Formation energies of TeO and $Te(OH)_6$ molecules

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We have chosen TeO and $Te(OH)_6$ molecules for our study. The main goal of our project is to find the formation energies of these two molecules. This work have been divided into 4 parts: At the first step, the structure has been built, and convergence tests have been done on structures. The second step is fully geometry optimization to find the stress, total force, unit cell volume and shape, and total energy for formation energy calculations. The third step is supercell size determination for molecules and the modulus calculations have been done. Finally, in the fourth step, these calculations have been repeated for a different molecule. These calculations have been done by the Density Functional Theory (DFT) by the Quantum Espresso (QEs) package.

I. INTRODUCTION

The electronic behavior, geometry optimization, bulk modulus, and formation energies were calculated for two different TeO and $Te(OH)_6$ molecules. The main aim of this paper is to calculate the formation energy of different Te-O-H molecules to find the most stable one. In this job we divided our calculation into 4 parts: At the first step, the structure has been built, and convergence tests have been done on structures. The second step is fully geometry optimization to find the stress, total force, unit cell volume and shape, and total energy for formation energy calculations. The third step is supercell size determination for molecules and the modulus calculations have been done. Finally, in the fourth step, these calculations have been repeated for a different molecule. These calculations have been done by the Density Functional Theory (DFT) by the Quantum Espresso (QEs) package.

II. COMPUTATIONAL METHODS

Our DFT calculations were performed with Quantum Espresso code. A Generalized Gradient Approximation (GGA) exchange-correlation functional with Perdew-Burke-Ernzerhof (PBE) pseudo potential [ref : 10.1103/PhysRevB.50.17953] were used. For

$Te(OH)_6$, charge and potential kinetic cut off energy is set to 90 Ry and 450 Ry, respectively with a 4×4×4 Monkhorst-Pack grid for Brillouin zone sampling. The full geometry optimization has done so that the force convergence acting on each atom was less than meV/A.

III. RESULTS AND DISCUSSIONS

A. Convergence Testing

The results of the convergence testing of $Te(OH)_6$ molecules for ecutwfc is presented in Fig. 1 and corresponding plot of the energy for different ecutfc is shown in the Fig. 2.

Ecut (Ry)	Total energy (Ry)	Time	Pressure (Kbar)
30	-283.0446788	20.57s	-267.42
35	-283.3357864	24.04s	-60.23
40	-283.4144861	29.07s	21.00
45	-283.4299882	34.84s	44.98
50	-283.4319513	38.07s	48.21
55	-283.4331565	47.73s	46.99
60	-283.4351944	56.13s	45.70
65	-283.4374571	1m 2.79s	45.42
70	-283.439295	1m 9.70s	46.03
75	-283.4405083	1m10.28s	46.86
80	-283.4411581	1m16.31s	47.57
85	-283.4414207	1m34.39s	48.06
90	-283.4414785	1m32.90s	48.28
95	-283.441488	2m 4.13s	48.22

FIG. 1. Convergence testing of ecutfc

From the total energy for different ecutwfc value as shown from the Fig. 2 we can say 90 is a good choice for ecutwfc. After find the value for ecutwfc we have to find the good choice for ecutrho and for that we fixed the value of ecutwfc and varied the value of ecutrho with different multiplication factor for ecutwfc. The multiplication factors were

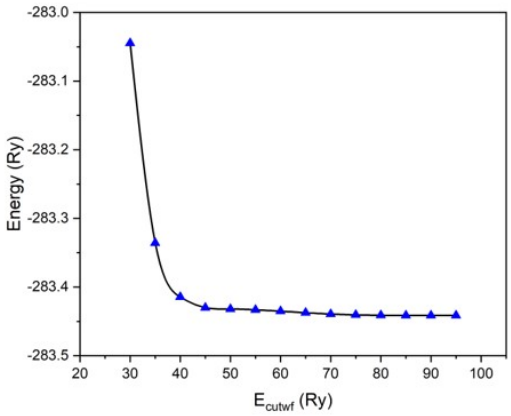

FIG. 2. Energy vs ecutfc

varied from 2 to 9 as shown in the Fig. 2 and we found that 5 is a good choice. Therefore, we have chosen ecutrho as 450 for further calculations. Corresponding results are shown in the Fig. 3 and Fig. 4.

Multiplied	Ecutrho (ry)	Total energy (Ry)	time	Pressure (Kbar)
2	180	-283.44214722	58.91s	47.77
3	270	-283.44140399	1m19.16s	48.18
4	360	-283.44141143	1m16.08s	48.21
5	450	-283.44147851	1m15.14s	48.28
6	540	-283.44148366	1m27.74s	48.14
7	630	-283.44143391	1m38.38s	48.23
8	720	-283.44145937	1m30.72s	48.24
9	810	-283.44143616	1m36.42s	48.19

FIG. 3. Convergence testing of ecutrho

Finally we have plotted energy as function of k points for $Te(OH)_6$ molecules in the Fig. 6 and corresponding data are given in Fig. 5. We found that $4 \times 4 \times 4$ is a good choice for k-mesh.

Therefore, from the convergence test we can say ecutwfc = 90, ecutrho = 450 and k-

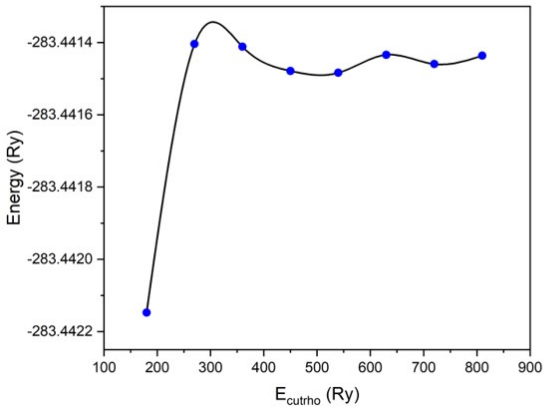

FIG. 4. Energy vs ecutrho

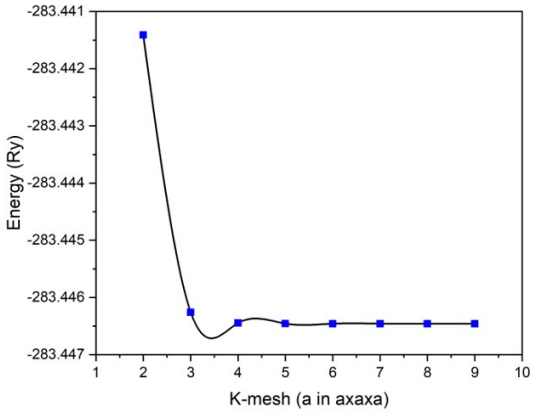

FIG. 6. Energy vs k-points

k-point	Energy (Ry)	Pressure (Kbar)	time
2	-283.44141143	48.21	1m29.12s
3	-283.44625851	47.40	2m10.81s
4	-283.44644715	47.40	5m 5.96s
5	-283.44645707	47.40	8m36.44s
6	-283.44645772	47.40	14m29.74s
7	-283.44645777	47.40	21m14.04s
8	-283.44645778	47.40	30m 8.23s
9	-283.44645776	47.40	33m42.02s

FIG. 5. Convergence testing of k-points

mesh $= 4 \times 4 \times 4$ are good choice for the $Te(OH)_6$ molecule. But with these parameters, pressure is not zero. So we have to find the lattice parameters as well as positions of each atoms with pressure zero, which is called geometry optimization.

B. Geometry Optimization

Using the value of charge and potential kinetic cut off energy is set to 90 Ry and 450 Ry, respectively with a $4 \times 4 \times 4$ Monkhorst-Pack grid for Brillouin zone sampling for $Te(OH)_6$, we did geometry optimization. For geometry optimization we have used bfgs dynamics and found the Cell parameters and position of the atoms for relaxed condition with zero pressure. Corresponding results are given in Fig. 7 and Fig. 8.

- the applied pressure target = 0.0 Kbar and the threshold parameter is 0.5 Kbar.
- The calculated volume after optimizing the shape of unit cell is
- 962.38836 a.u.^3 (142.61124 Ang^3)
- The cell parameters and atoms coordinates calculated as:

```
CELL_PARAMETERS (alat= 10.30811590)
   0.943280402  -0.034116555   0.095099064
  -0.051523378   0.968811789   0.090832657
  -0.337025525  -0.344802936   0.893884460

ATOMIC_POSITIONS (crystal)
Te            0.9901875574        0.9907081597        0.9953531230
O             0.1805883021        0.1914278247        0.8041375588
O             0.7542708705        0.7579483892        0.6747594990
O             0.7160564131        0.2376860223       -0.0152696657
O             0.7983746829        0.7878205889        0.1835979460
O             0.2255482841        0.2182097426        0.3195405074
O             0.2647900526        0.7442261037        0.9991327569
H             0.3787259633        0.1932263919       -0.1290975157
H             0.7936260130        0.8119929398        0.5258830406
H             0.7949478693        0.4183156954        1.0887604221
H             0.6013971865        0.7944130535        1.1220235205
H             0.1867506913        0.1593208414        0.4667970301
H             0.1870221139        0.5669902470        0.8895687770
```

FIG. 7. Cell parameters and position of the atoms after geometry optimization

C. Cohesive Energy of $Te(OH)_6$

Cohesive energy was calculated as shown in the Fig. 9. Cohesive energy was found -3.54486 eV per atom for $Te(OH)_6$. To calculate the cohesive energy we have first calculated the total energy of the $Te(OH)_6$

```
Computing stress (Cartesian axis) and pressure

      total   stress  (Ry/bohr**3)                   (kbar)     P=        0.30
  -0.00000548   0.00000121   0.00000329          -0.81        0.18        0.48
   0.00000121  -0.00001897  -0.00000443           0.18       -2.79       -0.65
   0.00000329  -0.00000443   0.00003055           0.48       -0.65        4.49


  atom    1 type  3   force =     0.00107084    0.00281927    0.00008731
      atom    2 type  1   force =     0.00186459   -0.00091314    0.00061620
      atom    3 type  1   force =     0.00095331    0.00098289   -0.00027816
      atom    4 type  1   force =    -0.00151562   -0.00174696   -0.00064889
      atom    5 type  1   force =    -0.00821214   -0.00030126    0.00550154
      atom    6 type  1   force =     0.00298429    0.00330870   -0.00410518
      atom    7 type  1   force =    -0.00056799   -0.00141697    0.00016975
      atom    8 type  2   force =     0.00010954   -0.00249639    0.00257078
      atom    9 type  2   force =     0.00306707   -0.00075995   -0.00558501
      atom   10 type  2   force =    -0.00023198    0.00030925   -0.00076014
      atom   11 type  2   force =     0.00434239   -0.00164921   -0.00398611
      atom   12 type  2   force =    -0.00463320    0.00092154    0.00236215
      atom   13 type  2   force =     0.00076889    0.00094223    0.00405578

      Total force =     0.017217     Total SCF correction =     0.000034
```

FIG. 8. Pressure and forces after geometry optimization

molecule and then the energy for individual single atoms.

```
E_cohesive= E_single atoms - E_structure =((6*-0.99984054)+(6*-26.31744327)-( -283.4874876456)= 3.39 Ry/formula unit.=  46.123316443401ev/formula unit
Cohesive energy per atom (eV) = 3.55 eV. (its for my calculations)-without the volume optimization for single atoms

The Te single atom volume convergence
The cell parameter is : 16 ang  and the total energy calculated as: -26.27217079 Ry
total energy of Te(OH)6 after full geometry calculation =-283.48151194 Ry

6O -247.77796386
6H -5.99904462
Te -26.31744408
TeO6H6-283.48151194
The cohesive energy = -3.38705938 Ry
Cohesive energy per atom (eV) = -3.54486 eV
```

FIG. 9. Calculation of cohesive energy for $Te(OH)_6$

D. Band Structure

We have calculated the band structure and density of states for $Te(OH)_6$ as shown in the Fig. 10 and Fig. 11.

E. Convergence test of TeO_6

After calculating the cohesive energy of the $Te(OH)_6$ molecule, our next target was TeO_6 molecule. Here also we follow the same steps like convergence test to find proper values of ecutwfc, ecutrho and k-mesh.

We did convergence test for TeO_6 similarly as $Te(OH)_6$ and we found $E_{cutfc} = 90$

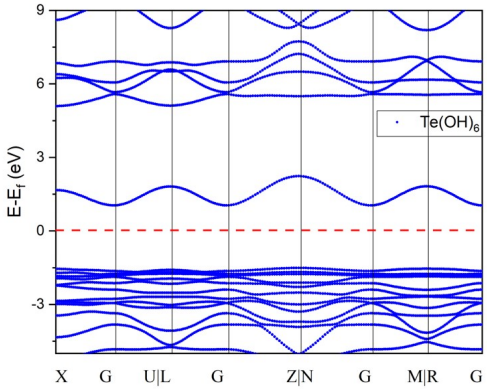

FIG. 10. Band structure of $Te(OH)_6$

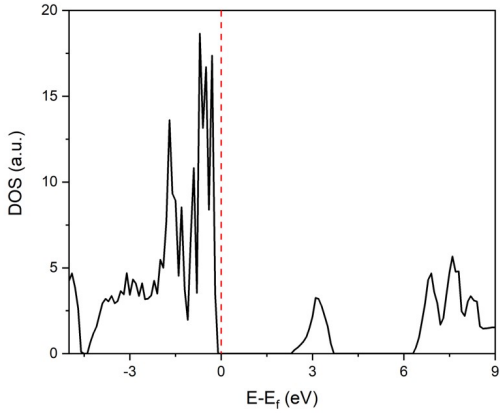

FIG. 11. Calculated density states of $Te(OH)_6$

$E_{cutrho} = 450$ and $K - mesh = 4 \times 4 \times 4$

F. Geometry Optimization of TeO_6

The results of the geometry optimization of TeO_6 are shown in the Fig. 12 to Fig. 14

```
total   stress  (Ry/bohr**3)                   (kbar)     P=        0.19
 0.00000130   0.00000000   0.00000000           0.19        0.00        0.00
 0.00000000   0.00000130   0.00000000           0.00        0.19        0.00
 0.00000000   0.00000000   0.00000124           0.00        0.00        0.18
```

FIG. 12. Stress tensor and pressure of TeO_6 after geometry optimization

```
• Forces acting on atoms (cartesian axes, Ry/au):
• atom   1 type  1   force =    0.00000000   0.00000000   0.00000000
  atom   2 type  2   force =   -0.00007136  -0.00004120   0.00005901
  atom   3 type  2   force =    0.00007136  -0.00004120   0.00005901
  atom   4 type  2   force =    0.00000000   0.00008239   0.00005901
  atom   5 type  2   force =    0.00007136   0.00004120  -0.00005901
  atom   6 type  2   force =   -0.00007136   0.00004120  -0.00005901
  atom   7 type  2   force =   -0.00000000  -0.00008239  -0.00005901
  Total force =     0.000248    Total SCF correction =     0.000014
```

FIG. 13. Forces acting on each atom $Te(OH)_6$ after geometry optimization

```
• CELL_PARAMETERS (alat= 10.02991042)
• 0.972190537  -0.000000000  -0.000000000
•  0.486095268   0.841941702  -0.000000000
• 0.486095268   0.280647234   0.793786594
• ATOMIC_POSITIONS (crystal)
• Te     -0.000000000  -0.000000000   0.000000000
• O       0.723045894   0.723045894   0.276954332
• O       0.276953879   0.723045894   0.276954332
• O       0.723045894   0.276953879   0.276954332
• O       0.276954106   0.276954106   0.723045668
• O       0.723046121   0.276954106   0.723045668
• O       0.276954106   0.723046121   0.723045668
• End final coordinates
```

FIG. 14. Cell parameters and atomic position of TeO_6 after geometry optimization

Geometry optimization was done to find the cell parameters and position of the atoms in the TeO_6 molecule for zero pressure. Then we used those parameters to find the energy of the TeO_6 molecule.

G. Cohesive Energy of TeO_6

Finally we have calculated the Cohesive energy of TeO_6 as shown in the Fig. 15. To calculate the cohesive energy we have first calculated the total energy of the TeO_6 molecule and then same for the individual single atoms.

```
• The total energy is: -275.1050088307 Ry
• 6O -247.77796386
• Te -26.31744408
• Cohesive energy = 1.0096008907
• Cohesive energy per atom (eV) = 1.9615103 eV
```

FIG. 15. Calculation of cohesive energy TeO_6

IV. CONCLUSIONS

We have calculated the formation energy of $Te(OH)_6$ and TeO_6 molecules using DFT calculation. We found that formation energy of TeO_6 and $Te(OH)_6$ molecules for per atom are -3.54486 eV and -1.9615103 eV respectively.

V. ACKNOWLEDGEMENTS

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