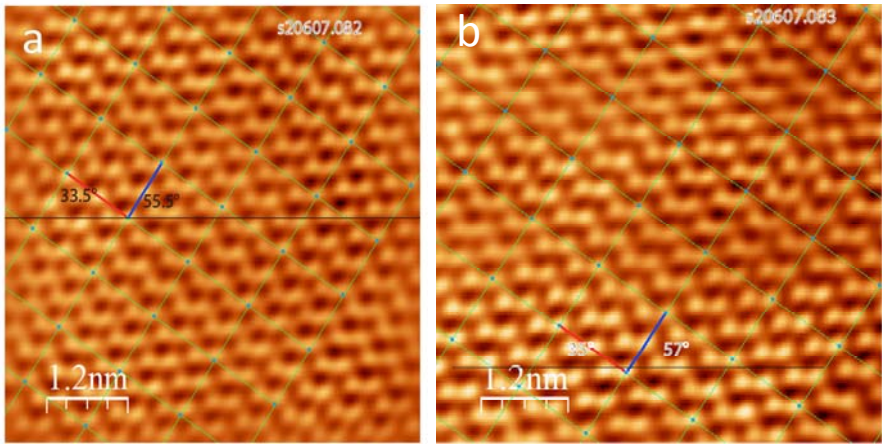


Fig. S6. Filtered consecutive STM images of selenium adlayer a) in upward direction, b) in downward direction. Shown are the doubled vectors $\vec{c}$ (red) and $\vec{d}$ (blue).

After drift correction, the Se adlattice is:

$$L_{cd} = \begin{pmatrix} c_x & c_y \\ d_x & d_y \end{pmatrix} = \begin{pmatrix} -0.428 & 0.292 \\ 0.250 & 0.374 \end{pmatrix}$$ with the lengths and angles:

$$\left|\vec{c}\right| = \sqrt{c_x^{\,2} + c_y^{\,2}} = 0.518 \qquad \left|\vec{d}\right| = \sqrt{d_x^{\,2} + d_y^{\,2}} = 0.450$$

$$\theta_\alpha = \tan^{-1}(c_y/c_x) = 34.2^\circ \qquad \theta_\beta = \tan^{-1}(d_y/d_x) = 56.2^\circ$$

Therefore angle between vector $\mathbf{l_c}$ and $\mathbf{l_d}$ is = 180-34.2-56.2 = **89.6°**

After correction for calibration with $L_{CD} = M_{cal} \cdot L_{cd}$

$$L_{CD} = \begin{pmatrix} C_x & C_y \\ D_x & D_y \end{pmatrix} = \begin{pmatrix} -0.402 & 0.370 \\ 0.282 & 0.408 \end{pmatrix}$$

With the lengths and angles

$$|L_C| = 0.547 \qquad |L_D| = 0.496$$

$$\theta_\alpha = \tan^{-1}(C_y/C_x) = 42.6^\circ \qquad \theta_\beta = \tan^{-1}(D_y/D_x) = 55.3^\circ$$

Therefore angle between vector L_C and L_D is = 180-42.6-55.3 = **82.1°**

D) Evaluation of the adlayer structure (Using Sulfate adlattice)

The two lattice vectors $\mathbf{z_1}$ and $\mathbf{z_2}$ are considered for the substrate (Rh(111)) as per model.

The substrate vectors (matrix L_Z) and the sulfate vectors (matrix L_{AB}) are related by

$$L_{AB} = S \cdot L_Z \qquad \text{S.12}$$

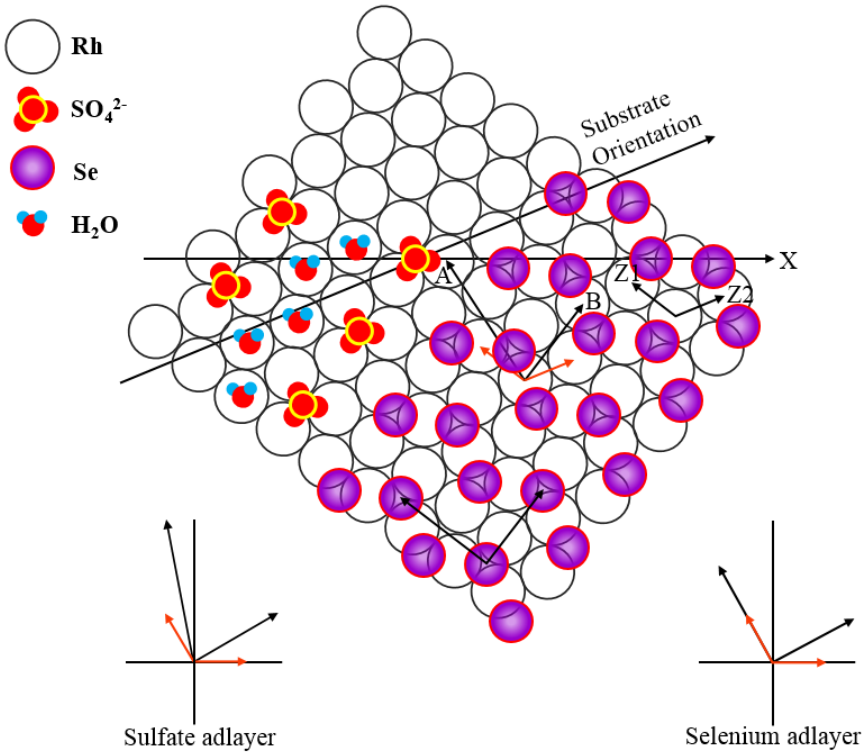


Fig. S7. Sulfate and Se adlatice model on Rh(111)

The sulfate adlayer Matrix was given above:

$$L_{AB} = \begin{pmatrix} A_x & A_y \\ B_x & B_y \end{pmatrix} = \begin{pmatrix} -0.390 & 0.592 \\ 0.282 & 0.368 \end{pmatrix}$$

These matrices relate each other with eq. S.13 which is used to get Matrix L_Z for substrate

$$L_{AB} = S_{SO_4} \cdot L_Z \Leftrightarrow L_Z = S_{SO_4}{}^{-1} \cdot L_{AB} \qquad \text{S.13}$$

Where $S_{SO_4} = \begin{pmatrix} 3 & 1 \\ 1 & 2 \end{pmatrix}$

The matrix (T_{Se}) of the Se adlayer is then calculated from

$$L_{CD} = T_{Se} \cdot L_Z \Leftrightarrow T_{Se} = L_{CD} \cdot L_Z{}^{-1} = \; L_{CD} \cdot L_{AB}{}^{-1} \cdot S_{SO_4} \qquad \text{S.14}$$

$$T_{Se} = \begin{pmatrix} 2.138 & 0.211 \\ 1.160 & 2.135 \end{pmatrix} \sim \begin{pmatrix} 2 & 0 \\ 1 & 2 \end{pmatrix}$$

Without using the calibration matrix

$$T_{Se} = L_{cd} \cdot L_{AB}{}^{-1} \cdot S_{SO_4} = T_{Se} = \begin{pmatrix} 1.868 & -0.122 \\ 1.074 & 1.931 \end{pmatrix} \sim \begin{pmatrix} 2 & 0 \\ 1 & 2 \end{pmatrix}$$