

Computational Materials Physics: Project 2021-2022

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Abstract

Nowadays, it is almost impossible to publish a decent experimental paper, where the results of performed measurements are not being confronted with outcomes of numerical calculations. This only confirms ab-initio methods, such as Density Functional Theory (DFT), to attract every year more and more researchers from various fields to its community. Here we provide a thorough analysis of numerically obtained properties for the TeHO_3 known crystal system. Having these results in agreement with data available in the literature, we encourage ourselves to dive into the unknown, since we attempt to study the stability of molecules from TeO_5H_x family (x ranging from zero to five). It is even more intriguing, for these compounds are only speculated to occur in nature. Finally, we aim to use presented results as a basis for an efficient, fully relativistic study of corresponding polonium-based molecules.

I. INTRODUCTION

In this work, the stability of simple molecules built from oxygen, hydrogen and tellurium is investigated through use of Density Functional Theory (DFT). Since tellurium is chemically analogous to polonium, the results obtained in this work can serve as basis for an efficient study of corresponding polonium-based molecules, which is one of the ongoing research projects at Ghent University.

This report consists of two main parts. In Section II, the crystal structure of TeHO_3 , one of the five known stable Te-O-H crystals, is investigated. In Section III, the stability of new free Te-O-H molecules is recognized. Conclusions based on these stability calculations are formulated in Section V.

All the computations in this work have been performed using Quantum Espresso as DFT code of choice [9, 10]. To describe the nuclei and core electrons, the projected augmented wave method (PAW) has been used [4]. The wave-functions of the valence electrons are expanded on a plane wave basis set, and Perdew-Burke-Ernzerhof (PBE) functionals are used to evaluate the exchange-correlation energy [12].

II. INVESTIGATION OF THE TeHO_3 CRYSTAL STRUCTURE USING DFT

The ternary phase diagram of the Te-O-H system, as found on <https://www.materialsproject.org>, is shown in Figure 1 [6, 7]. In this phase diagram, there occur five stable mixed crystals: $\text{Te}(\text{OH})_6$, TeHO_3 , TeO_2 , Te_2O_5 , and TeO_3 . The ternary TeHO_3 crystal, shown in the right panel of Figure 1, will be investigated more closely in this work. In the first step a convergence testing procedure is conducted to obtain good computational settings. Next, a full geometry optimization is performed, resulting in the equilibrium geometry and the corresponding total energy. Finally, the formation energy of this crystal is determined and compared to data found in the literature.

i. Convergence testing

The cif-file representing the TeHO_3 structure was obtained from <https://www.materialsproject.org> [7, 15], and the pseudopotentials for Te, O and H were obtained from the Quantum Espresso PSLibrary [5]. In this first approach, the relativistic effects were not taken

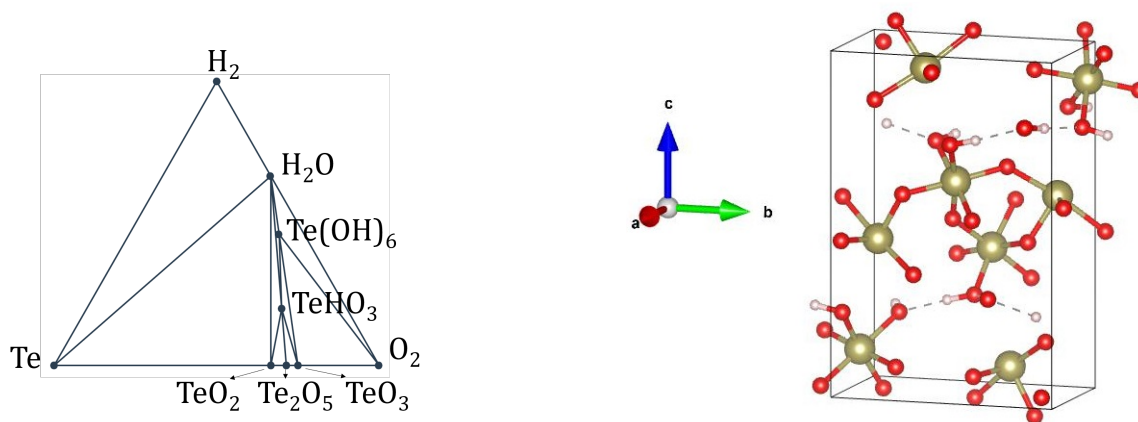


Figure 1: Left panel: Ternary phase diagram of the Te-O-H system, provided by <https://www.materialsproject.org> [6, 7]. Right panel: Visualization of the TeHO₃ structure prepared with VESTA [8]. The Te atoms are shown in yellow, the O atoms - in red, and the H atoms - in white.

into consideration. The pseudopotentials of choice are [1], [2] and [11] for Te, O, and H, respectively. The convergence target is to predict the reliable hydrostatic pressures. The number of points in the k-mesh, the kinetic energy cutoff for the wavefunctions (ecutwfc) and charge densities (ecutrho) are varied independently until the fluctuations in hydrostatic pressure are below 1 kbar. The results are shown in Figure 2. From this analysis, a k-point mesh of size 3x3x3 was chosen. For the basis set, based on the analysis in Figures 4 and 3, ecutwfc and ecutrho were determined to be 60 Ry and 300 Ry respectively. However, based on the combined efforts from all teams involved in the project, ecutwfc and ecutrho were set for further calculations to 87 Ry and 435 Ry, respectively.

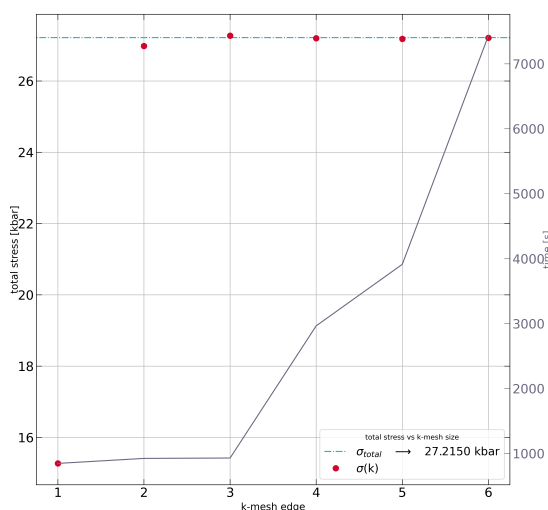


Figure 2: Convergence of k-mesh size.

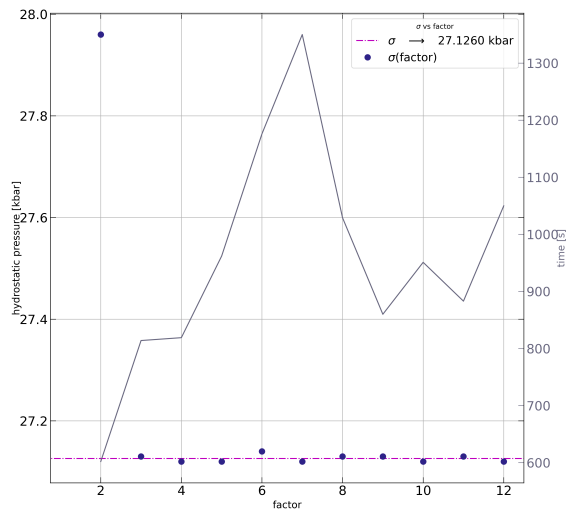


Figure 3: Convergence of ecutrho.

ii. Geometry Optimization

TeHO₃ crystallizes in the Pna2₁ (33) Hermann-Mauguin space group. Therefore, the lattice constants *a*, *b* and *c* can be varied independently, while the angles are fixed to 90°. In addition, for each of the atoms in the unit cell, the *x*, *y*, and *z* positions must be determined independently, i.e. all of them are free coordinates.

The geometry of TeHO₃ is optimized using the “vc-relax” setting in Quantum Espresso, with the target pressure set to 0.5 kbar. This setting optimizes the volume of the unit cell to obtain the lattice parameters that correspond to the target pressure. In addition, in an iterative way, the atomic positions are optimized to

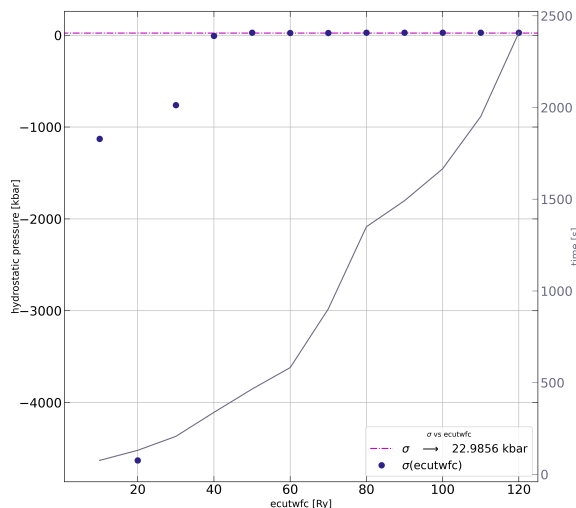


Figure 4: Convergence of $ecutwfc$.

obtain minimal forces on the atoms. With this setting, the minimal total energy, i.e. the ground state energy, can be found as well. The optimized lattice parameters are $a = 9.2216 \text{ \AA}$, $b = 15.5632 \text{ \AA}$, and $c = 23.3816 \text{ \AA}$. The equilibrium volume of the unit cell $V_0 = 497.25731$ [arb. u.] and the ground state energy $E_0 = -3909.3802$ Ry. However, this unit cell contains eight molecules of TeHO_3 (see Figure 1). Therefore, the total ground state energy per molecule is $E_0 = -362.6067$ Ry.

iii. Formation Energy

The formation energy of the TeHO_3 crystal from the elemental phases in the corners of the phase diagram in Figure 1 is defined as:

$$E_{form} = E(\text{TeHO}_3) - \frac{1}{n}E(\text{Te}_{solid}) - \frac{1}{2}E(\text{H}_2) - \frac{3}{2}E(\text{O}_2), \quad (1)$$

where n denotes the number of Te atoms in a solid tellurium unit cell.

To obtain the total energy of solid Te, a “vc-relax” optimization calculation was performed using the cif-file obtained for the elemental solid tellurium in the corner of the phase diagram presented in Figure 1 [3, 14]. The total ground state energy per atom for this crystal with parameters $a = 4.5703 \text{ \AA}$, $b = 4.5703 \text{ \AA}$, $c = 5.8930 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ is given in Table 1.

To calculate the total energies for free O_2 and H_2 molecules, the convergence tests needed to be performed in the first place to determine an appropriate supercell size. For this cell size, the distance between a single molecule and its periodic images was so large that any interaction between them was negligible. However,

when free molecules are studied using periodic DFT code, a spurious background interaction is unavoidable. To make these interactions as isotropic as possible, a supercell with FCC symmetry is used. In addition, to obtain the correct ground state total energy, the calculations must be performed in “spin-polarized” mode. Figures 5 and 6 show the results of the supercell convergence tests for O_2 and H_2 , respectively. The convergence criterion was set to 0.01 eV/atom . Based on this criterion, the supercell shape for O_2 is fixed to $a = b = c = 11.3384 \text{ \AA}$, $\alpha = \beta = \gamma = 60^\circ$, and to $a = b = c = 13.2281 \text{ \AA}$, $\alpha = \beta = \gamma = 60^\circ$ for H_2 . The atomic positions are relaxed for both molecules, and the ground state energies are given in Table 1.

From the ground state energies in Table 1, the formation energy of TeHO_3 can be calculated according to Equation 2. The results are shown in Table 2. The value calculated in this work is compared to the value provided by <https://www.materialsproject.org> [6]. The difference between the calculated value and the value from literature $< 0.1 \text{ eV/atom}$. It can therefore be concluded that there is a good agreement between performed calculations and the published data. Moreover, the remaining difference can be attributed to precision settings, such as choice of the k-point mesh or the basis set of the exchange-correlation functionals.

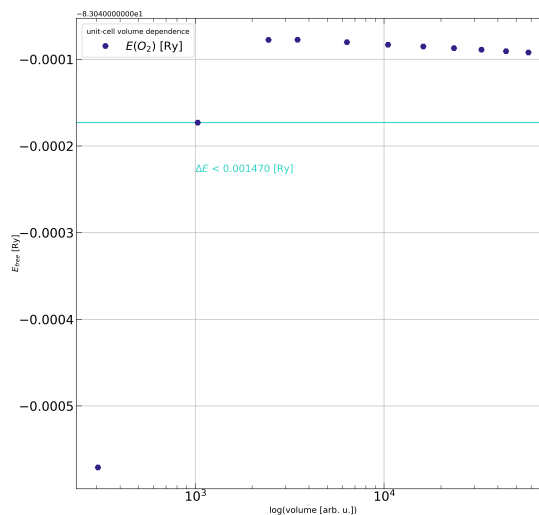


Figure 5: Total energy for the free O_2 molecule as a function of the supercell size.

III. MOLECULAR CALCULATIONS USING DFT

In this section a family of molecules will be investigated by performing free molecule calculations. The calculations are carried out with a periodic DFT code

TeHO ₃ [Ry/molecule]	solid Te [Ry/atom]	H ₂ [Ry/molecule]	O ₂ [Ry/molecule]
-488.6725	-362.6067	-2.0000	-83.0412

Table 1: Total ground state energies of one TeHO₃, H₂, and O₂ molecule, and one Te atom in crystallized form.

E _{form} [Ry/molecule]	E _{form} [Ry/atom]	E _{form} [eV/atom]	E _{form} [eV/atom] [6]
-0.504	-0.1008	-1.371	-1.385

Table 2: Comparison of the formation energy of TeHO₃ calculated in this work to the formation energy obtained from <https://www.materialsproject.org> [6].

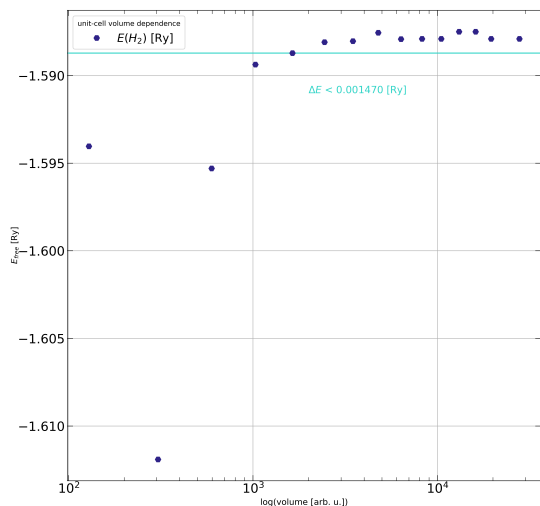


Figure 6: Total energy for the free H₂ molecule as a function of the supercell size.

using supercells approach. The molecules studied in this work consist of a single tellurium atom at the center of a square-based pyramid (made out of oxygen atoms), with zero to five hydrogen atoms (Te(OH)₅ to TeO₅). The k-mesh chosen for these calculations is 1x1x1 and the basis set size is the same as the one determined above for the TeHO₃ crystal. As already mentioned in Section iii, one can not avoid a spurious background interaction when free atoms or molecules are studied using periodic DFT code. In an ideal case, the interactions are considered as isotropic as possible by using supercell with FCC symmetry. However, the approach proposed here uses a supercell with simple cubic symmetry due to complexity of the TeO₅H_x molecules.

i. Supercell size determination

First, the size of the supercell was determined by studying the convergence of the total energy as a function of the supercell size parameter A . The convergence criterion was set to 0.01 eV/atom. In order to perform a

satisfactory determination of A value, the convergence of the total energy retrieved from DFT calculations is investigated for Te(OH)₅. The converged supercell size found for this molecule, being the “biggest” representative of the studied family of compounds, is assumed to be adequate for smaller molecules as well. Figure 7 shows the total energy retrieved from the DFT calculations of the free molecule as a function of the supercell size (A^1). From those results A turned to be equal 9 Å as a good choice for the supercell size. Choosing a smaller value for A would decrease the precision of the calculations, while a larger A would result in more expensive calculations bringing no significant increase to the precision.

ii. New Te-O-H molecules

The overall goal of the project was to identify the most stable molecules consisting of Te, O and H. The general formula for the family of molecules studied here can be expressed by TeO₅H_x, with x ranging from zero to five. In order to study the various molecules, a supercell with the same size as the one determined in Section i is used. A key parameter when performing free molecule calculation is the initial guess for the atomic positions. If the initial atomic positions are too far from the optimal ones, the DFT calculation does not converge. In this work the geometry investigated is the one where Te lies at the center of a square-based pyramid, with zero to five oxygen atoms. Consecutive TeO₅H_x molecules were investigated using the following approach:

- Find the atomic positions (with pen and paper) of all the atoms in Te(OH)₅ based on the atomic positions of Te, O and H in the stable Te(OH)₆ crystal [13].
- Build a simple cubic supercell for the studied geometry with tellurium atom at the center, and insert these positions in a Quantum Espresso input file.
- Geometry optimize Te(OH)₅ and extract the obtained total energy.

¹See input parameters of the &SYSTEM block of a Quantum Espresso input file.

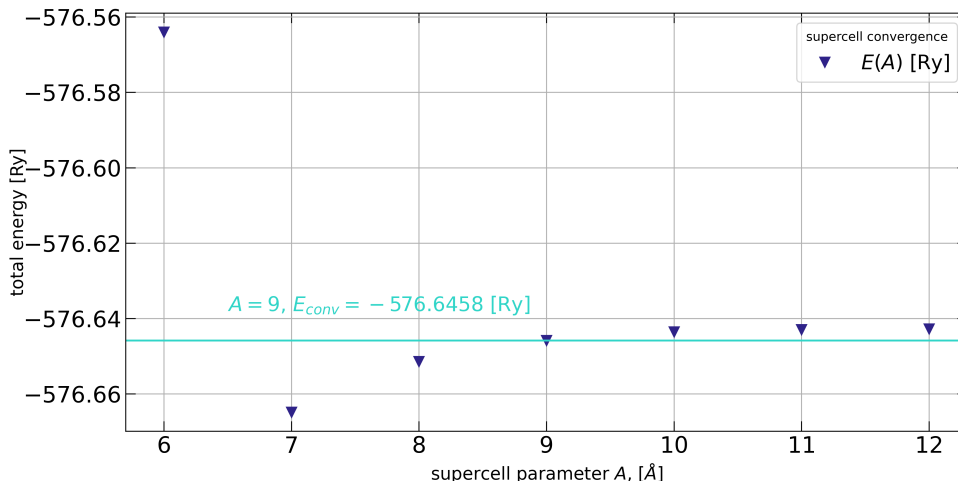


Figure 7: Total energy resulting from the free molecule calculations for $\text{Te}(\text{OH})_5$ as function of the supercell size.

- Use the final atomic positions found after geometry optimization and create a new input file, removing one hydrogen (strategically chosen²) atom to form the TeO_5H_4 molecule.
- Geometry optimize TeO_5H_4 and note the total energy.
- Repeat the two previous steps until all of the hydrogen atoms are taken out from the molecule so as to obtain TeO_5 .

The final configurations obtained for all molecules after geometry optimization for the atomic positions are shown in Table 3. These results give a first indication that when there are less than two hydrogen atoms present in the $\text{Te} - \text{O} - \text{H}$ molecule, it tends to dissociate into O_2 and TeO_3H for TeO_5H , or TeO_3 for TeO_5 . Yet, a fully converged result was not reached for all the molecules within the relaxed calculations. Therefore, these results can only give a first glimpse. Surely they can be reviewed and improved. That's why future studies on this topic are highly recommended.

The formation energies of all new TeO_5H_x molecules, where $0 < x < 5$, can be obtained by the following equation:

$$E_{\text{form}} = E(\text{TeO}_5\text{H}_x) - E(\text{Te}_{\text{solid}}) - \frac{x}{2}E(\text{H}_2) - \frac{5}{2}E(\text{O}_2). \quad (2)$$

The total ground state energies of solid Te (per atom), O_2 and H_2 were already calculated in section iii, and are given in Table 1. The total ground state energies of the

free TeO_5H_x molecules are presented in Table 4. Again, these results give only a first guidepost, since not all molecule calculations reached a fully converged result. A visual overview of the formation energies is given in Figure 8.

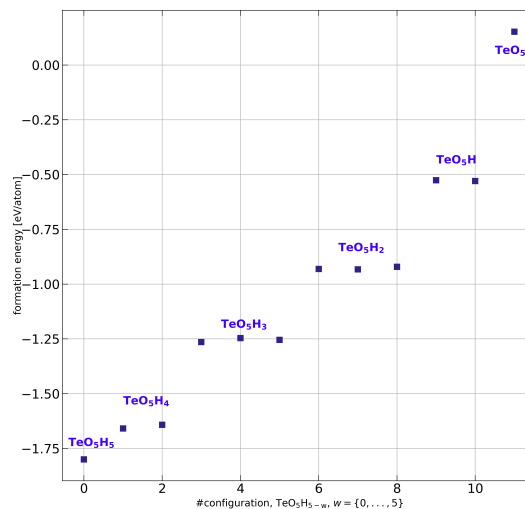


Figure 8: Comparison of formation energies for the studied new $\text{Te} - \text{O} - \text{H}$ molecules.

IV. FURTHER WORK

This report shows an amateur attempt to find new stable molecules from the TeO_5H_x family. In this section, a few possible research paths are proposed for future work. Firstly, the molecules obtained here can be further

²Multiple configurations can be formed that way, only a few of them could be handled in this project. For more information about the different configurations investigated in this project: see Tables 3 and 4 in Appendix.

investigated, especially the molecules that dissociate in order to see, if other configurations would result in a stable molecule. Then, instead of using a simple cubic unit cell for the supercell calculations, a FCC cell can be used so as to make the interactions between the molecule's periodic copies the most isotropic as possible. This can be done using a coordinate transformation to a non-orthogonal basis. Finally, other geometries could be investigated such as the one where Te lies at the center of a triangle with one O atom on top and one O atom beneath the triangle's plane (see Figure 9). By changing the orientations of the O-H bindings many other configurations can also be investigated. It is also advisable to perform magnetic calculations so as to be able to determine, whether the molecules from this family display magnetic behavior.

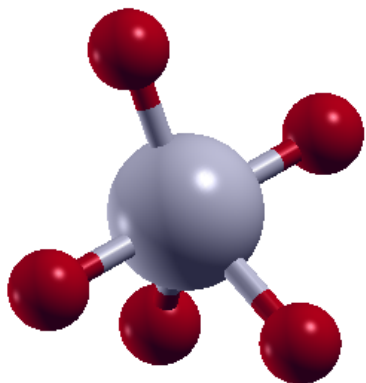


Figure 9: Possible geometry for a TeO_5 molecule.

V. CONCLUSION

The present results are significant in at least three major aspects. In section II, it was shown that the formation energy calculated in this work for the known stable Te-crystal TeHO_3 agreed well with the formation energy provided in the literature. The difference between these two values was smaller than 0.1 eV/atom, which can be attributed to precision settings. In section ii, it has been also demonstrated that Te-molecules with 5 oxygen atoms can be investigated using *ab-initio* methods. Eventually, this study provides a preliminary conclusion that adding hydrogen atoms to the oxygen atoms might stabilize entire TeO_5H_x structures.

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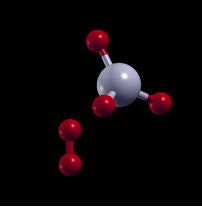
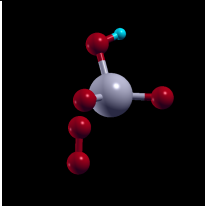
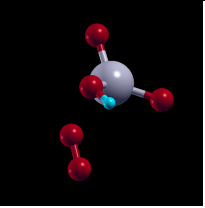
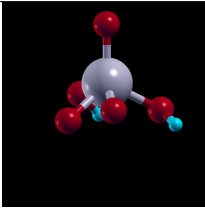
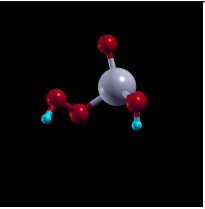
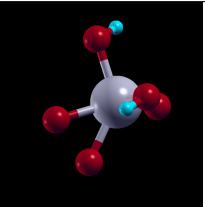
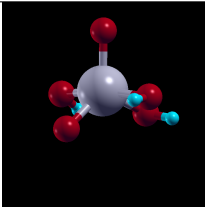
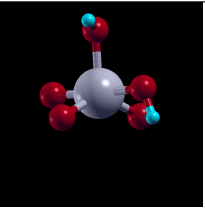
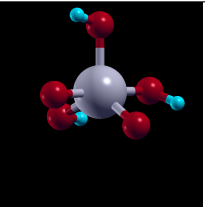
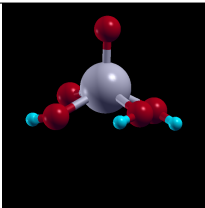
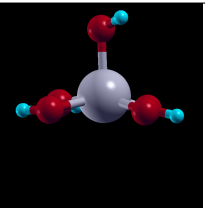
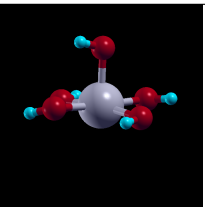
Configuration 1	Configuration 2	Configuration 3
TeO ₅		
		
TeO ₅ H ₁		
		
TeO ₅ H ₂		
		
TeO ₅ H ₃		
		
TeO ₅ H ₄		
		
Te(OH) ₅		
		

Table 3: Visualization of the molecules with final atomic positions obtained after a geometry optimization for the atomic position using a periodic DFT code and following the workflow presented in Section ii. For each molecule there is one, two or three possible configurations depending on the number of hydrogen atoms present. Configuration 1 for TeO₅H₂, TeO₅H₃, TeO₅H₄ is the one where the top hydrogen atom is removed. For TeO₅H₁ the concept of "top" hydrogen atom loses its sense, as the atomic positions have changed too much.

Configuration 1	Configuration 2	Configuration 3
TeO ₅		
-570.1426 Ry		
TeO ₅ H ₁		
-571.4802 Ry		-571.4820 Ry
TeO ₅ H ₂		
-572.7571 Ry	-572.7582 Ry	-572.7511 Ry
TeO ₅ H ₃		
-574.0461 Ry	-574.0343 Ry	-574.0396 Ry
TeO ₅ H ₄		
-575.4288 Ry		-575.4167 Ry
TeO ₅ H ₅		
-576.6650 Ry		

Table 4: Formation energies of the free TeO₅H_x molecules. The configurations correspond to the ones described in Table 3.