Supporting Information

Understanding the thermodynamic, dynamic, bonding and electrocatalytic properties of low dimensional $MgPSe_3$

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Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

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1 Electron localization function analysis

To analyze the ionic and covalent contributions to chemical bonding, we have used an electron localization function index (ELF). ELF is a relative measure of the likelihood of finding an electron in a given point of space[1–4], which is determined using the dimensionless localization index $\chi(\vec{r})$:

$$\chi(\vec{r}) = \frac{t_p(\vec{r})}{t_w(\vec{r})} = \frac{t(\vec{r}) - \frac{1}{8}\frac{|\nabla\rho(\vec{r})|^2}{\rho}}{c_F\rho^{5/3}(\vec{r})} \tag{1}$$

where c_F denotes the Fermi constant. The ELF is defined in terms of χ by mapping its values on to the range $0 \leq ELF \leq 1$ by defining the electron localization function as :

$$\eta(\vec{r}) = \frac{1}{1+\chi^2(\vec{r})} \tag{2}$$

ELF can also provide maps along the bond path and rationalize the bonding schemes. In order to achieve an accurate description of existing bonds, we have used the 1D-ELF profile. We have provided in Figure 4 of the manuscript the 3D isosurface as well as the corresponding 1D-ELF profile for P–P, Mg–Se, and P–Se bonds in Figure S5 (see below).

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2 Hydrogen Evolution Reaction (HER)

The characterization of the HER electrocatalytic activities of $MgPSe_3$ structure has been carried out by calculating the Gibbs free energy of hydrogen adsorption (ΔG_H) under standard conditions. The best value of ΔG_H for an ideal catalyst should be close to zero, this can be obtained by[5]

$$\Delta G_H = \Delta E_H + \Delta G_H^{ZPE} - T\Delta S_H \tag{3}$$

Here, ΔG_H is the hydrogen adsorption energy, ΔG_H^{ZPE} and T ΔS_H are the zero-point energy difference and entropy difference between adsorbed an H^* atom and gas-phase H_2, respectively. In detail, ΔE_H, ΔE_H^{ZPE} and ΔS_H are given by

$$\Delta E_H = E_{H^*} - E^* - \frac{1}{2}E_{H_2} \tag{4}$$

$$\Delta E_H^{ZPE} = E_{H^*}^{ZPE} - \frac{1}{2}E_{H_2}^{ZPE} \tag{5}$$

$$\Delta S_H = S_{H^*} - \frac{1}{2}S_{H_2} \tag{6}$$

where E_{H^*}, E^* , and E_{H_2} are the energies of catalyst with one adsorbed H^*, catalyst, and gas-phase H_2, respectively. $E_{H^*}^{ZPE}$ and $E_{H_2}^{ZPE}$ are the zero-point energies of adsorbed H^* without the contribution of catalyst and gas-phase H_2, respectively. S_{H^*} and S_{H_2} represent the entropies of adsorbed H^* atom and gas-phase H_2 at standard condition, respectively.

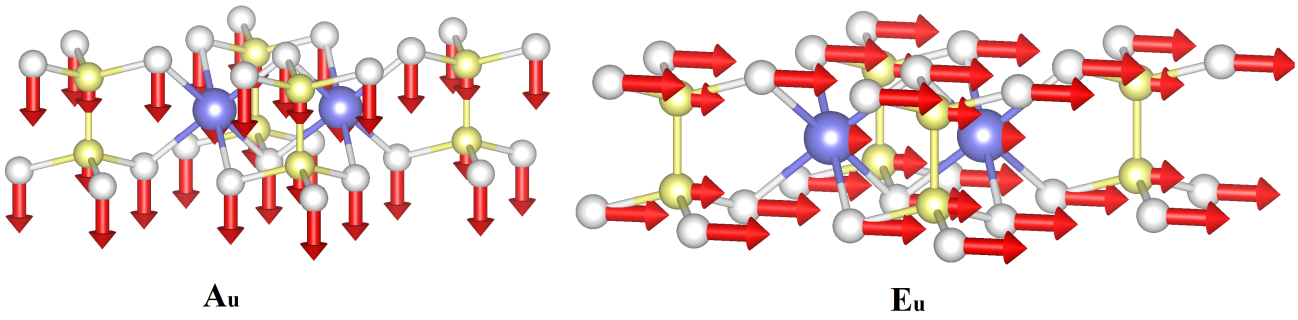

Figure S1 : Vibrational eigenvectors of the zone-centered acoustic phonon modes shown in the low dimensional $MgPSe_3$ structure. The light blue, white, and yellow balls represent Mg, Se, and P atoms, respectively.

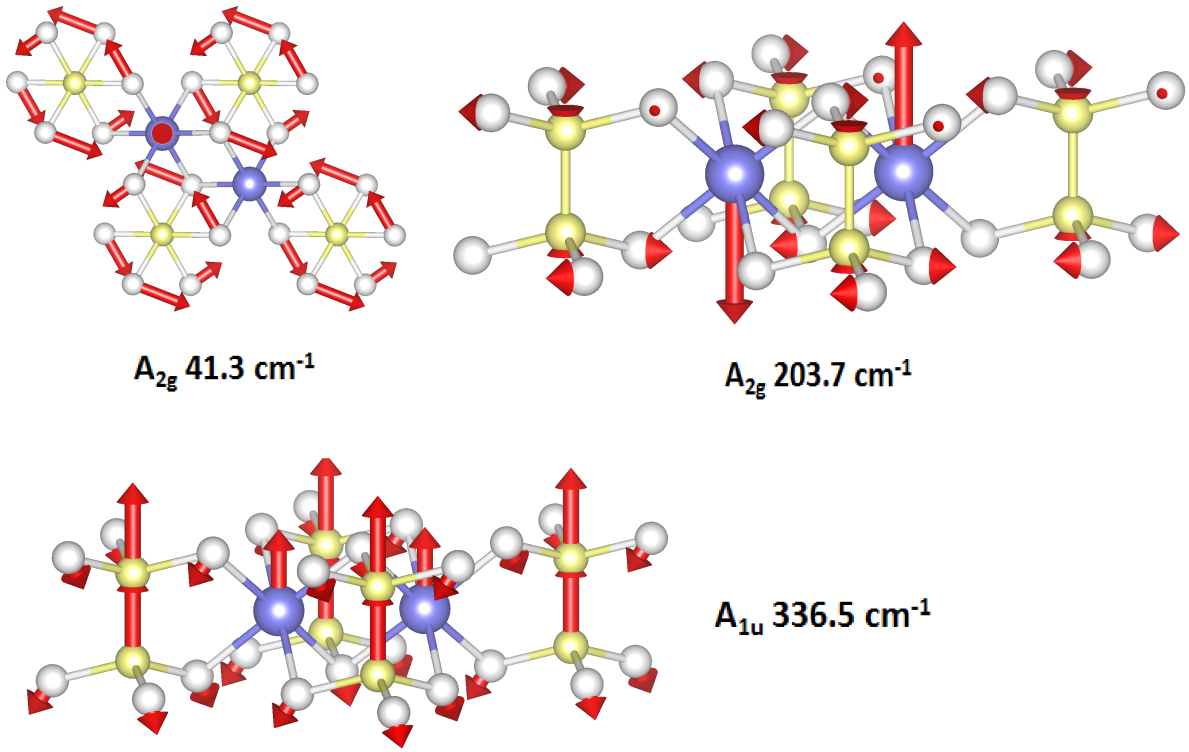

Figure S2: Vibrational eigenvectors of the zone-centered silent phonon modes shown in the low dimensional $MgPSe_3$ structure. The light blue, white, and yellow balls represent Mg, Se, and P atoms, respectively.

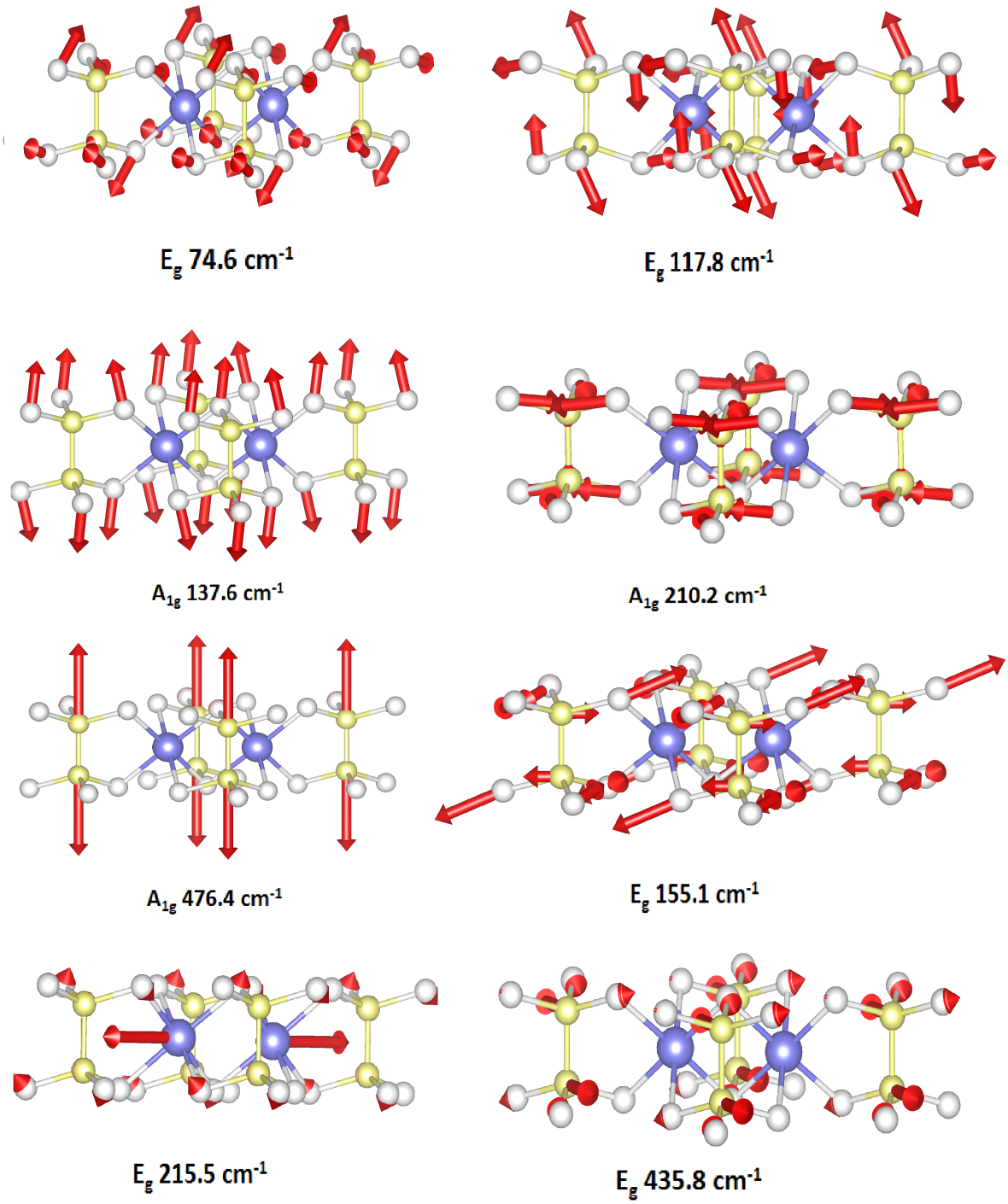

Figure S3: Vibrational eigenvectors of the zone-centered Raman phonon modes shown in the low dimensional $MgPSe_3$ structure. The light blue, white, and yellow balls represent Mg, Se, and P atoms, respectively.

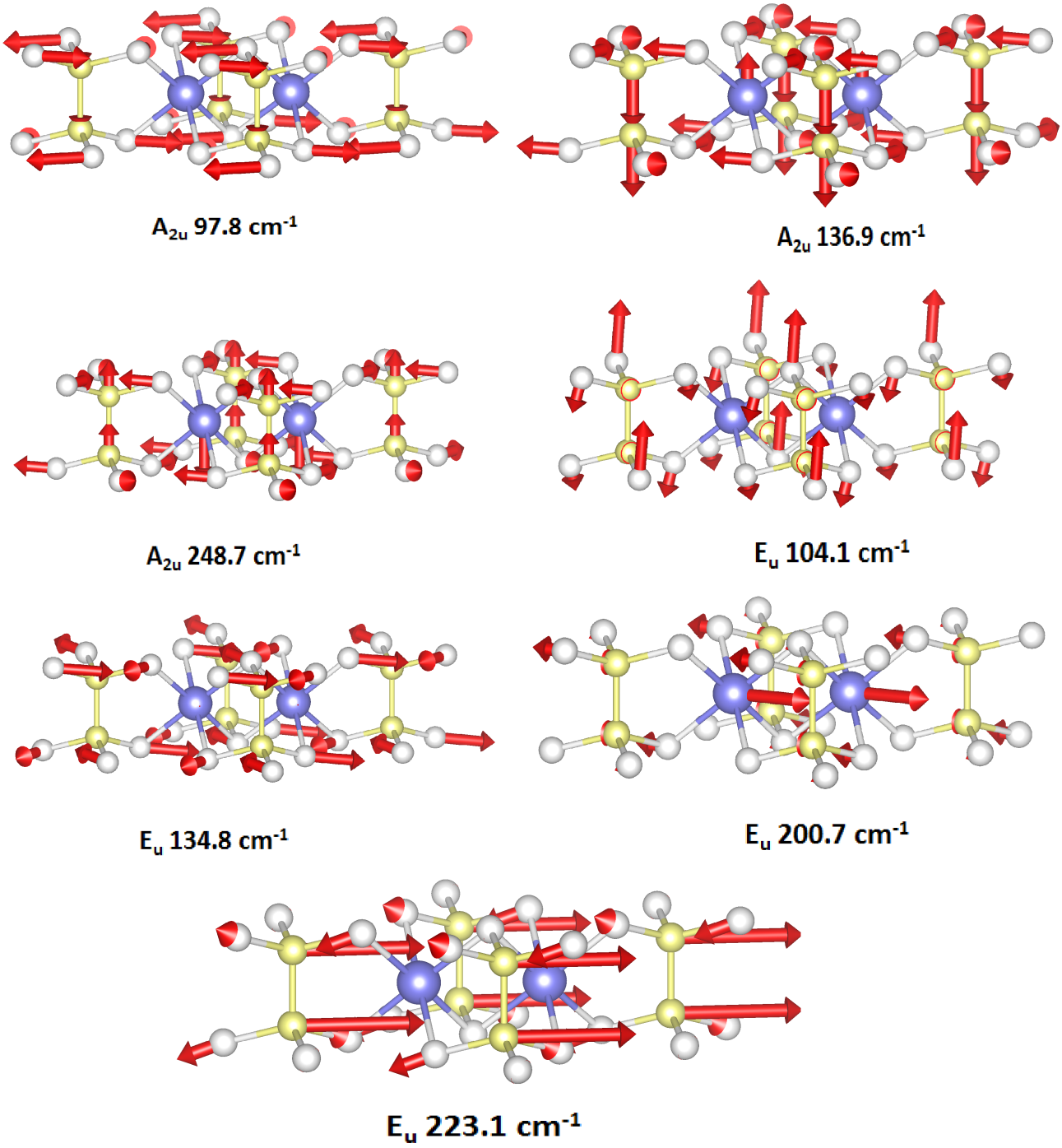

Figure S4: Vibrational eigenvectors of the zone-centered Infrared phonon modes shown in the low dimensional $MgPSe_3$ structure. The light blue, white, and yellow balls represent Mg, Se, and P atoms, respectively.

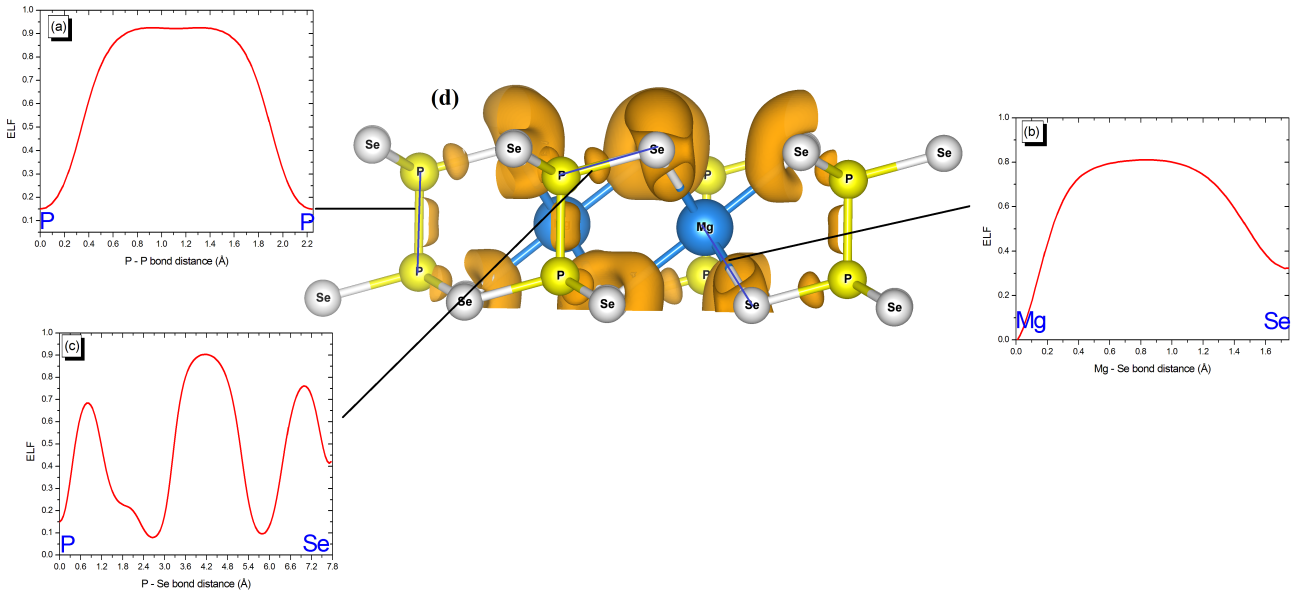

Figure S5:1D ELF profile analyzed for the (a) P–P, (b) Mg–Se and (c) P–Se bonds. The plot in (d) depict 3D ELF isosurface for η=0.84.The profile near the P and Se in (c) represents only the shadow of the other bonds' directions. It is noted that due to the fact that our work is done within the PAW method, only valence electrons are taken into account in the calculation, and for this reason, we have a zero value in the ELF profile in the core of the atoms.

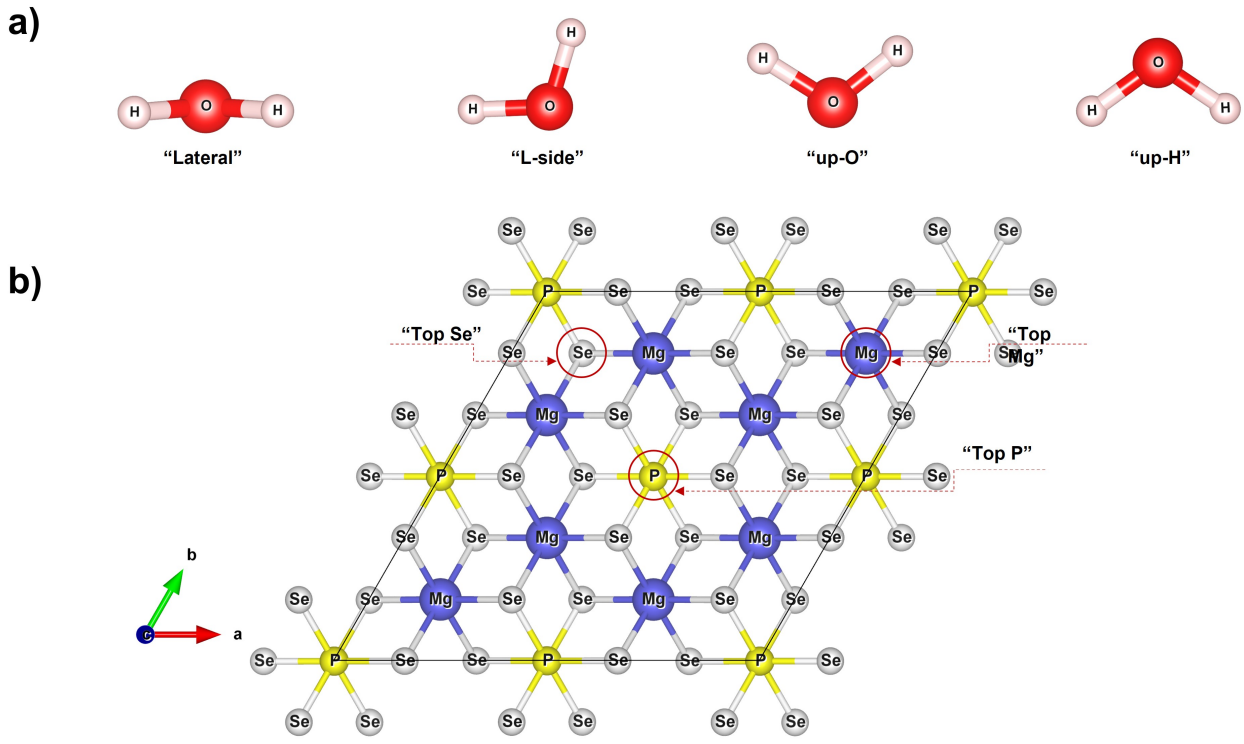

Figure S6: The plot shows the active sites and different spatial orientations of H_2O molecule used to study its adsorption on the the low dimensional $MgPSe_3$ structure.

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