

## Supporting information

Mechanism of tautomerisation and geometric isomerisation in thioformic acid and its water complexes: Exploring chemical pathways for water migration

**Gurpreet Kaur and Vikas\***

*Quantum Chemistry Group, Department of Chemistry & Centre of Advanced Studies in*

*Chemistry, Panjab University, Chandigarh- 160014 INDIA.*

Email: qlabspu@pu.ac.in, qlabspu@yahoo.com

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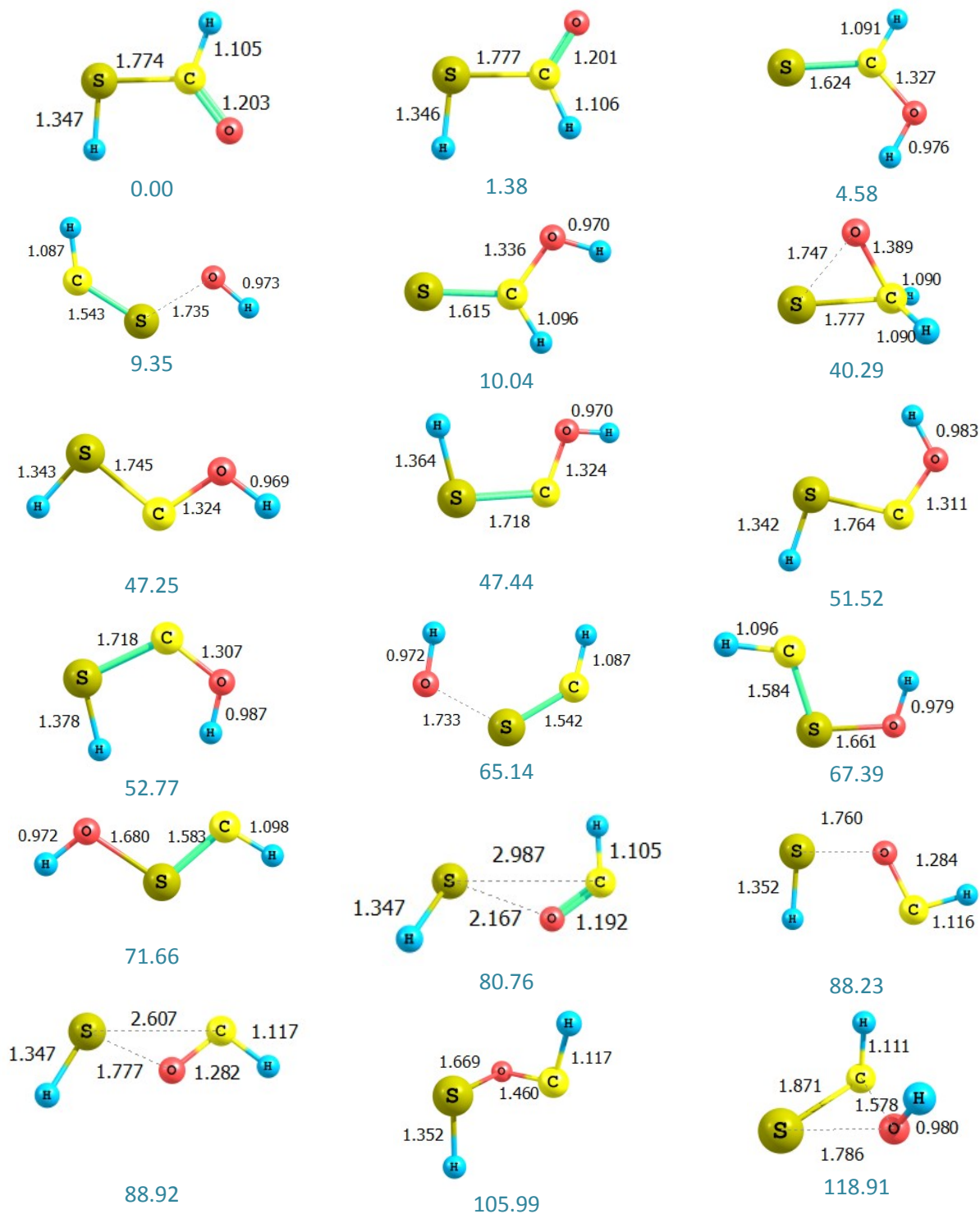


Figure 1. The geometries (with bond length in Å) of isomers of TFA and the values in parenthesis refer to ZPE corrected relative energies (in kcal/mol) with respect to *trans*-TFA(thiol) obtained at DFT/PBE1PBE/6-31+G(d) level.

**Table S1.** Second order interaction energies,  $E^{(2)}$  (in kcal/mol), representing the strength of H-bond formed between *trans*-TFA(thione) and two-water molecules at B3LYP/6-311++G(2d,2p) depicted in Figure 11.

| Bicomplex | Donor<br>TFA                             | Acceptor<br>H <sub>2</sub> O | $E^{(2)}$ | Donor<br>H <sub>2</sub> O                | Acceptor<br>TFA | $E^{(2)}$ | Donor<br>H <sub>2</sub> O                | Acceptor<br>H <sub>2</sub> O | $E^{(2)}$ |
|-----------|--|------------------------------|-----------|--|-----------------|-----------|--|------------------------------|-----------|
| 0         | $n_{S1(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 1.63      | $n_{O3(1)} \rightarrow \sigma^*_{O1-H2}$ |                 | 0.70      | $n_{O2(1)} \rightarrow \sigma^*_{O3-H6}$ |                              | 0.31      |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 10.67     | $n_{O3(2)} \rightarrow \sigma^*_{O1-H2}$ |                 | 31.50     | $n_{O2(2)} \rightarrow \sigma^*_{O3-H6}$ |                              | 17.79     |
| 1         | $n_{S1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 1.59      | $n_{O2(1)} \rightarrow \sigma^*_{O1-H2}$ |                 | 0.63      | $n_{O3(1)} \rightarrow \sigma^*_{O2-H4}$ |                              | 0.26      |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 10.38     | $n_{O2(2)} \rightarrow \sigma^*_{O1-H2}$ |                 | 30.67     | $n_{O3(2)} \rightarrow \sigma^*_{O2-H4}$ |                              | 15.95     |
| 2         | $n_{S1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 0.22      | $n_{O3(1)} \rightarrow \sigma^*_{O1-H2}$ |                 | 0.80      | $n_{O2(1)} \rightarrow \sigma^*_{O3-H6}$ |                              | 0.11      |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 3.16      | $n_{O3(2)} \rightarrow \sigma^*_{O1-H2}$ |                 | 31.53     | $n_{O2(2)} \rightarrow \sigma^*_{O3-H6}$ |                              | 9.99      |
| 3         | $n_{S1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 0.26      | $n_{O3(1)} \rightarrow \sigma^*_{O1-H2}$ |                 | 0.81      | $n_{O2(1)} \rightarrow \sigma^*_{O3-H4}$ |                              | 0.08      |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 3.57      | $n_{O3(2)} \rightarrow \sigma^*_{O1-H2}$ |                 | 31.54     | $n_{O2(2)} \rightarrow \sigma^*_{O3-H4}$ |                              | 9.44      |
| 4         | $n_{S1(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 0.41      | $n_{O2(1)} \rightarrow \sigma^*_{O1-H2}$ |                 | 0.58      |  |                              |           |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 4.62      | $n_{O2(2)} \rightarrow \sigma^*_{O1-H2}$ |                 | 23.48     |  |                              |           |
|           | $n_{S1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 0.13      | $n_{O3(1)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.07      |  |                              |           |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 3.69      | $n_{O3(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.46      |  |                              |           |
| 5         | $n_{S1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 0.66      | $n_{O3(1)} \rightarrow \sigma^*_{O1-H2}$ |                 | 0.84      | $n_{O3(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 4.19      |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 7.94      | $n_{O3(2)} \rightarrow \sigma^*_{O1-H2}$ |                 | 18.62     | $n_{O3(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 0.64      |
| 6         | $n_{S1(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 0.46      | $n_{O3(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.12      |  |                              |           |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 5.86      | $n_{O2(1)} \rightarrow \sigma^*_{O1-H2}$ |                 | 0.62      |  |                              |           |
|           | $n_{O1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 1.90      | $n_{O2(2)} \rightarrow \sigma^*_{O1-H2}$ |                 | 24.92     |  |                              |           |
| 7         | $n_{S1(1)} \rightarrow \sigma^*_{O3-H6}$ |                              | 0.44      | $n_{O2(1)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.20      | $n_{O3(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 0.16      |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O3-H6}$ |                              | 7.51      | $n_{O2(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 4.09      | $n_{O3(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 10.50     |
| 8         | $n_{O1(1)} \rightarrow \sigma^*_{O3-H6}$ |                              | 2.94      | $n_{O2(1)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.19      | $n_{O3(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 0.12      |
|           |  |                              |           | $n_{O2(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 3.18      | $n_{O3(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 8.84      |
| 9         | $n_{S1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 0.27      | $n_{O3(1)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.12      | $n_{O3(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 0.14      |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 6.23      |  |                 |           | $n_{O3(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 8.18      |
| 10        | $n_{S1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 0.09      | $n_{O2(1)} \rightarrow \sigma^*_{C1-H1}$ |                 | 1.71      |  |                              |           |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 2.29      | $n_{O2(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.27      | $n_{O2(2)} \rightarrow \sigma^*_{O3-H6}$ |                              | 5.07      |

where  $n$  denotes the donation of lone pair from lewis structure to  $\sigma^*$  antibond of non-lewis structure

**Table S2.** Same as Table S1, but for bicomplexes of *trans*-TFA(thiol) with two-water molecules depicted in Figure 12.

| Bicomplex | Donor<br>TFA                             | Acceptor<br>H <sub>2</sub> O | E <sup>(2)</sup> | Donor<br>H <sub>2</sub> O                | Acceptor<br>TFA | E <sup>(2)</sup> | Donor<br>H <sub>2</sub> O                | Acceptor<br>H <sub>2</sub> O | E <sup>(2)</sup> |
|-----------|--|------------------------------|------------------|--|-----------------|------------------|--|------------------------------|------------------|
| 0         | $n_{O1(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 5.18             | $n_{O3(1)} \rightarrow \sigma^*_{S1-H4}$ |                 | 0.60             | $n_{O2(1)} \rightarrow \sigma^*_{O3-H2}$ |                              | 0.20             |
|           | $n_{O1(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 3.86             | $n_{O3(2)} \rightarrow \sigma^*_{S1-H4}$ |                 | 13.45            | $n_{O2(2)} \rightarrow \sigma^*_{O3-H2}$ |                              | 13.91            |
| 1         | $n_{O1(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 5.10             | $n_{O3(1)} \rightarrow \sigma^*_{S1-H4}$ |                 | 0.58             | $n_{O2(1)} \rightarrow \sigma^*_{O3-H2}$ |                              | 0.15             |
|           | $n_{O1(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 3.90             | $n_{O3(2)} \rightarrow \sigma^*_{S1-H4}$ |                 | 13.22            | $n_{O2(2)} \rightarrow \sigma^*_{O3-H2}$ |                              | 12.14            |
| 2         | $n_{O1(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 1.67             | $n_{O3(1)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.20             | $n_{O2(1)} \rightarrow \sigma^*_{O3-H2}$ |                              | 0.14             |
|           | $n_{O1(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 7.05             | $n_{O3(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 3.23             | $n_{O2(2)} \rightarrow \sigma^*_{O3-H2}$ |                              | 10.41            |
| 3         | $n_{O1(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 1.75             | $n_{O2(1)} \rightarrow \sigma^*_{S1-H4}$ |                 | 0.30             |  |                              |                  |
|           | $n_{O1(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 3.47             | $n_{O2(2)} \rightarrow \sigma^*_{S1-H4}$ |                 | 7.08             |  |                              |                  |
|           | $n_{O1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 0.57             | $n_{O3(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.10             |  |                              |                  |
|           | $n_{O1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 4.22             |  |                 |                  |  |                              |                  |
| 4         | $n_{O1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 2.82             | $n_{O3(1)} \rightarrow \sigma^*_{S1-H4}$ |                 | 1.70             | $n_{O3(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 2.34             |
|           | $n_{O1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 5.40             | $n_{O3(2)} \rightarrow \sigma^*_{S1-H4}$ |                 | 2.24             | $n_{O3(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 5.54             |
| 5         | $n_{O1(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 1.03             | $n_{O2(1)} \rightarrow \sigma^*_{S1-H4}$ |                 | 0.47             | $n_{O3(1)} \rightarrow \sigma^*_{O2-H6}$ |                              | 0.09             |
|           | $n_{O1(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 2.72             | $n_{O2(2)} \rightarrow \sigma^*_{S1-H4}$ |                 | 10.54            | $n_{O3(2)} \rightarrow \sigma^*_{O2-H6}$ |                              | 7.53             |
| 6         | $n_{S1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 0.42             | $n_{O2(1)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.42             | $n_{O3(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 0.14             |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 2.34             | $n_{O2(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 1.94             | $n_{O3(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 8.69             |
|           |  |                              |                  | $n_{O2(2)} \rightarrow \sigma^*_{S1-H4}$ |                 | 0.18             |  |                              |                  |
|           |  |                              |                  | $n_{O2(1)} \rightarrow \sigma^*_{S1-H4}$ |                 | 0.21             |  |                              |                  |
| 7         | $n_{O1(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 2.25             | $n_{O2(2)} \rightarrow \sigma^*_{S1-H4}$ |                 | 5.25             |  |                              |                  |
|           | $n_{O1(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 4.67             | $n_{O3(1)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.45             |  |                              |                  |
|           |  |                              |                  | $n_{O3(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 1.26             |  |                              |                  |
|           |  |                              |                  | $n_{O3(1)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.19             | $n_{O2(1)} \rightarrow \sigma^*_{O3-H2}$ |                              | 0.14             |
| 8         | $n_{S1(1)} \rightarrow \sigma^*_{O2-H3}$ |                              | 0.46             | $n_{O3(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 2.65             | $n_{O2(2)} \rightarrow \sigma^*_{O3-H2}$ |                              | 8.79             |
|           | $n_{S1(2)} \rightarrow \sigma^*_{O2-H3}$ |                              | 2.39             |  |                 |                  | $n_{O2(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 0.05             |
| 9         | $n_{O1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 1.25             | $n_{O2(1)} \rightarrow \sigma^*_{S1-H4}$ |                 | 2.04             | $n_{O2(1)} \rightarrow \sigma^*_{O3-H2}$ |                              | 0.99             |
|           | $n_{O1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 1.04             | $n_{O2(2)} \rightarrow \sigma^*_{S1-H4}$ |                 | 1.78             | $n_{O2(2)} \rightarrow \sigma^*_{O3-H2}$ |                              | 3.36             |
| 10        | $n_{O1(1)} \rightarrow \sigma^*_{O3-H5}$ |                              | 0.33             | $n_{O2(1)} \rightarrow \sigma^*_{C1-H1}$ |                 | 1.24             |  |                              |                  |
|           | $n_{O1(2)} \rightarrow \sigma^*_{O3-H5}$ |                              | 2.42             | $n_{O2(2)} \rightarrow \sigma^*_{C1-H1}$ |                 | 0.22             | $n_{O2(2)} \rightarrow \sigma^*_{O3-H2}$ |                              | 4.90             |

where  $n$  denotes the donation of lone pair from lewis structure to  $\sigma^*$  antibond of non-lewis structure

**Table S3.** Vibrational frequencies (in  $\text{cm}^{-1}$ ) corresponding to three highest intensities (in  $\text{km/mol}$ ) of bicomplexes of *trans*-TFA(thione) with two-water molecules depicted in Figure 11 at DFT/B3LYP/6-311++G(2d,2p) level of the theory.

| Bicomplex | Frequency | IR intensity | Assignment  |
|-----------|-----------|--------------|---|
| 0         | 3010.10   | 1267.34      | $\nu(\text{O-H})$ in TFA  |
|           | 3535.33   | 858.119      | $\nu_{\text{asym}}(\text{O-H})$ in water  |
|           | 3415.59   | 635.748      | $\nu(\text{O-H})$ in TFA.   |
| 1         | 3034.13   | 1239.06      | $\nu(\text{O-H})$ in TFA  |
|           | 3542.58   | 850.724      | $\nu_{\text{asym}}(\text{O-H})$ in water  |
|           | 3443.89   | 576.170      | $\nu_{\text{asym}}(\text{O-H})$ in water  |
| 2         | 3010.49   | 1236.92      | $\nu_{\text{sym}}(\text{O-H})$ and $\nu_{\text{sym}}(\text{C-H})$ in TFA                    |
|           | 3719.63   | 506.078      | $\nu_{\text{asym}}(\text{O-H})$ in H(5)O(3)H(6)   |
|           | 3623.28   | 331.001      | $\nu_{\text{sym}}(\text{O-H})$ in H(5)O(3)H(6)  |
| 3         | 3001.98   | 1221.75      | $\nu(\text{O-H})$ in TFA  |
|           | 3713.11   | 548.120      | $\nu_{\text{asym}}(\text{O-H})$ in H(5)O(3)H(6)   |
|           | 3629.95   | 277.438      | $\nu_{\text{sym}}(\text{O-H})$ in H(5)O(3)H(6)  |
| 4         | 3213.17   | 758.517      | $\nu(\text{O-H})$ and $\nu(\text{C-H})$ in TFA  |
|           | 3642.8    | 341.475      | $\nu_{\text{asym}}(\text{O-H})$ in H(3)O(2)H(4)   |
|           | 1308.23   | 308.591      | $\nu(\text{C=O})$ with $\omega(\text{H1})$ and $\omega(\text{H2})$ in TFA                   |
| 5         | 3541.76   | 682.442      | $\nu(\text{O-H})$ in TFA and $\nu_{\text{asym}}(\text{O-H})$ in water                       |
|           | 3309.14   | 500.876      | $\nu(\text{O-H})$ in TFA and $\nu(\text{O-H})$ in H(5)O(3)H(6)                              |
|           | 1291.82   | 297.652      | $\nu(\text{C=O})$ with $\omega(\text{H1})$ and $\omega(\text{H2})$ in TFA                   |
| 6         | 3174.00   | 598.164      | $\nu(\text{O-H})$ and $\nu(\text{C-H})$ in TFA  |
|           | 1287.13   | 378.141      | $\nu(\text{C=O})$ with $\omega(\text{H1})$ and $\omega(\text{H2})$ in TFA                   |
|           | 3604.57   | 376.367      | $\nu_{\text{sym}}(\text{O-H})$ in H(3)O(2)H(4)  |
| 7         | 3630.95   | 573.839      | $\nu_{\text{asym}}$ in water  |
|           | 1249.74   | 419.118      | $\nu(\text{C=O})$ with $\omega(\text{H1})$ and $\omega(\text{H2})$ in TFA                   |
|           | 3585.09   | 360.591      | $\nu_{\text{asym}}$ in water  |
| 8         | 1209.27   | 442.799      | $\nu(\text{C=O})$ in TFA  |
|           | 3641.32   | 324.122      | $\nu_{\text{asym}}$ in H(3)O(2)H(4)   |
|           | 3747.79   | 274.437      | $\nu_{\text{asym}}$ in H(5)O(3)H(6)   |
| 9         | 3643.31   | 651.648      | $\nu_{\text{asym}}$ in H(5)O(3)H(6)   |
|           | 1236.05   | 329.964      | $\nu(\text{C=O})$ with $\omega(\text{H1})$ and $\omega(\text{H2})$ in TFA                   |
|           | 3685.61   | 231.755      | $\nu_{\text{asym}}$ in H(3)O(2)H(4)   |
| 10        | 1236.16   | 384.954      | $\nu(\text{C=O})$ with $\omega(\text{H1})$ and $\omega(\text{H2})$ in TFA                   |
|           | 220.363   | 217.887      | $\omega(\text{O-H})$ in Water   |
|           | 1467.85   | 174.211      | $\omega(\text{H1})$ and $\omega(\text{H2})$ and $\nu(\text{C=O})$ and $(\text{C=S})$ in TFA |

\*  $\nu_{\text{sym}}$  for symmetric stretch,  $\nu_{\text{asym}}$  for asymmetric stretch,  $\omega$  for wagging.

| <b>Table S4.</b> Same as Table S3, but for bicomplexes of <i>trans</i> -TFA(thiol) with two-water molecules depicted in Figure 12. |           |              |   |
|--|-----------|--------------|---|
| Bicomplex  | Frequency | IR intensity | Assignment  |
| 0  | 3627.66   | 633.309      | $\nu_{\text{asym}}(\text{O-H})$ in H(3)O(2)H(6)                                   |
|  | 2390.93   | 576.619      | $\nu(\text{S-H})$ in TFA  |
|  | 3508.69   | 441.723      | $\nu_{\text{asym}}(\text{O-H})$ in H(2)O(3)H(5)                                   |
| 1  | 3630.05   | 645.466      | $\nu_{\text{asym}}(\text{O-H})$ in H(3)O(2)H(6)                                   |
|  | 2398.17   | 563.623      | $\nu(\text{S-H})$ in TFA  |
|  | 3536.30   | 384.986      | $\nu_{\text{asym}}(\text{O-H})$ in H(2)O(3)H(5)                                   |
| 2  | 3634.54   | 688.054      | $\nu_{\text{asym}}(\text{O-H})$ in H(3)O(2)H(6)                                   |
|  | 1711.27   | 382.886      | $\nu(\text{C=O})$ in TFA and $\delta(\text{OH})$ in water                         |
|  | 3581.44   | 342.385      | $\nu_{\text{asym}}(\text{O-H})$ in H(2)O(3)H(5)                                   |
| 3  | 3726.81   | 234.727      | $\nu_{\text{asym}}(\text{O-H})$ in H(2)O(3)H(5)                                   |
|  | 1695.05   | 233.241      | $\nu(\text{C=O})$ and $\omega(\text{H4})$ in TFA and $\delta(\text{OH})$ in water |
|  | 3693.89   | 230.970      | $\nu_{\text{asym}}(\text{O-H})$ in H(3)O(2)H(6)                                   |
| 4  | 3618.25   | 448.402      | $\nu_{\text{asym}}(\text{O-H})$ in H(2)O(3)H(5)                                   |
|  | 1722.19   | 335.817      | $\nu(\text{C=O})$ in TFA and $\delta(\text{OH})$ in water                         |
|  | 3696.90   | 289.200      | $\nu_{\text{asym}}(\text{O-H})$ in H(3)O(2)H(6)                                   |
| 5  | 3769.96   | 475.728      | $\nu_{\text{asym}}(\text{O-H})$ in H(3)O(2)H(6)                                   |
|  | 2448.87   | 411.217      | $\nu_{\text{asym}}(\text{O-H})$ in H(2)O(3)H(5)                                   |
|  | 1725.28   | 304.288      | $\nu(\text{C=O})$ in TFA and $\delta(\text{OH})$ in water                         |
| 6  | 1771.83   | 402.874      | $\nu(\text{C=O})$ in TFA  |
|  | 3644.60   | 302.831      | $\nu_{\text{asym}}(\text{O-H})$ in H(3)O(2)H(6)                                   |
|  | 3740.15   | 209.222      | $\nu_{\text{asym}}(\text{O-H})$ in H(2)O(3)H(5)                                   |
| 7  | 1716.50   | 330.606      | $\nu(\text{C=O})$ TFA and $\delta(\text{OH})$ in H(3)O(2)H(6)                     |
|  | 3658.82   | 258.819      | $\nu_{\text{asym}}(\text{O-H})$ in in H(3)O(2)H(6)                                |
|  | 135.428   | 210.496      | $\omega(\text{O-H})$ in Water and $\omega$ in TFA                                 |
| 8  | 1774.26   | 400.225      | $\nu(\text{C=O})$ in TFA  |
|  | 3641.90   | 308.003      | $\nu_{\text{asym}}(\text{O-H})$ in H(3)O(2)H(6)                                   |
|  | 1750.65   | 350.256      | $\nu(\text{C=O})$ in TFA and $\delta(\text{OH})$ in H(2)O(3)H(5)                  |
| 9  | 216.735   | 223.429      | $\omega(\text{O-H})$ in Water   |
|  | 564.120   | 178.369      | $\omega(\text{H4})$ in TFA and $\omega(\text{O-H})$ in Water                      |
|  | 1744.62   | 335.601      | $\nu(\text{C=O})$ in TFA and $\delta(\text{OH})$ in H(2)O(3)H(5)                  |
| 10   | 229.967   | 245.223      | $\omega(\text{O-H})$ in Water   |
|  | 1686.70   | 193.296      | $\delta(\text{OH})$ in water  |

\*  $\nu_{\text{sym}}$  for symmetric stretch,  $\nu_{\text{asym}}$  for asymmetric stretch,  $\omega$  for wagging,  $\delta$  for scissoring or bending.



**TFA**1. *trans*-TFA(thiol)

Energy = -512.7857 a.u.

ZPE= 0.0277 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.734071436187 | 0.110600180986  | 0.028747947586  |
| H | 1.298824215401  | -0.902816454052 | -0.489339588272 |
| S | 0.981866295972  | -0.063841899224 | 0.511294721150  |
| O | -1.259402703966 | -0.419349498284 | -0.907109435483 |
| H | -1.261243311492 | 0.786100201184  | 0.720774508383  |

2. *cis*-TFA(thiol)

Energy = -512.7845 a.u.

ZPE= 0.0276 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.711348653652 | 0.223042117400  | -0.047140789198 |
| H | 1.089357195518  | 1.248425426805  | 1.038295953978  |
| S | 1.010925929607  | 0.055529458836  | 0.427048175381  |
| O | -1.301423903029 | -0.622806448424 | -0.651919878391 |
| H | -1.165015194585 | 1.174077246947  | 0.271857784220  |

3. *trans*-TFA(thione)

Energy = -512.7824 a.u.

ZPE= 0.0316 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.431435468211 | 0.296936802966  | 0.059336063211  |
| H | -0.784999551482 | -1.544639782155 | -0.037232450248 |
| S | 1.183314855100  | 0.181555778383  | 0.186111584168  |
| O | -1.290101910609 | -0.715540477373 | -0.047490586008 |
| H | -0.968743213266 | 1.240201103151  | 0.050427667481  |

4. *cis*-TFA(thione)

Energy = -512.7744 a.u.

ZPE= 0.0312 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.422231424004 | 0.279192639778  | 0.059367180103  |
| H | -2.140853720467 | -0.524089780024 | -0.109786954462 |
| S | 1.185842397854  | 0.197650691135  | 0.186957083921  |
| O | -1.216799520555 | -0.796771309407 | -0.044563406984 |
| H | -0.960817829244 | 1.226563638546  | 0.050341168320  |

## 5. IM1

Energy = -512.6642 a.u.

ZPE= 0.0237 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -1.724122977770 | 0.478298600479  | -0.027697060497 |
| H | 1.599792085817  | 0.093575909417  | -0.890384814613 |
| S | 1.185178069481  | -0.316955800687 | 0.319047805776  |
| O | -0.923553886881 | -0.274576010812 | -0.457789483902 |
| H | -1.539362144714 | 1.222546161065  | 0.763290418580  |

## 6. IM2

Energy = -512.6181 a.u.

ZPE= 0.0255 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.997936725097 | 0.663612183559  | 0.119253448890  |
| H | 1.345450610535  | 0.691570656279  | -0.629207292191 |
| S | 0.766157933960  | -0.085154526889 | 0.312451057751  |
| O | -0.592629804315 | -0.606345073433 | -0.511160688965 |
| H | -1.443771855004 | 0.340675989605  | 1.082779071379  |

## 7. TS0

Energy = -512.7696 a.u.

ZPE= 0.0265 a.u.

one imaginary frequency= -420.5028  $\text{cm}^{-1}$

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.715805489720 | 0.254557703662  | -0.155326217921 |
| H | 0.664938756781  | -0.200405097942 | 1.676933153360  |
| S | 1.047918981671  | 0.098021180379  | 0.424323643620  |
| O | -1.349072275653 | -0.651597132751 | -0.586537069682 |
| H | -1.103446687687 | 1.281791566270  | -0.086115953593 |

## 8. TS1

Energy = -512.7595 a.u.

ZPE= 0.0294 a.u.

one imaginary frequency= -660.8805  $\text{cm}^{-1}$

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.409834660038 | 0.294819867173  | 0.001337028769  |
| H | -1.453562769106 | -1.108095988504 | -0.852289443569 |
| S | 1.185730156706  | 0.191384474979  | 0.199816205051  |
| O | -1.273157855845 | -0.762060608725 | 0.028923586527  |
| H | -0.915532003133 | 1.254273989819  | -0.101344555910 |

## 9. TS2

Energy = -512.7328 a.u.

ZPE= 0.0254 a.u.

one imaginary frequency= -1738.7204  $\text{cm}^{-1}$

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.528238729586 | 0.383860116650  | 0.054684092824  |
| H | 0.101050898072  | -1.179943069311 | 0.048156903780  |
| S | 1.136383745194  | 0.123506480149  | 0.180169126751  |
| O | -1.175520958672 | -0.694507893968 | -0.037430421184 |
| H | -1.031822070673 | 1.348267151188  | 0.049283926571  |

## 10. TS3

Energy = -512.6129 a.u.

ZPE= 0.0244 a.u.

one imaginary frequency= -675.3042 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.945002271808 | 0.585304205842  | 0.097485724369  |
| H | 1.400085872022  | 0.780200881096  | -0.535915290967 |
| S | 0.807029949492  | -0.051713197034 | 0.345355627712  |
| O | -0.717648160862 | -0.602631927950 | -0.546759833880 |
| H | -1.490253316485 | 0.410872778158  | 1.046660266466  |

## 11. TS4

Energy = -512.6118 a.u.

ZPE= 0.0239 a.u.

one imaginary frequency= -471.6962 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -1.241873334284 | 0.642956105724  | 0.010990392989  |
| H | 1.236000175168  | 0.854160196060  | -0.517468681074 |
| S | 0.870087723623  | -0.140120277447 | 0.318163112614  |
| O | -0.613294885580 | -0.499711854536 | -0.449411439914 |
| H | -1.398891252035 | 0.475412445920  | 1.098896463677  |

## 12. TS5

Energy = -512.6089 a.u.

ZPE= 0.0235 a.u.

one imaginary frequency= -525.7945 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -1.302033834855 | 0.483076334282  | 0.231221558215  |
| H | 1.393244240419  | 0.663870139019  | -0.557361095248 |
| S | 0.866879847874  | -0.259365687290 | 0.277483580739  |
| O | -0.632857755752 | -0.449889832356 | -0.536509772736 |
| H | -0.888944710073 | 1.471864736436  | -0.086323059134 |

### Complexes of TFA with single-water molecule

#### 1. *trans*-TFA(thiol)-H<sub>2</sub>O (complex 1)

BSSE corrected energy = -589.2572 a.u.

ZPE= 0.0527 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.632141582783  | 0.973428525904  | -0.362413296478 |
| H | 1.476606458097  | 1.642965261287  | -0.582174741513 |
| S | 1.160949889326  | -0.714836602176 | -0.275813462677 |
| O | -0.490964307061 | 1.389252910764  | -0.208835501423 |
| H | -1.854413415014 | 0.022866411346  | 0.224162519273  |
| H | -0.070131049030 | -1.215474549432 | -0.012252831952 |
| O | -2.092462240728 | -0.897570029425 | 0.418880330548  |
| H | -2.870663923868 | -1.090668729537 | -0.110015615438 |

#### 2. *trans*-TFA(thiol)-H<sub>2</sub>O (complex 2)

BSSE corrected energy = -589.2542 a.u.

ZPE= 0.0517 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.106697127979  | -0.072260770727 | 0.351657145467  |
| H | 1.082180392953  | -0.497003806402 | 0.627891471840  |
| S | -1.223971300766 | -0.893804211082 | 1.197841713396  |
| O | -0.013457847137 | 0.836233207218  | -0.429151927217 |
| H | -2.195350668184 | -0.148883642666 | 0.642482660686  |
| H | 3.287918884741  | 1.775400406425  | -1.257702929458 |
| O | 2.822997367459  | 0.998879965335  | -0.938269070646 |
| H | 1.881377913731  | 1.216287786159  | -0.987304936095 |

#### 3. *trans*-TFA(thiol)-H<sub>2</sub>O (complex 3)

BSSE corrected energy = -589.2513 a.u.

ZPE= 0.0506 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.504554790097 | 0.668355920375  | -0.050706698063 |
| H | 0.439257697388  | 1.116071542293  | -0.388149199342 |
| S | -0.187081688937 | -0.923398230492 | 0.725243339361  |
| O | -1.583652042336 | 1.171556815644  | -0.182798741474 |
| H | -1.479725964389 | -1.166949934982 | 1.001283629204  |
| H | 3.306441188251  | 0.444767423893  | 0.522025560769  |
| O | 2.777019578411  | 0.446632970385  | -0.280394696482 |
| H | 3.201317011172  | -0.185805440364 | -0.867019549497 |

4. *cis*-TFA(thiol)-H<sub>2</sub>O (complex 4)

BSSE corrected energy = -589.2533 a.u.

ZPE= 0.0515 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.299940096657  | 0.090289482427  | -0.252733186608 |
| H | -0.149704490945 | -0.630808048512 | -0.948760054815 |
| O | -0.352401040235 | 0.801241370020  | 0.465037510264  |
| S | 2.081336845239  | 0.127051619833  | -0.268207739860 |
| H | 2.215744807753  | -0.823827504333 | -1.206641407137 |
| H | -2.240000554199 | 0.248673651797  | 0.009904999542  |
| O | -2.815267400913 | -0.329396745254 | -0.510786952737 |
| H | -3.709698941643 | -0.016731221724 | -0.358162582540 |

5. *cis*-TFA(thiol)-H<sub>2</sub>O (complex 5)

BSSE corrected energy = -589.2520 a.u.

ZPE= 0.0509 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.319124277226  | 0.984065876009  | 0.503668599420  |
| H | -0.773042252527 | 0.868866671257  | 0.436882726002  |
| O | 0.862255433626  | 1.812247147273  | 1.177623082110  |
| S | 1.205000661807  | -0.201889612181 | -0.505366129855 |
| H | 0.090141187725  | -0.795209660253 | -0.970699203601 |

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| H | -2.524844820832 | -1.935124537800 | -0.892709823073 |
| O | -2.083097154248 | -1.153701763568 | -1.237300455587 |
| H | -2.539641226596 | -0.938694046594 | -2.055763434764 |

6. *cis*-TFA(thiol)-H<sub>2</sub>O (complex 6)

BSSE corrected energy = -589.2522 a.u.

ZPE= 0.0514 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.727925935477  | -0.741138307992 | 0.043578510428  |
| H | 1.610252852560  | -1.396834736129 | 0.057744402172  |
| O | -0.394872381866 | -1.167055215690 | -0.010336025256 |
| S | 1.110956594778  | 0.995936888982  | 0.107573450101  |
| H | 2.441261122978  | 0.817696664512  | 0.149845593462  |
| H | -3.588620211709 | 0.140455782116  | -0.090247662618 |
| O | -2.753301419767 | 0.612851925984  | -0.065190695612 |
| H | -2.071056152952 | -0.072161206594 | -0.052397030598 |

7. *trans*-TFA(thione)-H<sub>2</sub>O (complex 7)

BSSE corrected energy = -589.2591 a.u.

ZPE= 0.0568 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.641195909233  | 0.866104972262  | -0.359047146274 |
| H | 1.347783302557  | 1.659834693589  | -0.585599969769 |
| S | 1.126529315797  | -0.702269030499 | -0.290208127196 |
| O | -0.562587861938 | 1.351353774948  | -0.167188836762 |
| H | -1.209700806467 | 0.624039367363  | 0.039289949089  |
| H | -1.171611571858 | -1.328822641556 | 0.256294883460  |
| O | -2.004790596754 | -0.844634364472 | 0.403788033043  |
| H | -2.645317646022 | -1.209705865506 | -0.214177463380 |

8. *trans*-TFA(thione)-H<sub>2</sub>O (complex 8)

BSSE corrected energy = -589.2500 a.u.

ZPE= 0.0553 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.017762682991 | 0.710843750012  | -0.238664230857 |
| H | -1.044651775188 | 0.680038058721  | 0.112213137000  |
| S | 0.932162054576  | -0.611536425401 | -0.326026637908 |
| O | 0.333660916102  | 1.945753946718  | -0.575095911354 |
| H | 1.253584170846  | 1.934501920185  | -0.884898413437 |
| H | -1.231506549191 | -1.696569459413 | 0.468647178360  |
| O | -2.155638601097 | -1.514736662005 | 0.689502248152  |
| H | -2.353292290727 | -2.070706800449 | 1.447265620084  |

9. *trans*-TFA(thione)-H<sub>2</sub>O (complex 9)

BSSE corrected energy = -589.2479 a.u.

ZPE= 0.0546 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.567177997778 | -0.259449327654 | 0.321554267414  |
| H | 0.105412384099  | 0.269823217854  | 0.988059289558  |
| S | -2.185411059755 | -0.240263180957 | 0.434856767947  |
| O | 0.140227334059  | -0.924636453998 | -0.600731986503 |
| H | -0.482379532594 | -1.388496953639 | -1.183539546794 |
| H | 2.300455016271  | -0.442146047340 | -0.096842522870 |
| O | 2.624473723939  | 0.116353314769  | 0.617221422448  |
| H | 3.582327137907  | 0.100599029756  | 0.550632285267  |

10. *cis*-TFA(thione)-H<sub>2</sub>O (complex 10)

BSSE corrected energy = -589.2492 a.u.

ZPE= 0.0553 a.u.

no imaginary frequency

Cartesian coordinates

|   |                |                 |                 |
|---|----------------|-----------------|-----------------|
| C | 0.060654934777 | -0.381031388288 | -0.097836670403 |
| H | 1.053308655179 | -0.826760773653 | -0.168134415129 |



|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| S | -1.270171730025 | -1.292291936998 | 0.092921102141  |
| O | 0.060621234980  | 0.944708103745  | -0.182525096034 |
| H | 0.974407403123  | 1.279836948981  | -0.294912708408 |
| H | 2.844429839084  | 2.347561546541  | -1.322130153428 |
| O | 2.649114237069  | 1.886471549736  | -0.500692318055 |
| H | 3.000043509949  | 2.438489694645  | 0.204732721819  |

11. *cis*-TFA(thione)-H<sub>2</sub>O (complex 11)

BSSE corrected energy = -589.2433 a.u.

ZPE= 0.0551 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.382116854467 | 0.596809163333  | -0.056841496692 |
| H | 0.461646687899  | 1.280212462954  | -0.138713464288 |
| S | -0.183445377523 | -1.013304680800 | -0.068860811842 |
| O | -1.576138970526 | 1.186598142805  | 0.052111282074  |
| H | -1.475015251258 | 2.146928711470  | 0.035050782021  |
| H | 2.190280796304  | -0.263671770868 | -0.422199228769 |
| O | 2.770584459251  | 0.504684445162  | -0.530236066934 |
| H | 3.602647537618  | 0.259422205345  | -0.118330239647 |

12. *cis*-TFA(thione)-H<sub>2</sub>O (complex 12)

BSSE corrected energy = -589.2409 a.u.

ZPE= 0.0544 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 1.293927911023  | 0.553430018319  | 0.121753389154  |
| H | 2.281779922068  | 1.012085029843  | 0.120692798008  |
| S | -0.061212278490 | 1.434178839058  | 0.227381091344  |
| O | 1.302208320561  | -0.778177417331 | 0.030184460744  |
| H | 2.206707555687  | -1.112658191435 | -0.022525600261 |
| H | -1.696927650879 | -0.578625650271 | 0.126183588666  |
| O | -2.357887089995 | -1.283348025054 | 0.087879520394  |
| H | -3.203698123755 | -0.829050731096 | 0.113117260235  |

## 13. Complex TS1/2

BSSE corrected energy = -589.2525 a.u.

ZPE= 0.0509 a.u.

One imaginary frequency = -50.5322 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.643122851154  | 0.073076059944  | 0.437231335670  |
| H | 1.085063276185  | -0.079012450953 | 1.433565945661  |
| S | 1.879868998462  | -0.073475932662 | -0.833888599376 |
| O | -0.521941855920 | 0.306604047948  | 0.264216851340  |
| H | 1.029935626720  | 0.148733505524  | -1.851404893005 |
| H | -3.935512606844 | 0.293515134914  | 0.693674017965  |
| O | -3.475990688200 | -0.353368936650 | 0.153171524038  |
| H | -2.545628176208 | -0.103694378573 | 0.200984364133  |

## 14 Complex TS1/3

BSSE corrected energy = -589.2493 a.u.

ZPE= 0.0504 a.u.

One imaginary frequency = -41.8938 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 1.521569000000  | 0.209620000000  | 0.382843000000  |
| H | 1.964685000000  | -0.066961000000 | 1.352460000000  |
| H | -2.198905000000 | 0.236810000000  | 0.455289000000  |
| O | -3.023383000000 | 0.445851000000  | 0.004009000000  |
| H | -3.259248000000 | 1.328513000000  | 0.301545000000  |
| S | 0.227841000000  | -0.950545000000 | -0.069851000000 |
| H | -0.072154000000 | -0.350338000000 | -1.234624000000 |
| O | 1.872228000000  | 1.154522000000  | -0.260773000000 |

## 15. Complex TS4/5

BSSE corrected energy = -589.2504 a.u.

ZPE= 0.0504 a.u.

One imaginary frequency = -38.7121 cm<sup>-1</sup>

## Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.391115604812  | 0.477774475125  | 0.095731810825  |
| H | -0.489056102131 | 0.020142364450  | -0.376425889725 |
| O | 0.334831992789  | 1.230538589279  | 1.025995152045  |
| S | 1.952645228594  | -0.005765906818 | -0.656814411159 |
| H | 1.400028751623  | -0.814722655639 | -1.574763204602 |
| H | -3.079242890566 | -0.495451029058 | 0.171183934553  |
| O | -2.662500152740 | -0.742871452150 | -0.659496141103 |
| H | -3.311495541672 | -0.539327252145 | -1.338717620857 |

## 16. Complex TS1/5

BSSE corrected energy = -589.2365 a.u.

ZPE= 0.0497 a.u.

One imaginary frequency = -330.5483  $\text{cm}^{-1}$

## Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 1.106468000000  | 0.541920000000  | 0.426269000000  |
| H | 1.268609000000  | 0.628440000000  | 1.511239000000  |
| O | 1.288110000000  | 1.445255000000  | -0.325772000000 |
| S | 0.562130000000  | -1.148291000000 | -0.100975000000 |
| H | -0.737335000000 | -0.801018000000 | 0.020782000000  |
| H | -3.445332000000 | -0.005956000000 | 0.159550000000  |
| O | -2.556062000000 | 0.350891000000  | 0.082221000000  |
| H | -2.575204000000 | 0.930506000000  | -0.685168000000 |

## 17. Complex TS2/4

BSSE corrected energy = -589.2371 a.u.

ZPE= 0.0502 a.u.

One imaginary frequency = -432.3564  $\text{cm}^{-1}$

## Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.127557000000 | -0.061224000000 | -0.054931000000 |
| H | 0.391806000000  | -1.024921000000 | -0.141143000000 |
| O | 0.452850000000  | 0.978096000000  | 0.007863000000  |
| S | -1.976899000000 | -0.190067000000 | -0.066434000000 |
| H | -2.030628000000 | -0.259505000000 | 1.274371000000  |

|   |                |                 |                 |
|---|----------------|-----------------|-----------------|
| H | 2.453753000000 | 0.368917000000  | 0.026238000000  |
| O | 3.006691000000 | -0.422728000000 | 0.035855000000  |
| H | 3.904470000000 | -0.119018000000 | -0.116685000000 |

## 18. Complex TS7/8

BSSE corrected energy = -589.2464 a.u.

ZPE= 0.0544 a.u.

One imaginary frequency = -78.6109 cm<sup>-1</sup>

## Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.514635973861  | 0.795870946259  | 0.142775183483  |
| H | 0.593464261318  | 1.125689095001  | 1.173912770880  |
| S | 1.053821213261  | -0.650387374368 | -0.382703592458 |
| O | -0.064850100448 | 1.732602943216  | -0.592933857495 |
| H | -0.143154254084 | 1.407770469272  | -1.504947627554 |
| H | -1.482846256674 | -1.376443317045 | 0.214720349294  |
| O | -2.420009381046 | -1.203213379819 | 0.356587305075  |
| H | -2.791402666587 | -2.040457248486 | 0.646589146291  |

## 19. Complex TS8/9

BSSE corrected energy = -589.2475 a.u.

ZPE= 0.0544 a.u.

One imaginary frequency = -38.3425 cm<sup>-1</sup>

## Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -1.744451762905 | 0.173836403379  | 0.049212581986  |
| H | -0.714575573305 | -0.142615078095 | 0.178320339904  |
| S | -3.038882568348 | -0.795689465895 | 0.218762541322  |
| O | -1.782705534747 | 1.469966999777  | -0.268724277343 |
| H | -2.713258363106 | 1.725001199243  | -0.376884906855 |
| H | 1.502471200612  | 1.444284254776  | -0.200593521135 |
| O | 1.513619363729  | 0.542409041966  | 0.132367132383  |
| H | 2.376649627086  | 0.191399075864  | -0.103073256311 |

## 20. Complex TS7/9

BSSE corrected energy = -589.2472 a.u.

ZPE= 0.0546 a.u.

One imaginary frequency =  $-26.8929 \text{ cm}^{-1}$

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.490215632275  | 0.220760871909  | -0.692427998641 |
| H | 0.126625739149  | 0.520962737120  | -1.670051857630 |
| S | 2.051028634442  | -0.036781266816 | -0.345069385213 |
| O | -0.536446625440 | 0.102994072858  | 0.157697410696  |
| H | -0.193201550843 | -0.175161151193 | 1.022790994836  |
| H | -2.657866314056 | -0.052467972202 | 0.192829093103  |
| O | -3.532551963107 | -0.305947304067 | 0.507001115410  |
| H | -4.070938524014 | 0.485858878269  | 0.432817855447  |

21. Complex TS10/11

BSSE corrected energy =  $-589.2410 \text{ a.u.}$

ZPE=  $0.0543 \text{ a.u.}$

One imaginary frequency =  $-41.6435 \text{ cm}^{-1}$

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.282825483859 | 0.321242959326  | 0.002160391908  |
| H | 0.747472985264  | 0.668072321292  | -0.059331924828 |
| S | -0.675502910316 | -1.250213724672 | -0.002681856923 |
| O | -1.189983874688 | 1.306782929620  | 0.077892984027  |
| H | -0.742350410881 | 2.162380176933  | 0.055667100803  |
| H | 3.078918667590  | 0.199727424000  | -1.100056981550 |
| O | 2.937120046076  | 1.014726488440  | -0.609069794993 |
| H | 3.661595899777  | 1.057729766102  | 0.021349729637  |

22. Complex TS10/12

BSSE corrected energy =  $-589.2405 \text{ a.u.}$

ZPE=  $0.0540 \text{ a.u.}$

One imaginary frequency =  $-83.9158 \text{ cm}^{-1}$

Cartesian coordinates

|   |                |                 |                |
|---|----------------|-----------------|----------------|
| C | 1.239247363365 | 0.631001867755  | 0.130273640353 |
| H | 2.295217131258 | 0.894111695045  | 0.172006673975 |
| S | 0.059571115425 | 1.734081872237  | 0.209922070323 |
| O | 1.001966573928 | -0.680788689394 | 0.007246788234 |

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| H | 1.826334702260  | -1.183371983141 | -0.020418931616 |
| H | -1.464080747102 | -0.777870440122 | 0.068792406717  |
| O | -2.209610163923 | -1.388915490101 | 0.078853430762  |
| H | -2.983960353003 | -0.826057877543 | 0.157285437710  |

## 23. Complex TS7/10

BSSSE corrected energy = -589.2235 a.u.

ZPE= 0.0534 a.u.

One imaginary frequency = -429.6389 cm<sup>-1</sup>

Cartesian coordinates

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.626126000 | 0.621180000  | 0.362091000  |
| H | 1.261012000  | 0.551680000  | -0.147824000 |
| S | -1.709679000 | -0.507843000 | -0.061508000 |
| O | 0.424146000  | 1.013385000  | -0.378669000 |
| H | -0.741792000 | 1.180059000  | 1.292302000  |
| H | 2.646556000  | -1.174781000 | -0.564800000 |
| O | 2.704546000  | -0.431948000 | 0.044727000  |
| H | 2.916310000  | -0.810045000 | 0.903440000  |

## 24. Complex TS8/11

BSSSE corrected energy = -589.2270 a.u.

ZPE= 0.0532 a.u.

One imaginary frequency = -681.6726 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.666465000000 | -0.457716000000 | -0.057059000000 |
| H | 0.103904000000  | -1.221573000000 | -0.149838000000 |
| S | -0.292054000000 | 1.114114000000  | 0.008046000000  |
| O | -1.935401000000 | -0.946911000000 | -0.086029000000 |
| H | -2.266907000000 | -1.164162000000 | 0.792583000000  |
| H | 2.056203000000  | 0.181828000000  | 0.039772000000  |
| O | 2.612691000000  | -0.608477000000 | 0.088472000000  |
| H | 3.360127000000  | -0.432518000000 | -0.488451000000 |

## 25. Complex TS1/7

BSSE corrected energy = -589.2380 a.u.

ZPE= 0.0509 a.u.

One imaginary frequency = -1055.0623 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.546702016679  | 0.894253067488  | -0.346566678927 |
| H | 1.338328778226  | 1.608864377288  | -0.587925182046 |
| S | 1.019718765675  | -0.752768130289 | -0.263401629543 |
| O | -0.602493562983 | 1.349210849538  | -0.158163079262 |
| H | -1.444541450579 | 0.268274556243  | 0.140096959425  |
| H | -0.609726581322 | -1.095733000537 | 0.117630588111  |
| O | -1.717752180839 | -0.758892326619 | 0.341632860409  |
| H | -2.296467993236 | -1.076752300080 | -0.362781909775 |

## 26. Complex TS2/8

BSSE corrected energy = -589.1990 a.u.

ZPE= 0.0481 a.u.

One imaginary frequency = -1728.8280 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.128437873322 | 0.209528653713  | 0.101839763923  |
| H | 0.935520470800  | 0.284588606354  | -0.117468227751 |
| S | -0.871740781319 | -0.904314331812 | 1.139851521894  |
| O | -0.970644878812 | 0.991772570596  | -0.421714572048 |
| H | -1.803632700236 | 0.221548698977  | 0.343749915337  |
| H | 3.867178383685  | 0.339279387061  | -0.177519196713 |
| O | 3.076444129732  | 0.613041574889  | -0.650391054758 |
| H | 3.340134042475  | 1.373641895702  | -1.175747766054 |

## 27. Complex TS7/7{1}

BSSE corrected energy = -589.2577 a.u.

ZPE= 0.0559 a.u.

One imaginary frequency = -288.4560 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.645027540001  | 0.863203522476  | -0.354895134647 |
| H | 1.358489054116  | 1.650627923769  | -0.581275917460 |
| S | 1.114446212187  | -0.707265330326 | -0.283790325290 |
| O | -0.554084768355 | 1.366309892896  | -0.166620891680 |
| H | -1.211079691063 | 0.658751034836  | 0.039966951590  |
| H | -1.237081852165 | -1.415344455790 | 0.262867245954  |
| O | -2.012094862486 | -0.839655954562 | 0.356085158307  |
| H | -2.779824090577 | -1.375368780406 | 0.567349942810  |

## 28. Complex TS7/7{2}

BSSE corrected energy = -589.2565 a.u.

ZPE= 0.0561 a.u.

One imaginary frequency = -174.4400 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.677429531836  | 0.878240324198  | -0.368320860440 |
| H | 1.335028903047  | 1.714828108773  | -0.589317275554 |
| S | 1.232201783066  | -0.663034654126 | -0.338846434771 |
| O | -0.549121176504 | 1.299347429076  | -0.146392362266 |
| H | -1.153928956559 | 0.539188021729  | 0.056002625695  |
| H | -1.695263381536 | -1.260359765127 | 1.125001535027  |
| O | -2.171361166279 | -0.830957972353 | 0.404916966702  |
| H | -2.010136087621 | -1.402994210395 | -0.354250510614 |

## 29. Complex TS8/8

BSSE corrected energy = -589.2480 a.u.

ZPE= 0.0547 a.u.

One imaginary frequency = -138.3938 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.419799666851 | 0.483512847921  | 0.010912068464  |
| H | 0.429863662150  | 1.087954623070  | -0.292924665237 |
| S | -0.278300780198 | -1.058278067472 | 0.517715075373  |



|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| O | -1.553974313672 | 1.169395552170  | -0.090608638693 |
| H | -2.285839712074 | 0.595678793219  | 0.188504990854  |
| H | 2.896148833500  | 0.357128863901  | 0.465496204126  |
| O | 2.852096739945  | 0.670949495424  | -0.442766529136 |
| H | 2.722046740433  | -0.128594525317 | -0.961595693614 |

## 30. Complex TS3/DC

BSSE corrected energy = -589.1880 a.u.

ZPE= 0.0453 a.u.

One imaginary frequency = -1180.8948 cm<sup>-1</sup>

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.287590566720 | 0.996175473875  | -0.354629781061 |
| H | 1.100037171741  | 0.992779382926  | -0.448661863849 |
| S | 0.170979375867  | -1.181593638246 | 0.769174123072  |
| O | -1.373171534906 | 1.331874268225  | -0.455852168338 |
| H | 0.103786298906  | -0.597178130657 | 1.976893834780  |
| H | 1.753406250235  | -0.278369051193 | 0.260298564304  |
| O | 2.202212364433  | 0.577392844133  | -0.201091821296 |
| H | 2.672039919735  | 0.291984711172  | -0.994281095649 |

## 31. DC

BSSE corrected energy = -589.2465 a.u.

ZPE= 0.0453 a.u.

No imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.780934847726 | 2.252319636236  | -1.071217054782 |
| H | 1.195710065968  | 1.123217339769  | -0.563362272078 |
| S | 0.762559786172  | -2.343661646081 | 1.369342770388  |
| O | -1.774045880632 | 2.757970675545  | -1.213902418790 |
| H | 1.199327546719  | -1.990354537615 | 2.587177601376  |

|   |                |                 |                 |
|---|----------------|-----------------|-----------------|
| H | 1.256627344183 | -1.228526074202 | 0.795600212228  |
| O | 1.924586477680 | 0.606298034830  | -0.200867627604 |
| H | 2.571125184422 | 0.533825212912  | -0.907981169848 |

### BiComplexes of TFA with two-water molecule

#### BiComplexes of TFA(thione) with two-water molecule

##### 1. BiComplex 0

BSSE corrected energy = -665.7353 a.u.

ZPE= 0.0817 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -1.117980700809 | 0.561065885586  | -0.750957261905 |
| H | -2.084721660057 | 0.917045070165  | -1.098584226034 |
| S | -0.111692861420 | 1.599828865349  | 0.036933097902  |
| O | -0.952133581934 | -0.695900670384 | -1.050944359914 |
| H | -0.078752123475 | -1.094894328623 | -0.750702602572 |
| O | 2.645289603099  | -0.014292975082 | 0.836427626221  |
| H | 1.893166981939  | 0.584322160050  | 0.654780328815  |
| H | 3.410638504852  | 0.384116191565  | 0.412568833048  |
| H | 1.104876751804  | -2.736928190662 | 0.175056620007  |
| O | 1.249026566555  | -1.973825890788 | -0.390803499335 |
| H | 1.887934766409  | -1.389662807980 | 0.076520975350  |

##### 2. BiComplex 1

BSSE corrected energy = -665.7344 a.u.

ZPE= 0.0815 a.u.

no imaginary frequency

Cartesian coordinates

|   |                |                 |                 |
|---|----------------|-----------------|-----------------|
| C | 1.871273710620 | -0.163134554504 | 0.347284341361  |
| H | 2.927851882501 | -0.163360168700 | 0.603553686243  |
| S | 1.001338337639 | -1.552039254594 | 0.504226678655  |
| O | 1.493517551547 | 1.016152881928  | -0.058760700831 |

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| H | 0.524362292348  | 1.086127890037  | -0.314607710709 |
| O | -0.991134581000 | 1.461474466313  | -0.807225929959 |
| H | -1.410387346247 | 2.221200164021  | -0.395482014885 |
| H | -1.583613393441 | 0.690562142447  | -0.667001344152 |
| H | -1.238371354289 | -1.273460375995 | -0.099311645694 |
| O | -2.121250656419 | -0.966079053535 | -0.386171052950 |
| H | -2.729888057555 | -1.215786028609 | 0.314322198370  |

### 3. BiComplex 2

BSSE corrected energy = -665.7306 a.u.

ZPE= 0.0808 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.859663838622 | 1.531623636510  | -0.798678234409 |
| H | -1.763450993597 | 1.828562311486  | -1.324991798713 |
| S | -0.524662461806 | 2.122516473089  | 0.698656835240  |
| O | -0.151947972625 | 0.692867452375  | -1.513846427086 |
| H | 0.682732026542  | 0.418177611115  | -1.024795070249 |
| O | 2.321007075248  | -2.496280456714 | 0.951171128650  |
| H | 3.164979313093  | -2.905781819768 | 0.739485644372  |
| H | 1.650251855577  | -3.156498326031 | 0.753942548764  |
| H | 1.638082203181  | 0.705572327605  | 0.650510313818  |
| O | 1.972416157840  | 0.138027733917  | -0.061304751570 |
| H | 2.072471568543  | -0.754462951439 | 0.313700780192  |

### 4. BiComplex 3

BSSE corrected energy = -665.7304 a.u.

ZPE= 0.0807 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -2.136957914344 | 0.656811519495  | 0.438326806697  |
| H | -3.217901572944 | 0.572487278435  | 0.518734453304  |
| S | -1.235836902108 | 1.152605523025  | 1.722984451674  |
| O | -1.725732941761 | 0.323056868888  | -0.758085079819 |
| H | -0.725194375365 | 0.399594592361  | -0.831756714555 |
| O | 2.550084173159  | -1.671952826194 | -0.796856658263 |
| H | 2.456338630866  | -2.386424724421 | -0.160397661337 |
| H | 3.495139907937  | -1.554809799119 | -0.928992110006 |

|   |                |                 |                 |
|---|----------------|-----------------|-----------------|
| H | 0.822780555624 | 0.921876979455  | 0.217354855577  |
| O | 0.886323645779 | 0.638891661011  | -0.708473262581 |
| H | 1.451358931346 | -0.153070424185 | -0.719207488660 |

## 5. BiComplex 4

BSSE corrected energy = -665.7265 a.u.

ZPE= 0.0802 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.111742789259  | 0.822192854472  | -0.138625913224 |
| H | -0.684402524564 | 1.507334619217  | -0.416290296978 |
| S | -0.234841465494 | -0.596675523286 | 0.628443671425  |
| O | 1.289109533473  | 1.275297766752  | -0.483873613674 |
| H | 2.009934658556  | 0.640292852697  | -0.223205079098 |
| O | 2.984036438685  | -0.616892177917 | 0.390100746375  |
| H | 2.203145995852  | -1.115121138131 | 0.686993361995  |
| H | 3.463648132573  | -1.193753177780 | -0.212157214654 |
| H | -2.578693914993 | 0.326223703040  | 0.524475744288  |
| O | -3.134929582416 | 1.068577744503  | 0.248862503939  |
| H | -3.916133010059 | 0.671058166350  | -0.143617135442 |

## 6. BiComplex 5

BSSE corrected energy = -665.7264 a.u.

ZPE= 0.0806 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 2.066397434704  | -0.310572889211 | 0.273166658997  |
| H | 3.132850713854  | -0.105566591992 | 0.296349861348  |
| S | 1.305205633883  | -0.989324513085 | 1.559984262364  |
| O | 1.545516673546  | 0.055758692017  | -0.876360519332 |
| H | 0.573981900771  | -0.132631814317 | -0.898490118170 |
| O | -3.651734311431 | 0.895942340903  | -0.458909415178 |
| H | -2.734063989149 | 0.598448567466  | -0.399293378530 |
| H | -3.611746544462 | 1.854513541614  | -0.493081708308 |
| H | -0.754456375430 | -0.898107402595 | 0.354157075463  |
| O | -1.088955574499 | -0.574399522240 | -0.506205710792 |
| H | -1.478416079180 | -1.334582238522 | -0.952046194343 |

## 7. BiComplex 6

BSSE corrected energy = -665.7251 a.u.

ZPE= 0.0802 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.122592038741  | 0.474006030615  | -0.112338895423 |
| H | 1.048932354002  | 1.039216393813  | -0.069648810784 |
| S | -1.336899354329 | 1.214546623724  | -0.214139493348 |
| O | 0.364918415586  | -0.822374831359 | -0.071705744191 |
| H | -0.481942787635 | -1.348168896106 | -0.102299982897 |
| O | -2.068079048353 | -1.911972263123 | -0.223442745629 |
| H | -2.399273090316 | -0.995130573627 | -0.238073217270 |
| H | -2.483203580316 | -2.340192160990 | 0.531583106192  |
| H | 2.445501652109  | -1.087751096024 | 0.101450092284  |
| O | 3.298750082504  | -0.663213111835 | 0.247937493665  |
| H | 3.918757966649  | -1.124208935490 | -0.322306026310 |

## 8. BiComplex 7

BSSE corrected energy = -665.7243 a.u.

ZPE= 0.0807 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.824433659472 | 0.541942104817  | 0.392952897980  |
| H | 0.138081092589  | 1.006725774674  | 0.188558553767  |
| S | -1.038904352502 | -1.074118587146 | 0.531946217587  |
| O | -1.785225986258 | 1.448032924318  | 0.507186008713  |
| H | -2.625329232666 | 0.995286536453  | 0.686312181035  |
| O | 2.281490504357  | 1.185751979776  | -0.174434394852 |
| H | 2.444856180160  | 0.225305582129  | -0.193936841882 |
| H | 2.754250160079  | 1.549811000390  | -0.926308884260 |
| H | 2.634748685750  | -2.070792873288 | 0.666437214112  |
| O | 2.221909129036  | -1.630490487486 | -0.081499002081 |
| H | 1.265904525377  | -1.647401765719 | 0.100445018707  |

## 9. BiComplex 8

BSSE corrected energy = -665.7210 a.u.

ZPE= 0.0804 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.814076022668  | 0.129900247633  | -0.015493764919 |
| H | 0.281638819089  | -0.804703334382 | 0.142134174232  |
| S | 2.426112950821  | 0.301822601481  | -0.029611972174 |
| O | -0.063543685460 | 1.135252562271  | -0.194385865868 |
| H | 0.440624673139  | 1.955445879653  | -0.322461434578 |
| O | -1.528306324095 | -2.093509128675 | 0.425175083014  |
| H | -2.188069007312 | -1.379907961793 | 0.404663636902  |
| H | -1.777599156652 | -2.667509210339 | 1.153150708744  |
| H | -3.457350884507 | 0.490807490910  | -0.643373459931 |
| O | -2.924244228906 | 0.364279164977  | 0.146055899113  |
| H | -2.084687054628 | 0.812332107230  | -0.026522761964 |

#### 10. BiComplex 9

BSSE corrected energy = -665.7197 a.u.

ZPE= 0.0797 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 1.654042762248  | -0.055400518903 | -0.181373718803 |
| H | 0.993775306639  | -0.643637635268 | -0.810894324380 |
| S | 1.228420479895  | 0.493900830608  | 1.293247497025  |
| O | 2.819904258131  | 0.140144642211  | -0.781819052222 |
| H | 3.389122788423  | 0.669948831056  | -0.200617591194 |
| O | -3.799270459784 | 0.732954832506  | -0.547176582303 |
| H | -3.046064643645 | 0.179527208195  | -0.286906428431 |
| H | -3.904685484186 | 0.589307021013  | -1.490260051694 |
| H | -0.941564727506 | -0.485953017575 | 0.848859805462  |
| O | -1.617274305559 | -0.963055618351 | 0.339754143472  |
| H | -1.983698819631 | -1.615918397871 | 0.942857926782  |

#### 11. BiComplex 10

BSSE corrected energy = -665.7173 a.u.

ZPE= 0.0794 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.024096425040  | -1.174553242556 | -0.100817101545 |
| H | -0.878934089544 | -0.571122162284 | -0.099518046804 |
| S | 1.529355585292  | -0.553677183531 | -0.098894556965 |
| O | -0.281957065711 | -2.469306202393 | -0.104204806203 |
| H | 0.543608995239  | -2.980249060040 | -0.105313999789 |
| O | -2.553457214280 | 1.170560813298  | -0.099657930706 |
| H | -3.089679591181 | 1.401664002834  | 0.664898611388  |
| H | -3.080630374006 | 1.408598898073  | -0.868377771122 |
| H | 0.668455016141  | 1.984941235528  | -0.088778543048 |
| O | 0.029329412769  | 2.707736963491  | -0.086104402325 |
| H | -0.828498151157 | 2.264859848800  | -0.088727318962 |

## BiComplexes of TFA(thiol) with two-water molecule

### 1. BiComplex 0

BSSE corrected energy = -665.7324 a.u.

ZPE= 0.0779 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 1.356573117200  | 0.237305774732  | -0.632970801058 |
| H | 2.391323691993  | 0.355223378165  | -0.987466734749 |
| S | 1.176263336116  | -1.257657207722 | 0.278854111766  |
| O | 0.510394024479  | 1.066774614747  | -0.879587675003 |
| H | -2.283017053632 | -0.239407641200 | 0.571707975313  |
| O | -2.245149391089 | 1.334681505018  | -0.305516818523 |
| H | -1.304442051485 | 1.332841782309  | -0.557714030702 |
| H | -0.150348655152 | -1.135252219253 | 0.583767500099  |
| H | -2.298258301308 | -0.989817239998 | 1.925554020363  |
| O | -2.038582432406 | -1.082363876622 | 1.005293288091  |
| H | -2.740462042949 | 1.452357269024  | -1.119843876283 |

### 2. BiComplex 1

BSSE corrected energy = -665.7316 a.u.

ZPE= 0.0777 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 1.361635415553  | 0.255065837430  | -0.609947080404 |
| H | 2.395242650175  | 0.367999020845  | -0.969376866983 |
| S | 1.158027084767  | -1.276338533531 | 0.233959780273  |
| O | 0.530907872500  | 1.112745505641  | -0.807544971634 |
| H | -2.297018986060 | -0.222383692312 | 0.628661224205  |
| O | -2.270748866866 | 1.236409202338  | -0.460722516056 |
| H | -1.311652786689 | 1.293541611798  | -0.618496158355 |
| H | -0.156455722052 | -1.129972505577 | 0.576124537059  |
| H | -2.238134413667 | -0.909979067853 | 2.015123352121  |
| O | -2.025022991597 | -1.041523632130 | 1.087908452138  |
| H | -2.567210869064 | 2.128008490382  | -0.264385287678 |

### 3. BiComplex 2

BSSE corrected energy = -665.7294 a.u.

ZPE= 0.0772 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.361876559651 | 0.238951286770  | -0.306071992696 |
| H | 0.034748566998  | -0.586874153477 | 0.301236538160  |
| S | -2.135063381489 | 0.201378182208  | -0.414164080713 |
| O | 0.345001176410  | 1.066598373674  | -0.831875697860 |
| H | 2.448728460316  | -0.910224026788 | 0.777478462931  |
| O | 3.084652698186  | 0.496711420324  | -0.280613509223 |
| H | 2.216946146159  | 0.836911341970  | -0.561996940499 |
| H | -2.233804419775 | 1.293007914619  | -1.192658731056 |
| H | 2.258833358525  | -2.395887090823 | 1.154909930598  |
| O | 1.846668372284  | -1.531947959266 | 1.226041934051  |
| H | 3.537941225043  | 1.236159414672  | 0.131855255689  |

### 4. BiComplex 3

BSSE corrected energy = -665.7255 a.u.

ZPE= 0.0766 a.u.

no imaginary frequency



Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.301655071293  | 0.702951660787  | 0.240079503489  |
| H | 1.227094166874  | 1.273312533794  | 0.393076339853  |
| S | -1.130267492011 | 1.720099280232  | 0.353199125104  |
| O | 0.324161237719  | -0.491452618009 | 0.020666677780  |
| H | 3.738617212410  | -1.207348101530 | -0.297393407796 |
| O | -2.417920950169 | -1.261353102979 | -0.347065286593 |
| H | -1.457394183793 | -1.354540248558 | -0.252885497921 |
| H | -2.015078336046 | 0.717232279626  | 0.129654508320  |
| H | 2.281635565065  | -0.939024176739 | 0.112262131375  |
| O | 3.196472619112  | -0.684604653021 | 0.297799734915  |
| H | -2.809698837541 | -1.945816041183 | 0.201497489859  |

5. BiComplex 4

BSSE corrected energy = -665.7263 a.u.

ZPE= 0.0768 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 1.981047080423  | 0.419587490902  | -0.313203338744 |
| H | 3.018128047033  | 0.375103209589  | -0.674957516673 |
| S | 1.699917759477  | -0.766250993701 | 0.972552321691  |
| O | 1.176881747049  | 1.196842166221  | -0.768362492096 |
| H | -1.717654644043 | 1.524700497976  | 0.908459783248  |
| O | -3.593292122525 | -0.309909364472 | -1.023651820484 |
| H | -2.795904615889 | -0.020180698093 | -0.554634832018 |
| H | 0.402866795235  | -0.439026840784 | 1.161922992138  |
| H | -0.603056584852 | 1.116636260796  | -0.085829743479 |
| O | -1.325895326709 | 0.766978159476  | 0.464637307751  |
| H | -3.682259666632 | -1.244083902550 | -0.822178921936 |

6. BiComplex 5

BSSE corrected energy = -665.7263 a.u.

ZPE= 0.0766 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 1.890871537420  | -0.988368600771 | 0.647241207000  |
| H | 2.878086472072  | -1.212739922844 | 1.078663912631  |
| S | 1.978335909275  | 0.377104592370  | -0.479679138228 |
| O | 0.905942839961  | -1.622321075294 | 0.937081633233  |
| H | -3.608803016104 | 1.814448822646  | 0.297994404569  |
| O | -1.174663494734 | -0.405348095005 | -0.720673821725 |
| H | -0.819272862933 | -1.005495853068 | -0.050133431871 |
| H | 0.651028242126  | 0.358269074659  | -0.782640556799 |
| H | -4.334181038500 | 0.622339881383  | -0.336415700182 |
| O | -3.607268958753 | 0.854234186653  | 0.248957200340  |
| H | -1.957529374360 | 0.012802103188  | -0.331012644570 |

## 7. BiComplex 6

BSSE corrected energy = -665.7236 a.u.

ZPE= 0.0761 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.094429685563 | -1.574022928661 | -0.014219936323 |
| H | 0.646027947241  | -1.165476031033 | -0.713644134420 |
| S | -0.192449623533 | -0.523585774245 | 1.464907169997  |
| O | -0.749833605154 | -2.557726910005 | -0.188653873872 |
| H | -1.549009078006 | 2.501119035840  | -0.838587369172 |
| O | 1.444459726576  | 0.910775692813  | -1.349407597539 |
| H | 0.775050020088  | 1.575666333091  | -1.116100185813 |
| H | -1.167423844256 | -1.242375257879 | 2.046589488406  |
| H | -0.948424967284 | 1.688766190327  | 0.321585538188  |
| O | -0.752533743304 | 2.393288691450  | -0.311100405807 |
| H | 2.277107186660  | 1.383562289200  | -1.417909014938 |

## 8. BiComplex 7

BSSE corrected energy = -665.7227 a.u.

ZPE= 0.0754 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.336718095342 | -0.584192560960 | -0.089898267524 |
| H | -1.409660706054 | -0.810679024108 | -0.087782627975 |
| S | -0.056949736450 | 1.127338408755  | 0.302405058124  |
| O | 0.512530145948  | -1.409744024841 | -0.330267573099 |

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| H | -3.949576385431 | 0.853289301048  | -0.328492125719 |
| O | 3.042141634281  | -0.098913845716 | -0.242901047950 |
| H | 2.355069220691  | -0.780853185626 | -0.323423015387 |
| H | 1.291738311006  | 1.052316928658  | 0.225981259300  |
| H | -3.767326579348 | 0.654045715365  | 1.176127614605  |
| O | -3.512977470351 | 0.295292616557  | 0.321268692783  |
| H | 3.712559138377  | -0.465013398491 | 0.339174388612  |

### 9. BiComplex 8

BSSE corrected energy = -665.7233 a.u.

ZPE= 0.0761 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 0.847752878013  | -0.980189273534 | 0.348584922642  |
| H | -0.170422703363 | -1.290394412974 | 0.618080164252  |
| S | 1.076927694934  | 0.787589259612  | 0.711846121170  |
| O | 1.687738669333  | -1.683747599348 | -0.126333438598 |
| H | -2.367687998954 | 0.118868493647  | -0.153297119958 |
| O | -1.763021780944 | 1.672296942251  | -1.087198119468 |
| H | -0.838698889694 | 1.678010710611  | -0.803000812825 |
| H | 2.318780215060  | 0.849905756340  | 0.203313968195  |
| H | -3.057282210800 | -1.247588062871 | 0.040013461411  |
| O | -2.392929884851 | -0.666874069196 | 0.418468592534  |
| H | -2.121487993103 | 2.523720805786  | -0.821065190230 |

### 10. BiComplex 9

BSSE corrected energy = -665.7223 a.u.

ZPE= 0.0759 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -1.792376174180 | -0.206634295764 | -0.264245399010 |
| H | -2.843903376113 | -0.489987630757 | -0.425552018461 |
| S | -0.771345314754 | -1.658334540568 | -0.125704697982 |
| O | -1.432266043886 | 0.937411378264  | -0.198014836305 |
| H | 1.721538711171  | 1.515344561592  | 0.287890219946  |
| O | 2.549609230188  | -0.368634195983 | 0.377061890146  |
| H | 3.228832453777  | -0.433279852289 | -0.301331615782 |

|   |                |                 |                |
|---|----------------|-----------------|----------------|
| H | 0.397125513830 | -1.010908589058 | 0.056399089217 |
| H | 0.333455353850 | 2.102672628832  | 0.092742259499 |
| O | 1.252693746899 | 2.356553679218  | 0.236864207775 |
| H | 3.009345313494 | -0.453574063796 | 1.217999306458 |

### 11. BiComplex 10

BSSE corrected energy = -665.7213 a.u.

ZPE= 0.0758 a.u.

no imaginary frequency

Cartesian coordinates

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | -0.640314471047 | -0.585512009188 | 0.063910907652  |
| H | -0.239713395468 | 0.436913801343  | 0.003383458342  |
| S | -2.414026583993 | -0.571093696262 | 0.262647982766  |
| O | 0.046650140482  | -1.569661777606 | 0.001572702566  |
| H | 2.539587805899  | 0.356869934221  | -0.313154612522 |
| O | 1.576594497286  | 2.174542138451  | -0.278318278119 |
| H | 1.957627410500  | 2.709565113984  | 0.424595019323  |
| H | -2.540644028440 | -1.908783004513 | 0.295605441691  |
| H | 2.137095619579  | -1.109345982250 | -0.230761678963 |
| O | 2.907262072838  | -0.535258310260 | -0.324416958980 |
| H | 1.783037182696  | 2.637464334941  | -1.096028142854 |