

First-principle study to estimate crystal formation energy of $\text{Te}_x\text{H}_y\text{O}_z$ family and stability of TeO_3H_x ($x = 0, 1, 3$) molecules

Chiku Parida*

*International Centre for Materials Science,
Jawaharlal Nehru Centre for Advanced Scientific Research,
Bangalore, India.*

Haseeb Ahmad†

*Department of Physics,
Lahore University of Management Sciences,
Lahore, Pakistan.*

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The stability of a molecule or compound is one of the most vital properties for any material scientist. In this study, we report the stability of TeO_3H_x molecules and some of the Te - O - H based crystals, calculated using Density Functional Theory (DFT) based electronic structure calculations, employing the Quantum ESPRESSO code. The calculations were carried out on the optimized structure after converging the relevant computational parameters. We found out the TeH_3O_3 has the smallest formation energy among the studied molecules and hence is most stable. Furthermore, the comparison with other ternary and binary systems suggests that TeO_2 is most stable among Te-H-O oxides.

I. INTRODUCTION

Predicting the stability of a system by computing the formation energies has been extensively employed in the literature [1]. We can estimate the stability of a system computationally before actually trying to synthesize it in the lab, hence saving a lot of time and expensive resources. Some experiments are even hard to perform in the lab due to extreme experimental conditions or some radioactive elements. The second reason (radioactivity) insinuates running computational trials for molecules containing polonium (Po), a radioactive element. Polonium, hydrogen, and oxygen-based molecules have been the topic of interest among some researchers recently, and the effort is going on to develop new molecules out of these elements. However, polonium is a heavy element, requires spin-orbit calculations, which is computationally demanding to use in all those calculations aimed to predict new molecules. In order to circumvent that issue, we in this work are reporting the calculations by picking up the tellurium (Te), which somewhat mimics the Po element and is also known for having a lot of binary and ternary stable oxides, such as in the form of TeO_2 , TeHO_3 , TeO_3 , Te_2O_5 , and $\text{Te}(\text{OH})_6$.

Out of the above-mentioned Te oxides, we will be dealing with TeO_3 . The Te atoms are polyvalent and hence have different oxidation states depending upon the environment, and also due to this, there is a multitude of Te-based oxides present. TeO_2 , TeO_3 , and their

mixture have found interesting applications, especially in the field of nonlinear optics [2], and their electronic and optical response has been explored already [2]. We have focused our attention to predict new TeO_3 based molecules by introducing the hydrogen atoms in an isolated TeO_3 . We are reporting results for isolated TeO_3 , TeO_3H and TeO_3H_3 . Furthermore, our prediction of these new hydrogen-based TeO_3 molecules will be the essence for the further computation of the similar systems but with polonium element instead of tellurium.

II. COMPUTATIONAL DETAILS

All the calculations are performed using plane-wave density functional theory code, Quantum Espresso (QE) [3]. The generalized gradient approximation (GGA) with Perdew, Burke, and Ernzerhof (PBE) functional [4] scheme is used for the exchange-correlation potential. The ultra-soft pseudopotential (USSP) potentials were selected to represent the interaction between valance and core electrons in all DFT calculations [5]. The electron wave functions are expanded in the form of a plane-wave basis set up to the cutoff energy 50 Ry, at which the total energy convergence was achieved up to 1.1×10^{-4} Ry/atom. A k-points sampling under the Monkhorst-Pack scheme [6] was used for the first Brillouin zone integration using $5 \times 5 \times 5$ k-mesh. The ionic positions and lattice parameters (for bulk systems) of the studied systems are fully relaxed until Hellmann-Feynman forces are smaller than $0.02 \frac{\text{eV}}{\text{\AA}}$ or predefined criteria. All the calculations were performed with non-spin polarized settings, and spin-orbit coupling was also not applied as we aimed to (qualitative) comparison

*Electronic address: charleschiku.98@gmail.com

†Electronic address: haseebphysics1@gmail.com

and to save computational time.

III. RESULTS AND DISCUSSION

A. Convergence Tests

To perform accurately and computationally feasible DFT calculations, we need to have optimal values of the cutoff of the wave function, charge density, and the number of k-points. Therefore, the convergence of these parameters was carefully studied to hydrostatic pressure, and the results are shown in the Appendix A. If these parameters are converged with pressure, they will be suitable for most of the properties of interest since the mentioned pressure is sensitive enough. Figs. (6), (7), and (8) suggests 50 Ry, 8, and 5x5x5 values for the kinetic energy cutoff, multiplicative factor for the charge density, and k-mesh size, respectively. And for all further calculations, these settings would be assumed except for the non-periodic isolated molecular calculations, in which we had used just gamma point ($k = 0 \ 0 \ 0$).

B. Geometry optimization

We need to have DFT-optimized relaxed structure (atomic positions and lattice parameters) for bulk systems. Therefore, the atoms and lattice constants were relaxed and allowed to obtain a minimum potential energy configuration. We have relaxed the bulk configuration of Te, and TeO_3 , while for the molecular O_2 and H_2 , we placed the isolated molecules in a supercell (15 Å cubic unit cell), and atomic position was optimized by computing the bond-length vs. total energy data as depicted in Fig. (2), which shows the minima at around 1.23 Å. The similar procedure for H_2 molecule gave the optimized bond length to be equal to 0.75 Å. The supercell size convergence was checked for O_2 molecule as well as TeO_3 molecule, and 15 Å was found to be converged as evident in Fig (1).

C. Formation Energies of Te-O-H Crystals

The formation energy is a vital number that elucidates the stability of a system. For all these calculations, we have used the following relation [1].

$$E_{\text{form}} = \frac{1}{x + y + z} (E_{\text{A}_x\text{B}_y\text{C}_z} - x\mu_{\text{A}} - y\mu_{\text{B}} - z\mu_{\text{C}}) \quad ,$$

where $E_{\text{A}_x\text{B}_y\text{C}_z}$ denotes the energy of material $\text{A}_x\text{B}_y\text{C}_z$ and μ is the energy per atom of the respective species. The calculated formation energies using the above formula for tellurium and hydrogen based oxides are given in Table (I).

Table (I) shows that TeO_2 has the least formation energy suggesting it to be most stable among others. The minute deviations of these energies from the previously

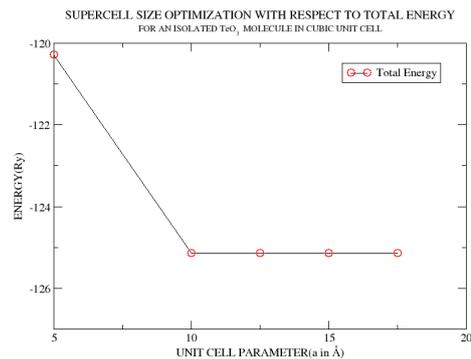


FIG. 1: Convergence of supercell size w.r.t. total energy for TeO_3 molecule. A 15 Å cubic unit cell was selected for further calculations.

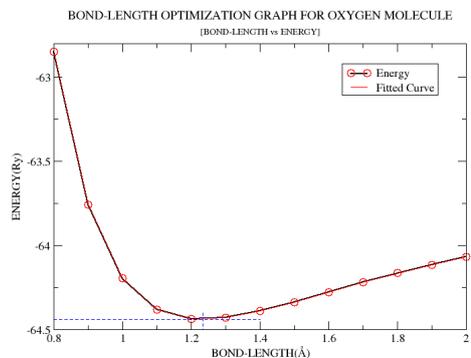


FIG. 2: Estimating the bond length of Oxygen molecule placed in a 15 Å unit cell. The optimal value of 1.23 Å was predicted by PBE functional.

obtained results [7] might be due to different pseudopotentials employed in our calculations.

D. Adding the Hydrogen atoms in an isolated TeO_3 molecule

To predict the new potential molecules out of Te, H, and O, we had inserted the isolated TeO_3 molecule in the 15 Å cubic unit cell and relaxed the geometry. The next step was to add the hydrogen atoms at the appropriate places. We have tested two systems in this study, namely, TeHO_3 and TeH_3O_3 . In an optimized TeO_3 molecule, all the oxygen atoms are almost identical at three corners of tetrahedron having bond-length of 1.82 Å with Te atom at the center of the tetrahedron. The O-Te-O angle is also around 120 degrees overall, as shown in Fig. (3). The added hydrogen atoms should be bonded with oxygen atoms of an isolated TeO_3 molecule. Since the hydrogen-oxygen bond-length is 0.97 Å, so we have placed hydrogen atoms in a different initial position around oxygen.

| Material | Formation Energy per atom (eV) |
|--------------------------------|--------------------------------|
| TeO ₂ | -2.39 |
| TeO ₃ | -1.95 |
| Te ₂ O ₅ | -2.14 |
| TeHO ₃ | -1.88 |
| Te(OH) ₆ | -1.47 |
| H ₂ O | -1.25 |

TABLE I: Formation energies per atom of tellurium and hydrogen based oxides.

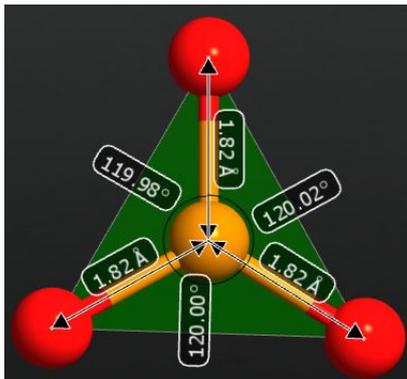


FIG. 3: The geometry of relaxed isolated TeO₃ molecule. The Te - O bond length is equal to 1.82 Å in all the bonds and the O - Te - O angles are almost of 120 degrees. Color Key: Yellow and Red shows Te and O atoms respectively.

For TeHO₃, different trials of picking atomic positions for a hydrogen atom resulted in different total energies, and the most stable relaxed structure is shown in Fig. (4). Similarly, for the TeH₃O₃, we initialized different atomic positions for three added hydrogens, and the most stable configuration is represented in Fig. (5). The calculated molecular formation energies as listed in Table (II) suggests that TeH₃O₃ is the most stable one among the studied molecular Te-O-H systems. Therefore, TeH₃O₃ like polonium based (PoH₃O₃) might be an ideal candidate to look for further calculations.

| Material | Molecular formation energy per atom (eV) |
|---------------------------------|--|
| TeO ₃ | -1.21 |
| TeHO ₃ | -1.32 |
| TeH ₃ O ₃ | -1.90 |

TABLE II: Formation energies per atom of TeO₃H_x oxides, where x = 0,1,3.

IV. CONCLUSION

The DFT can be used quite successfully to predict the lattice constants, atomic geometry, bond-length, and formation energies of the materials. In our work, we have found that TeO₂ is the most stable among the Te-

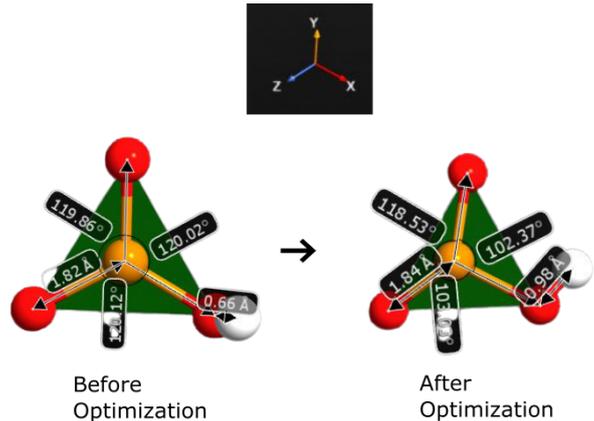


FIG. 4: The relaxed and starting configuration for the TeHO₃ molecule. Color Key: Yellow, Red and white shows Te, O, and H atoms respectively..

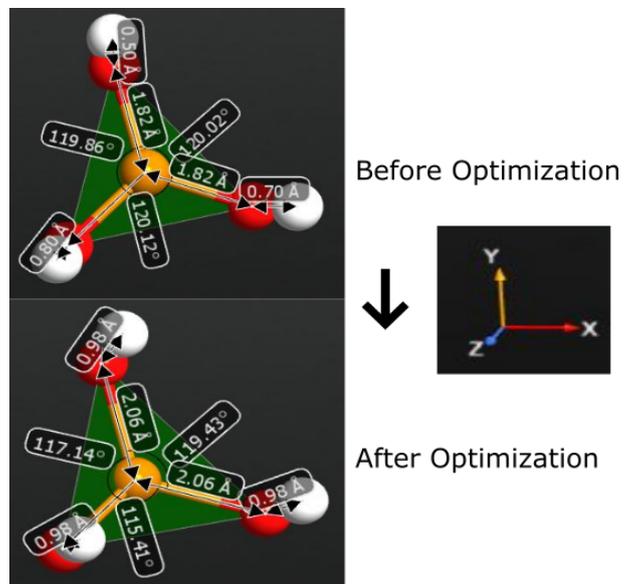


FIG. 5: The relaxed and starting configuration for the TeH₃O₃ molecule. Color Key: Yellow, Red and white shows Te, O, and H atoms respectively.

H-O crystal family based on formation energy calculations. We have used different geometrical configurations for hydrogen on isolated TeO₃ molecules to predict new molecules, which suggested TeH₃O₃ is the most thermodynamically favorable among the studied systems. Our study also paves the way to use the most stable molecular system found, with the polonium atom in future work.

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Appendix A: Convergence Results

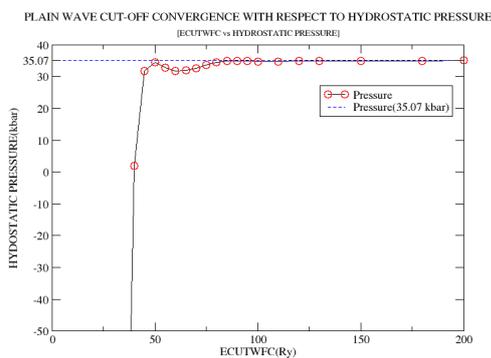


FIG. 6: Convergence of kinetic energy cutoff w.r.t. hydrostatic pressure. 50 Ry was selected for all further calculations.

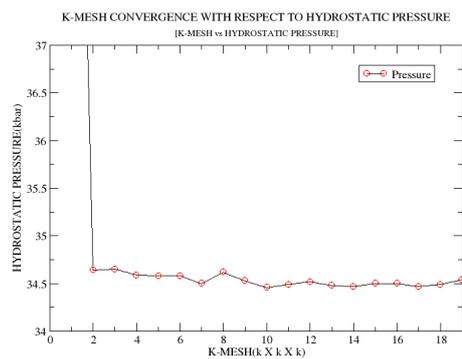


FIG. 8: Convergence of k-mesh grid w.r.t. hydrostatic pressure. The 5x5x5 was selected for all bulk periodic systems.

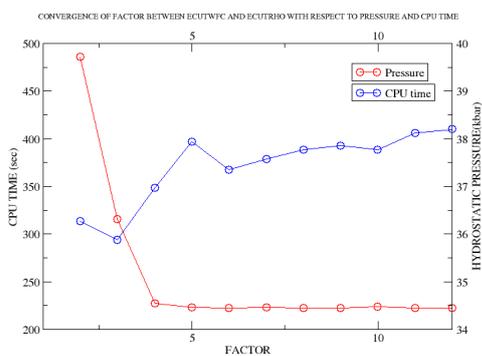


FIG. 7: Convergence of charge density multiplicative factor w.r.t. hydrostatic pressure. Here the factor signifies the multiplicative factor to be multiplied with the kinetic energy cutoff. The factor “8” was selected for all further calculations.