First Principles study on stability of $Te(OH)_6$ molecule

Abstract

In this work, the stability and hence the possibility of existence of $Te(OH)_6$ molecule are studied using density functional methods. Quantum Espresso package has been used to find the energy of formation of the molecules. Knowledge on Tellurium-based molecules is helpful in understanding heavy Polonium-based molecules as they are chemically similar.

Introduction

Polonium (Po) is a heavy atom with an atomic mass of 209 u. Since its discovery in 1898 [1], it is being used for various applications such as for eliminating static electricity in machinery and removing dust from photographic films [2]. However, due to high radioactive toxicity, experimental studies on Po are difficult. Additionally, strong relativistic effects associated with its heaviness makes computational calculations laborious. Te is chemically analogous to Po. Therefore, Te-based molecules, are often studied to understand the stability of Po-based molecules. The results obtained from studying Te-based molecules are subsequently used to study Po-O-H molecule with a fully relativistic molecular code.

The enthalpy of formation of the molecule is a key parameter to look at to establish the existence of a new molecule. In this paper, the stability test of $Te(OH)_6$ molecules are performed using DFT and these results can be extended to studying $Po(OH)_6$ molecule.

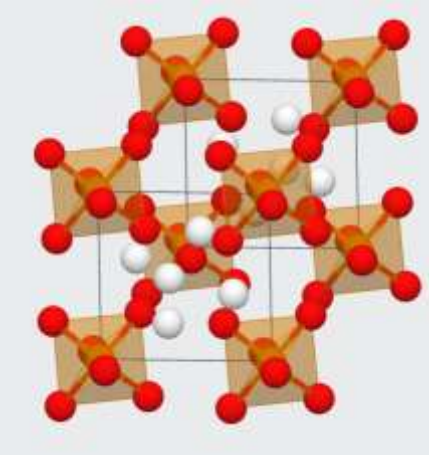

Figure 1. Image of $Te(OH)_6$ crystal [Credits: Materials Project: mp-626012 [3]]

Computational Details

Quantum espresso[4] is a software that used to perform electronic structure calculations and materials modelling. The plane wave density functionals are generated using a plane wave self-consistent field (PWscf) using appropriate pseudopotential files [5].

We use quantum espresso package which is based on density functional theory, plane waves and pseudopotentials. The calculations were done without spin-polarization using PBE exchange correlation functional. The plane waves were generated using a plane wave self-consistent field (PWscf) using respective pseudopotential files.

To determine the right computational settings, the stable crystal, TeO_2 is studied for convergence test to find the right basis set and K-point Monkhorst-Pack grids. Once these settings were optimised, volume optimisation is done by keeping b/a and c/a ratios same. With the lattice parameters corresponding to optimal volume, geometry optimization is done using vc-relax calculation. The total energy corresponding to this optimised geometry is determined. By creating a 2x1x1 supercell for O_2 molecule with vacuum = [1,0,0], where one O-atom placed at (0,0,0) position and the other one at (x,0,0), total energy corresponding to free oxygen atom is calculated. Similar method is followed to find the free atom energy of hydrogen also. Free atom calculation for finding total energy of Te is also performed. The energy values thus obtained is used to find energy of formation of the TeO_2 crystal. For all the supercells, K_points = 1x1x1 is used.

Having found good computational settings, $Te(OH)_6$ molecule is worked on. For these molecules, a 2x1x1 supercell is created with only one molecule and vacuum = [1, 0, 0]. The convergence of total energy on the size of the supercell is done for both the molecules and using the same size, geometry optimization is performed. Specifications of each calculation is discussed below.

Tasks and Results

The cif files used for each of the calculations below are given at the end of this article.

1. Convergence test for TeO_2 crystal is performed to find the right computational settings by finding stable hydrostatic pressure. The optimum value of basis sets and K_points are determined through this step.
   ecutwfc that converged hydrostatic pressure is found to be 87 Ry and erho to be 435.
   K_mesh is found to be 3x3x3.

2. With the same crystal, volume optimisation is done and hence found optimum volume and bulk modulus corresponding to minimum energy. The volume and total energy for various lattice parameters by keeping c/a and b/a ratio same is fit in Birch Murnaghan equation to find min energy and corresponding volume. The results are given below.
   Equation of state: birch first order.
   chisq = 0.2361D-07
   V0 = 2448.43 a.u.^{3}
   k0 = 1289 kbar,
   dk0 = 4.42
   d2k0 = 0.000
   emin =-3565.99909 Ry
   V0 = 362.82 Ang^3
   k0 = 128.9 GPa

Vol Ang^3	E_calc (Ry)	E_fit (Ry)	E_Diff (Ry)	P(GPa)	Enthalpy (Ry)
332.32	-3565.91020	-3565.91027	0.00007	13.75	-3563.81449
341.77	-3565.95910	-3565.95887	-0.00023	8.79	-3564.58065
351.09	-3565.98700	-3565.98720	0.00020	4.55	-3565.25361

360.89	-3565.99870	-3565.99878	0.00008	0.70	-3565.88362
370.87	-3565.99420	-3565.99401	-0.00019	-2.69	-3566.45268
380.71	-3565.97510	-3565.97517	0.00007	-5.58	-3566.94962

Optimised a=5.5079 A^0, b=11.7671 A^0, c= 5.5980 A^0

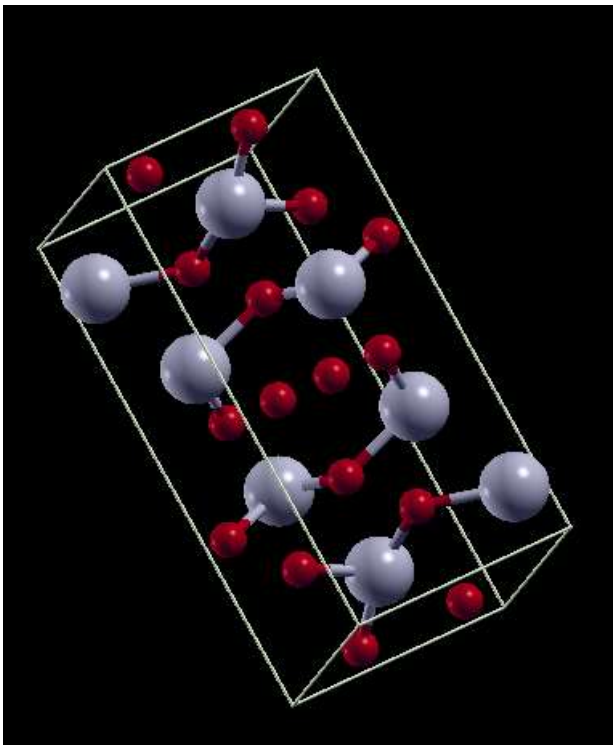

Figure 2. TeO_2 molecule with 8 Te atoms and 16 O atoms (xcrysden image)

3. The lattice parameters from the previous step are used to optimise geometry and find the total energy. The final total force, total energy, stress tensor, and Pressure are given below.

   Total force = 0.001813 Total SCF correction = 0.000008

Total Stress (Ry/bohr**3)			P(Kbar)		
-0.00000183	0	0	-0.27	0	0
0	0.00000058	0	0	0.09	0
0	0	0.00000156	0	0	0.23

   Total energy: -3566.89760264 Ry

4. Supercell for conventional unit cell of O_2 is found using a supercell=[2x1x1] and vacuum = [1,0,0]. ecutwfc = 87 Ry, ecutrho = 435 Ry are used, and spin polarisation is included. The results are below.

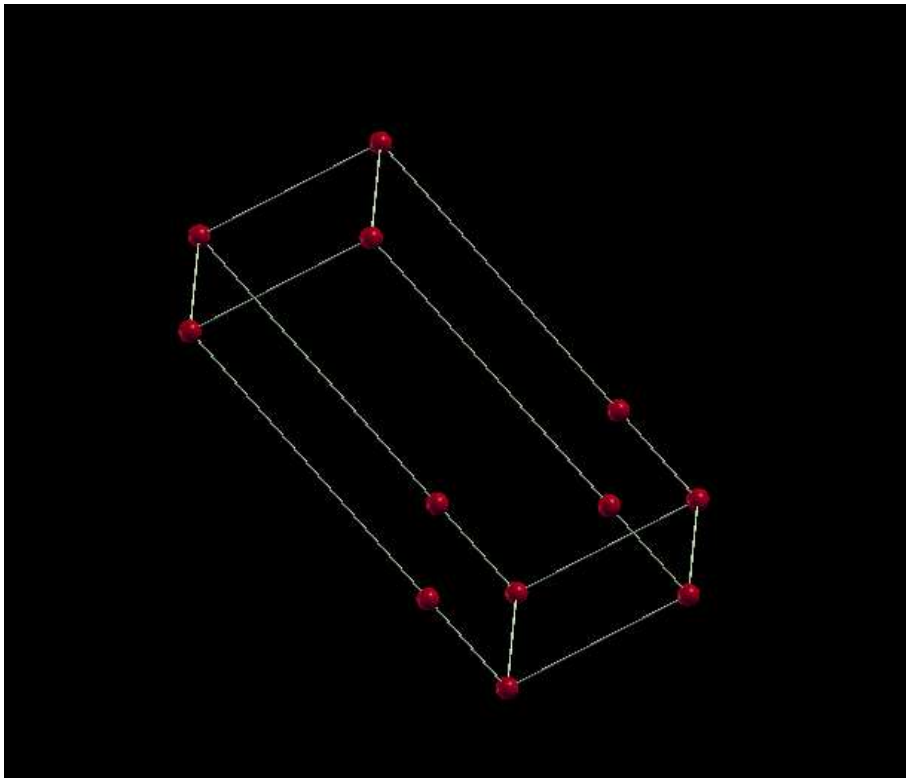

Figure 3. Image of O_2 supercell used for calculation. Supercell=[2,1,1] and supercell-vacuum=[1,0,1]. Generated using xcrysden

ATOMIC_POSITIONS (crystal)

O	0.000000	0.00000000	0.000000000
O	0.2500000	0.00000000	0.000000000

$$Total\ force\ =\quad 0.000180\quad Total\ SCF\ correction\ =\quad 0.000022$$

Total Stress (Ry/bohr^3)			P= 0 Kbar		
-0.00000029	-0.00000001	0.00000002	-0.04	0	0
0	0.00000075	0.00000001	0	0.11	0
0.00000002	-0.00000001	0.00000006	0	0	0.01

Total Energy = -82.5929123435 Ry

5. Free Te atom

Total energy of free atom Te is performed using ecutwfc = 42, ecutrho = 235, and K_points 3x3x3. The total Energy of this system is found to be -362.53708611 Ry.

6. Free atom hydrogen

A H_2 supercell, [2x1x1] and vacuum of [1,0,0] is used to generate conventional unit cell. The results found are shown below. Spin polarization calculation included.

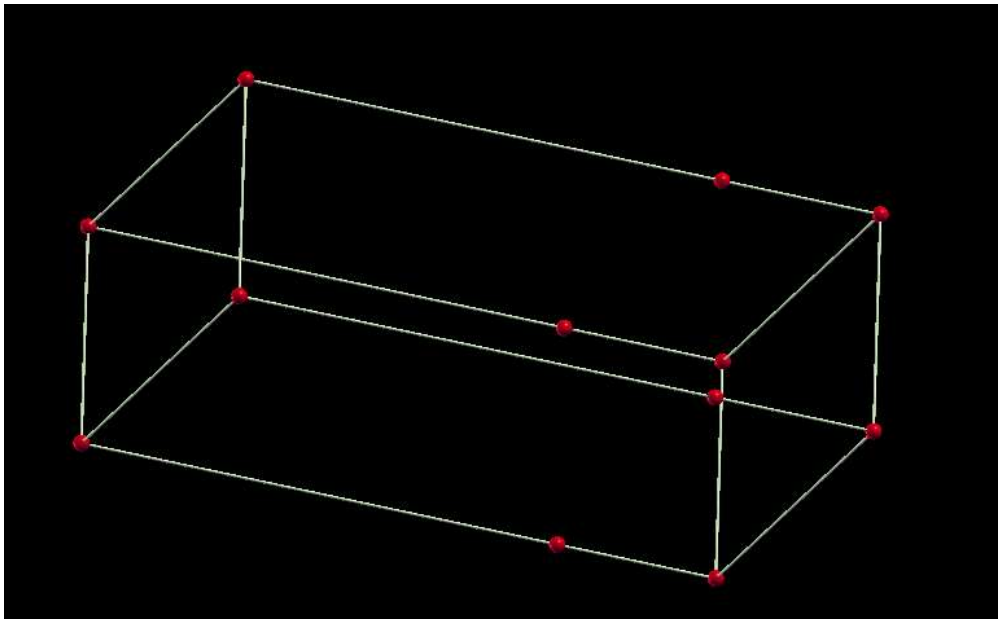

Figure 4. Image of H_2 2x1x1 supercell with vacuum = [1, 0, 0] plotted using xcrysden

ATOMIC_POSITIONS (crystal)

O	0.000000	0.00000000	0.000000000
O	0.2500000	0.00000000	0.000000000

Total force = 0.000049 Total SCF correction = 0.000002

Total Stress (Ry/bohr^3)			P= 0 Kbar		
-0.00000004	0.0000000	0.0000000	-0.01	0	0
0	-0.00000124	0.0000000	0	0.18	0
0.0000000	0.0000000	-0.00000001	0	0	0.00

Total Energy = -2.0010020601 Ry

7. Formation energy of TeO_2

Form the total energy of the TeO_2 and total energy of free Te and O atoms, the formation energy.

$$E_{coh} = \frac{1}{24}(E_{TeO_2} - [8xE_{Te} + \frac{16}{2}E_{O_2}])$$

$E_{coh} = -0.12612438\ Ry = -1.76010233\ eV$ (Without spin polarisation)

$E_{coh} = -0.22Ry = 2.9\ eV$ (With spin polarisation)

The formation energy calculated here with spin is almost double than the actual value of TeO_2 (1.505 eV).

8. $Te(OH)_6$

Total energy corresponding to optimised geometry of $Te(OH)_6$ is performed using relaxed calculation of [2,1,1] supercell with [1,0,0] vacuum created from conventional unit cell of $Te(OH)_6$ with one molecule. Spin polarisation calculation is performed here.

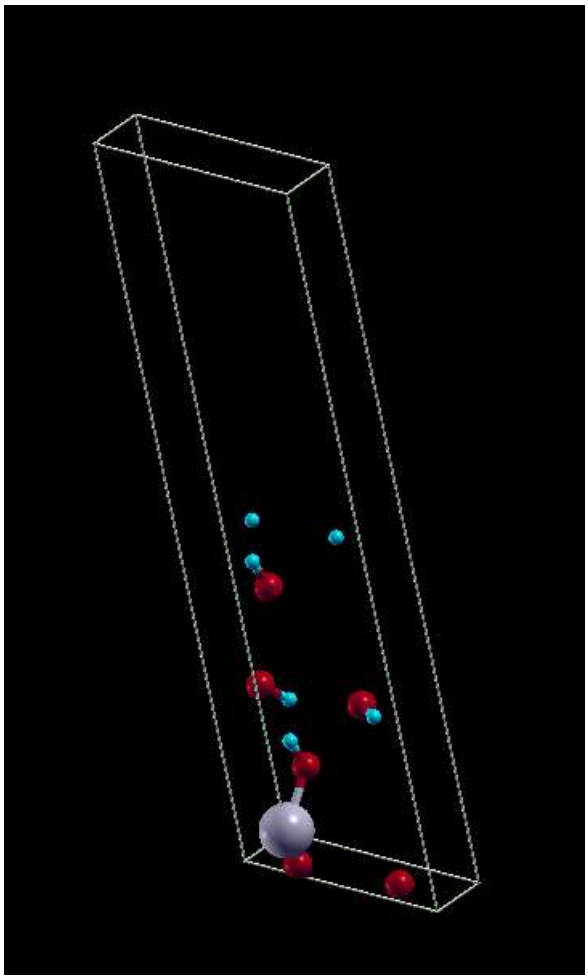

Figure 5. Image of $Te(OH)_6$ supercell using xcrysden

The calculated total energy = -618.809271 Ry

ATOMIC_POSITIONS (crystal)

Te	0.0075144967	0.0952546936	-0.0301436767
O	-0.0054222775	0.0616880220	0.6091213732
O	0.3060250181	0.3026555070	0.8499899512
O	0.1255870012	0.3042378181	0.2261781249
O	0.3358888935	0.2548883619	0.0937890943
O	-0.0114855257	0.7198354325	0.9317708946
O	0.2555830266	0.6643645880	0.8397544635
H	0.2684797466	0.5185263424	0.8259865303
H	0.5215332937	0.3807909971	0.9327480282
H	0.1461457831	0.2046691909	0.1706861507
H	0.3514735628	0.1151781327	0.0651483804
H	0.2227150059	0.6445609773	0.6394667910

H 0.5035909749 0.8598859366 0.5447028946

a_lattice parameter = 10.5211 a.u.

Unit-cell volume = 3542.8098 $(a.u.)^3$

crystal axes: (cart. coord. in units of alat)

a(1) = (4.000000 0.000000 0.000000)
a(2) = (-0.457563 0.892268 0.000000)
a(3) = (-0.485212 -0.292875 0.852345)

The formation energy of the molecule =

$$E_{coh} = \frac{1}{13}\{E_{Te(OH)_6} - [E_{Te} + \frac{6}{2}(E_O + E_H)]\} = -0.1849\ Ry = -2.514\ eV$$

Conclusion

This paper is an attempt to stud the stability of $Te(OH)_6$ molecule to check its possibility to exist in nature by calculating its formation energy using density functional theory methods. The cohesive energy of $Te(OH)_6$ is found to be -2.514 eV. The enthalpy of formation gives an insight on the chemical composition's stability. The results derived from this calculation can be extended to study Po $(OH)_6$ molecules.

[1] P. E. Figgins, "THE RADIOCHEMISTRY OF POLONIUM," *Nucl. Sci. Ser.*, 1961, doi: https://doi.org/10.2172/4034029.

[2] "https://www.livescience.com/39452-polonium.html."

[3] K. Persson, "Materials Data on Te(HO)6 (SG:1) by Materials Project," 2014, doi: 10.17188/1278534.

[4] A. D. C. Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavaz_zoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, C. Stefano de Gironcoli, Stefano Fabris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, F. Gougoussis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, C. Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, P. Sbraccia, Sandro Scandolo, Gabriele Sclauzero, Ari P Seitsonen, Alexander Smogunov, and and R. M. W. Umari, . ", 21(39):, 2009," *J. Phys. Condens. Matter*, 395502 (19pp).

[5] M. Pandit, "First Principle Calculation of Electronic National Institute of Technology Rourkela," no. May 2016, 2019.

List of cif files used

1. **Te**

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_chemical_formula_sum   Te1
_cell_volume   77.99912424
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 _atom_site_occupancy
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2. **O_2**

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_atom_site_label

_atom_site_symmetry_multiplicity

_atom_site_fract_x

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_atom_site_fract_z

_atom_site_occupancy

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_atom_site_symmetry_multiplicity

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_atom_site_fract_z

_atom_site_occupancy

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H H1 1 0.24329100 0.00000000 0.00000000 1

4. **TeO_2**

#--

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#$Revision: 130149 $

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This file is available in the Crystallography Open Database (COD),

http://www.crystallography.net/

#

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contributors.

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'Sawada, H'
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Kristallchemie (-144,1977)
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_journal_volume                  102
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1/2-x,1/2+y,-z

-x,-y,-z

1/2-x,y,1/2+z

x,1/2+y,1/2-z

1/2+x,1/2-y,z

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O2- 8 c 0.164 0.174 0.535 1. 0 d

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O2- -2.000

5. **$Te(OH)_6$**

generated using pymatgen

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_cell_angle_gamma 117.14917498

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_chemical_formula_sum 'Te1 H6 O6'

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_atom_site_symmetry_multiplicity

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_atom_site_fract_z

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H H6 1 0.17343700 0.34061500 0.42609200 1

O O7 1 0.00286100 0.22138900 0.74223600 1

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O O9 1 0.04982400 0.76484400 0.77438500 1

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6. TeO_6

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O O3 1 0.26192800 0.00000000 0.00000000 1

O O4 1 0.50000000 0.00000000 0.76192800 1

O O5 1 0.50000000 0.23807200 0.00000000 1

O O6 1 0.73807200 0.00000000 0.00000000 1