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Response to the Reviewer's reports:

Manuscript ID: CP-ART-08-2014-003481

Dear Sir/Madam,

This is in reference to a major revision of the manuscript entitled "**Mechanism of tautomerisation and geometric isomerisation in thioformic acid and its water complexes: Exploring chemical pathways for water migration**", by Gurpreet Kaur and Vikas. As per suggestions made by the reviewers, the manuscript has been thoroughly revised. Following the referee's suggestions, the major change in the manuscript include addition of new Tables 2, 4,5,7 and 8 reporting Gibbs free-energy change during the reaction pathways and their temperature dependence, while Tables 4-7 of the original manuscript are moved into the supporting information. The detailed response to all the comments of the reviewers, and the changes that have been made in the manuscript are described as follows:

	Reviewer's comments	**Response and list of changes**
	Reviewer # 1	
1.	The global reaction route mapping (GRRM) method was first introduced in the following paper, J. Phys. Chem. 2006, 110, 8933, which should be cited in this manuscript. A recent review on GRRM which appeared in a volume of PCCP, Phys. Chem. Chem. Phys. 2013, 15, 3683, should also be cited.	Reference, J. Phys. Chem. 2006, 110, 8933, has already been cited as Ref. 20 in the original manuscript, now Ref. 21 in the revised manuscript. Following reviewer's suggestion, Phys. Chem. Chem. Phys. reference, is cited in the revised manuscript as Ref. 33.
2.	In the descriptions about options in the use of GRRM, the meaning of UpDC(n) and DownDC(n) options with n=15 is not clear. What are these options related? Why the value of n is changed from the default setting? How the choice of n=15 yields an important effect? Probably this may be connected with the finding of the new pathways including IM1,	To make it clear, following explanation is provided on **Page 5** of the revised manuscript: "To further search any weak complexes which may be intermediates and dissociation channels along the reaction pathways, UpDC(*n*) and DownDC(*n*)[22,23] options in GRRM were employed for uphill walking by ADDF, and in the downhill walking by the conventional steepest descent methods, respectively,

	which is nearly dissociated, and this choice of n may also affect the searched results of loose water complexes.	with the value of parameter *n* adjusted to 15. Using these options, a weak complex along the *cis-trans* isomerisation pathways of TFA(thiol), and dissociation channels for TFA-water complexes were explored (see next section)”
3.	The use of 5 largest ADDs and 20 random starting structures may not be enough to explore the important reaction pathways of this study. Thus, the authors seemed to use saddle point optimization together with double ended TS search options. At least, the authors should describe the structures and pathways discovered by the additional searches. If numbers of largest ADDs or random starting structures were increased, the missing structures and the pathway would be covered without using the additional treatments.	We had also performed GRRM search by increasing the largest ADDs and random structures, however, no additional structures and pathways could be located. To make it clear, following explanation has been included on **Page 5** of the revised manuscript: “It should be noted that during exploration of the PES by GRRM, we employed 5 largest ADDs in ADDF search, starting from 20 random structures. In order to check the reliability of the chosen options for TFA-water complexes, GRRM search was also performed employing 10 largest ADDs around 30 random structures but we could not trace any additional structures and pathways.”
4.	Use of EQ only option may also limit the number of searched structures for two-water molecule complexes. Precise determination of TSs and the associated IRC traces may possibly lead to the more complex structures.	We had mistakenly mentioned the use of EQOnly option, the statement should read, as modified on Page **5** in the revised manuscript, as follows: “Further, since during search performed on the complexes of TFA with two-water molecules, the TSs obtained were very few in number, therefore, for the sake of simplicity further optimization of the TSs were avoided and these are not reported in this work.”
5.	Concerning with the barrier heights of TS0 and TS1 in the cis-trans isomerization for thiols and thiones, the energy difference of 4.27 between TS0 and TS1 does not indicate the energy difference of the barrier	In view of referee’s comments, standard Gibbs free-energy change during reaction pathways is provided for isomerisation and water migration in new Table 2 and Tables 4-5 (see also response to comment #8 below).

	heights. In the case of the kinetics, the barrier heights are responsible, but in the case of populations at a thermal equilibrium, heights of TSs should be compared. This point should be clarified.	Following this, the statement on TS0 and TS1 on Page 7 of the revised manuscript has been modified as follows: "However, geometric isomerisation in TFA(thione) is thermodynamically less favourable than that in the TFA(thiol) because as evident from Table 2, the standard Gibbs free-energy change to reach the transition state (TS1) along the pathway of TFA(thione) is relatively higher than that required for TS0 along the pathway of TFA(thiol)."
6.	Concerning with IM1, this intermediate structure seems to be a radical pair of SH and OCH. The DFT calculations of radical pairs may involve certain inaccuracies. UDFT calculations may cover interactions between the radicals.	Following the referee's suggestion, for IM1, we had performed the computations, including that to see any dispersion interactions, at the unrestricted level of UB3LYP/6-311++G(2d,2p). However, no difference is observed in the results between B3LYP and UB3LYP. To specify it, following explanation is included on Page 7 of the revised manuscript: "It should be noted that the intermediate, IM1, is nearly a dissociated structure with extensive stretching of C-S and S-O bonds with its dispersion interaction energy, using counterpoise calculations, found to be -11.30 kcal/mol both at B3LYP/6-311++G(2d,2p) and UB3LYP/6-311++G(2d,2p) levels of the theory**."**
7.	In the descriptions of water complexes, H20 should be replaced by H_2O.	As per the reviewer's suggestion, the error has been rectified in the revised manuscript.
8.	In the lists of two-water molecules, it is important to consider the effects of temperature, because energy differences among the structures are as small as 0.3-7 kcal/mol. The relative importance of the structures will crucially depend on the temperature. Free	Following the reviewer's suggestion, new Tables 5-8, report Gibbs free-energy change (ΔG) in kcal/mol at various temperatures for complexes of TFA with single- as well as two-water molecules relative to the isolated species. Besides this, the standard Gibbs free-energy change

	energies may be recommended to be shown at several temperatures. This is important for experimentalist, when they will use the vibrational frequencies listed in Tables 6 and 7.	during reaction pathways for isomerisation and water migration is also provided in new Table 2 and Tables 4-5. With inclusion of these tables, the results and discussion section is accordingly modified. A few the excerpts from the modified section are as follows: **Page 7** “From the standard Gibbs free-energy change along the new pathway explored, as listed in Table 2, it is clearly evident that the *trans*-TFA(thiol) is thermodynamically the most dominating species among the conformers of isolated TFA.” **Page 20** “This is supported by the net standard Gibbs free-energy change along the geometric pathways as evident in Table 4, depicting the favourability for *cis* form over *trans* form of TFA(thiol) in the complexes of TFA with single-water molecule, which is in contrast to that observed for isolated TFA, however, net standard Gibbs free-energy change in the two cases is within 1 kcal/mol for the most feasible pathways.” **Pages 20-21** “It should, however, be noted that dissociation of TFA-water complexes, except Complex 7 and Complex 10, towards separated speices (TFA and H_2O) at room temperature (298.15 K) is more favorable than the water migration as evident from ΔG values at different temperatures listed in Table 5. However, as the temperature decreases, the association between TFA and water seems to increase, though the dissociation still remains dominating at lower temperatures.” **Page 21** “As evident in Table 4, the net standard Gibbs free-energy change along these pathways favours

		trans form of TFA(thione) in the single-water molecule complexes of TFA(thione), in fact even more strongly than that observed in the case of isolated TFA(thione) indicating a catalytic effect of water.” **Page 21** “It should be noted that transition state TS2, in case of tautomerization of isolated TFA, lies higher than ComplexTS1/7 and ComplexTS2/8 by 18.45 and 1.51 kcal/mol, respectively, at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) indicating the positive catalytic effect of water in the tautomerisation of TFA, however, the standard Gibbs free-energy change, as evident in Tables 2 and 4, favors thiol form of TFA in both the cases.” **Page 28** “It should be noted that the association of TFA with two-water molecules increases as the temperature decreases which is evident from the increasingly positive Gibbs free-energy change with decrease in temperature as evident in Table 7. Interestingly, Bicomplexes 0-3 of TFA(thione) seem to be thermodynamically more feasible than the single-water molecule complexes of TFA.” **Pages 29-30** “For bicomplexes of TFA(thiol), the dissociation of water-complexes is more dominating, contrary to that observed for the Bicomplexes of TFA(thione), as indicated by Gibbs free-energy change relative to the isolated speices, at various temperatures in Table 8. The dissocation becomes even more dominating at higher temperatures.”
9.	The interaction energy of IM2 shown a 1920 kJ/mol should be shown in kcal/mole for the consistency of the energy scale.	As per the reviewer’s suggestion, 1920 kJ/mol has been converted to 458.89 kcal/mol.

	Reviewer # 2	
1.	However, significance of this work is unclear for several reasons summarized below. Therefore, I recommend publication of this paper in a more specialized journal in the field.......	Recently, we had revealed that single-molecule water catalysis may be operative during the reaction of TFA with hydroxyl radical [Ref. 10 of the original manuscript, **Gurpreet Kaur and Vikas, J. Phys. Chem. A, 2014, 118, 4019-4029**]. The same behaviour of water is also observed in the present work on geometric isomerisation and tautomerisation while analysing TFA-water complexes. Therefore, in order to explore the mechanism for water-assistance in the reactions of TFA, a detailed analysis is provided here for the water-migration pathways in the complexes of TFA with water molecules. Besides these, various complexes of TFA with two-water molecules has been explored for the first-time to study the hydrogen-bonding interactions (see also response to comment # 8 of reviewer #1 above).
2.	In gas-phase neutral complexes, water migrations compete with dissociations of a water molecule. Free- energy corrections at room temperature are usually comparable to binding energies of a water molecule. Therefore, importance of water migrations should be discussed using Gibbs free-energy relative to the dissociation limit, i.e., TFA + H2O and TFA + H2O + H2O. On the other hand, in [NH2CHO---H2O]+, strong charge-dipole interaction between H2O and NH2CHO+ allowed for the long-range water migration as well as water catalyzed tautomerization as reported in ref. 18	Following the reviewer's suggestion, new Tables 5,7 and 8, report Gibbs free-energy change (ΔG) in kcal/mol at various temperatures for complexes TFA with single- as well as two-water molecules On the basis of these tables, interesting observations are made, for details see response to comment # 8 of reviewer #1 above.

	(I mean that the reaction discussed in ref. 18 is not similar to the present example).	
3.	Tautomerization and cis-trans isomerization are no doubt of great significance. However, I don't think that those in TFA can be a representative example. Therefore, I strongly suggest to give discussions how tautomerization and cis-trans isomerization of TFA and those involving water molecules can be important in real chemical processes of TFA.	To make it clear, following explanation has been included on **Page 2** of the revised manuscript: "Thiol-thione tautomerisation in thioformic acids has been keenly studied in past[5-7] to investigate the role of specific solute-solvent interactions because there have been controversies regarding whether the thione form exists predominantly in polar solvents[5,7] or the most stable thiol form is the most dominant irrespective of the solvent polarity.[6,7] Moreover, due to the presence of -C(=O)S- and -C(=S)O- functionality, TFA can be used as a basic model to study the catalytic hydrolysis of substrates having RC(=O)O functionality, which is known to proceeds via formation of an enzyme reaction intermediate "thiolacyl-enzyme [RC(=O)S-Enz]" by enzymes like cysteine or serine protease.[8,9] Recently, we had revealed that single-molecule water catalysis may be operative during the reaction of TFA with hydroxyl radical.[10]"
4.	Cis-trans isomerization in vision involves rotation of double bonds on the electronic excited state.	The statement has been omitted in the text of the revised manuscript.
5.	I recommend to avoid using option names used in computational programs of the GRRM method. For example, "EQ only" should be mentioned as follows: In this search, TS optimizations were not made, in order to find only EQ structures as quick as possible.	This statement has been removed from the text. (see also response to comment # 8 of reviewer #1 above).
6.	Table 1 is not referred in the main text. In addition, there is nearly no discussion for some	In view of referee's suggestion, Tables 4-7 of the original manuscript are moved into the supporting

	tables. I think that some tables can be moved to Supporting information.	information of the revised manuscript. All the Tables included in the revised manuscript are appropriately addressed in the results and discussion section.
7.	The meaning "interaction energy of 1920 KJ/mol" in page 7 is unclear.	To clarify it, following explanation has been included on **Page 7** of the revised manuscript: "It should be noted that IM2 exhibits strong intramolecular interactions between the atoms as evident from counterpoise computed interaction energy of 458.89 kcal/mol for this intermediate species." (See also response to comments # 6 and 9 of Referee #1 above)
8.	Is the word "automerization" general?	"Automerisation" refers to self-isomerisation of an isomer. Its usage is general in the existing literature cited on exploration of isomerisation pathways.
9.	Ref. 12 is cited also as ref. 13.	Ref. 12 in the original manuscript was an introductory comment on Ref. 13 in the same issue of the journal. As per the reviewer's suggestion, Ref. 12 has been omitted in the revised manuscript. Ref. 13 is now cited as Ref. 14 in the revised manuscript.

The authors are obliged to all the referees for their highly useful comments in the improvement of the manuscript.

With regards,

Sincerely,

Vikas (Corresponding Author)

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

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Abstract

A systematic and automated search of chemical pathways for isomerisation between geometric and tautomeric forms of gas-phase thioformic acid (TFA) and its water complexes, is performed using global reaction route mapping (GRRM) method, and an uncovered pathway for *cis-trans* isomerisation in thiol form of TFA has been explored through computations performed at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of the coupled cluster and density functional theories. To explore the routes for water migration, a detail analysis of complexes of TFA with single-water molecule is presented. Notably, during the isomerisation process in TFA, a positive catalytic effect of water was observed that can arise either by the stabilization of the reactant and/or of the transition state through extensive hydrogen bonding. Interesting behavior of isomeric forms of TFA along the pathways analysed is revealed through Gibbs free-energy change and its temperature-dependence. The *cis* form of TFA(thiol) in the complexes of TFA with single-water molecule is found to be thermodynamically equally feasible as the *trans* form which though is known to be the most dominating among the isomeric forms of TFA. Besides these, various complexes of TFA with two-water molecules has also been explored to study the hydrogen-bonding interaction through natural bond-orbital (NBO) analysis. The complexes of TFA with two-water molecules have also been characterized using spectral features including vibrational frequency analysis, and the effect of complexation has been observed by noting frequency shifts.

Keywords: thioformic acid, tautomerisation, geometric isomerism, water migration, hydrogen bonding, GRRM**.**

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1. Introduction

Isomerisation in organic acids is a fundamental process which has been considerably investigated owing to its profound biochemical and medical applications.[1] In fact, geometric and tautomeric interconversions are keenly looked at both by the structural chemists and the biologist alike. *Cis-trans* isomerisation plays an important role in regulation of protein folding,[2] whereas tautomerism in ketones, and amides is known to regulate reactivity pattern and properties of organic compounds.[3,4] The organo-acid of interest in the present study is thioformic acid (TFA) which can exist in four geometric and tautomeric forms depicted in Figure 1.

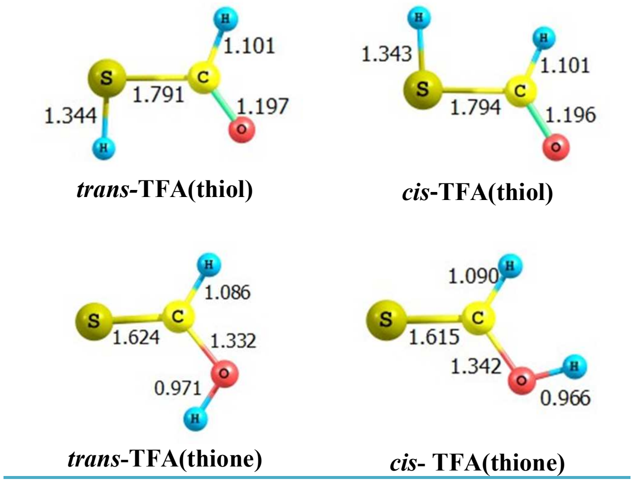


Figure 1. Geometric and tautomeric forms of thioformic acid (TFA). The geometries (with bond-lengths in Angstroms) depicted are optimized at DFT/B3LYP/6-311++G(2d,2p) level of the theory (for details see section on Computational Methodology).

Thiol-thione tautomerisation in thioformic acids has been keenly studied in past[5,6,7] to investigate the role of specific solute-solvent interactions because there have been controversies regarding whether the thione form exists predominantly in polar solvents[5,7] or the most stable thiol form is the most dominant irrespective of the solvent polarity.[6,7] Moreover, due to the presence of -C(=O)S- and -C(=S)O- functionality, TFA can be used as a basic model to study the catalytic hydrolysis of substrates having RC(=O)O functionality, which is known to proceeds via formation of an enzyme reaction intermediate “thiolacyl enzyme [RC(=O)S-Enz] ” by enzymes like cysteine or serine protease.[8,9] Recently, we had revealed that single-molecule water catalysis may be operative during the reaction of TFA with hydroxyl radical.[10] In the present work, reaction routes for the *cis-trans* and *thione-thiol* isomerisation in TFA and TFA-water complexes are reinvestigated[11] for exploring the mechanism of water migration in the gas phase reaction systems. To the best of our knowledge, the detailed mechanism of water migration and isomerisation in TFA-single water complexes presented here is being investigated for the first time. It is very-well known that the water plays a bifunctional role by acting as solvent as well as facilitating hydrogen-bonding.[12,13] Water has been proven to be an efficient catalyst exhibiting considerable lowering of the activation energy barrier by stabilizing the reactant and/or transition state of the reacting system.[10,14] Water catalysis has also been explored in variety of prototropic tautomerisations,[15-18] for example, amino-imino tautomerism in the gas phase and aqueous solution had been studied for tautomeric equilibria of formamide, thioformamide, selenoformamide, 2-amino-4-oxo-oxazoline, 2-amino-4-oxo-thiazoline and 5-fluorouracil.[18] In 2010, Maeda *et al*.,[19] has elucidated mechanism of long range migration of water leading to keto-enol tautomerisation of hydrated formamide cluster by employing global reaction route mapping (GRRM).[19-33]

The GRRM method is an emerging computational strategy for performing a systematic and automated search on a potential energy surface (PES), and it mainly involves two techniques: (i) uphill walking and (ii) downhill walking. The GRRM searches for the inter-connectivity between stable structures (EQs) via transition states (TSs) and dissociation channels (DCs). However, exploring a TS or DC from an EQ using uphill walking poses a major challenge, which though can reveal unconventional reaction pathways not explored by downhill walking methods.[20] The GRRM, as a compass for reaction pathways, has been quite successful in tackling this challenge through an anharmonic downward distortion following (ADDF)[20,27] approach based on a scaled hypersphere search (SHS) procedure.[20-22] ADDF, the basic component of GRRM follows the course of a reaction by noting maxima of ADD among all directions. This method has been successfully applied to explore a variety of physico-chemical systems including hydrogen-bonded[27-29] and catalytic systems.[30-33]

The present work, through automated search performed using GRRM, maps pathways for the geometric and tautomeric isomerisation in TFA, and also in the complexes of TFA with single-water molecule while exploring the mechanism of water migration in the complexes. Besides this, the complexes of TFA with two-water molecules were also analysed in order to explore specific hydrogen-bonded interactions of TFA with water, which can be significant for modeling conformational changes in the biological molecules.[11] The paper is organized as follows: Next section describes the Computational Methodology employed for exploring reaction routes through GRRM in the investigated systems. This is followed by Results and Discussion section which present detailed analysis on the mechanism of isomerisation and water migration in TFA-water complexes. Finally, the last section makes a few concluding remarks.

2. Computational methodology

In the present study, all the required computations are performed using GRRM program along with Gaussian 03 quantum chemistry software package.[34] The initial investigation of reaction pathways involving stationary and first order saddle points was performed at DFT/PBE1PBE/6-31+G(d) level of theory using a hybrid exchange-correlation (XC) functional of Perdew, Burke and Ernzerhof, which uses 25% exchange and 75% correlation weighting.[35,36] The geometries obtained were further optimized at DFT/B3LYP/6-311++G(2d,2p) level of theory using Becke, three-parameter, Lee-Yang-Parr (B3LYP)[37] hybrid XC functional where Becke stands for exchange part, Lee-Yang-Parr for correlation and 3 describes the particular way that the exchange and correlations are mixed together. Further, harmonic vibrational frequency analysis for each of the structure reported was performed to ensure if the optimized structure located is a stationary state or a transition state, and also to obtain zero-point energy (*ZPE*) correction. The intrinsic reaction coordinate (IRC)[38] calculations were also performed on all the traced transition states for the verification of right connectivity between reactants and products. All the stationary points that have been searched had all frequencies real, whereas all the interconnecting transition states had only one imaginary frequency. Single point energies were further refined using coupled-cluster (CC)[39] theory at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level. The result obtained using XC functional, B3LYP/6-311++G(2d,2p) are observed to be similar to those at MP2/6-311++G(2d,2p) level of the theory employed in a previous studies on TFA.[11]

It should be noted that during exploration of the PES by GRRM, we employed 5 largest ADDs in ADDF search, starting from 20 random structures. In order to check the reliability of the chosen options for TFA-water complexes, GRRM search was also performed employing 10 largest ADDs around 30 random structures but we could not trace any additional structures and pathways. To further search any weak complexes which may be intermediates and dissociation channels along the reaction pathways, UpDC(n) and DownDC(n)[22,23] options in GRRM were employed for uphill walking by ADDF, and in the downhill walking by the conventional steepest descent methods, respectively, with the value of parameter n adjusted to 15. Using these options, a weak complex along the *cis-trans* isomerisation pathways of TFA(thiol), and dissociation channels for TFA-water complexes were explored (see next section). Few other possible connections between EQs were obtained through saddle point optimization and double ended TS search option[24] in GRRM. Further, since during search performed on the complexes of TFA with two-water molecules, the TSs obtained were very few in number, therefore, for the sake of simplicity further optimization of the TSs were avoided and these are not reported in this work.

It should also be noted that the energy of the structures is corrected for basis set superposition error (BSSE) using counterpoise (CP) method of Boys and Bernardi.[40] The CP corrected stabilization energy is further analysed as:

$$\Delta E_{\mathrm{SE(CP)}} = E_{\mathrm{AB}}(\mathrm{AB}) - E_{\mathrm{A}}(\mathrm{AB}) - E_{\mathrm{B}}(\mathrm{AB}) - [E_{\mathrm{A}}^{0}(\mathrm{A}) - E_{\mathrm{A}}(\mathrm{A})] - [E_{\mathrm{B}}^{0}(\mathrm{B}) - E_{\mathrm{B}}(\mathrm{B})], \qquad (1)$$

where $E_{\mathrm{X}}(\mathrm{Y})$ is the energy of the fragment X computed in the basis of Y. E_{A}^{0} and E_{B}^{0} are the energies of the fragments A and B in their actual geometries within the complex whereas

E_A(A) and E_B(B) are the energies of the free fragments in their equilibrium geometries. NBO analysis[41] was also performed to compute second order interaction energies of complexes of *trans*-TFA with two-water molecules only since these interaction energies are already been reported for complexes of *trans*-TFA with single-water molecule in previous study.[11] The energetic importance of these interactions between donor Lewis-type NBOs and acceptor non-Lewis NBOs, are assessed by 2nd-order perturbation theory. Since these interactions involves deviation from the Lewis structure, they are known as "delocalization" corrections to the zeroth-order natural Lewis structure.

3. Results and Discussions

3.1. Pathways of tautomeric and geometric isomerisation in TFA

Through an automated search by GRRM on the singlet PES of TFA, 18 equilibrium structures (EQs) were obtained (see supporting information Figure 1). Six of the identified isomers are found to be potential isomers describing isomerism between geometric and tautomeric forms of TFA as depicted in Figure 2. It should be noted that four of the EQs searched are isomeric forms of TFA, namely, *trans*-TFA(thiol), *cis*-TFA(thiol), *trans*-TFA(thione) and *cis*-TFA(thione) which had already been well-studied in the literature.[11] The thiol form of TFA is known to be the most stable which can be present in *cis* and *trans* conformer. However, the trans-TFA(thiol) is thermodynamically more stable and is a global minima on the singlet PES of TFA. The relative abundance *cis*:*trans* conformers is roughly 1:3 at room temperature in gas phase favouring *trans* conformer.[42-44] They are found to be interconvertible via rotation of C-S bond in transition state TS0 which lies lowest among all other TSs traced at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory as evident in Figure 3 and Table 1 where the relative energies computed with respect to *trans*-TFA(thiol) are listed.

Interestingly, apart from the well-known pathway[11] via TS0 discussed above, the GRRM has traced a new pathway for *cis-trans* interconversion in TFA(thiol) as depicted in Figure 2, which involves two intermediate states (IM1 and IM2) though it requires high activation energy, and is observed to utilize strong interaction between oxygen (O) and sulfur (S) atoms. The first step along this pathway involves extensive rearrangement in *trans*-TFA(thiol) leading to intermediate IM1 via transition state TS5 involving simultaneous breaking of C-S bond and formation of S-O bond. It should be noted that the intermediate, IM1, is nearly a dissociated structure with extensive stretching of C-S and S-O bonds with its dispersion interaction energy, using counterpoise calculations, found to be -11.30 kcal/mol at B3LYP/6-311++G(2d,2p) and UB3LYP/6-311++G(2d,2p) levels of the theory**.** This is followed by interconversion of IM1 to another intermediate IM2 through TS4 involving shortening of C-S interatomic distance. It should be noted that IM2 exhibits strong intramolecular interactions between the atoms as evident from counterpoise computed interaction energy of 458.89 kcal/mol for this intermediate species. Finally, IM2 leads to *cis*-TFA(thiol) via TS3 through rotation of S-H bond along with S-O bond breaking and C-S bond formation. From the standard Gibbs free-energy change along the new pathway explored, as listed in Table 2, it is clearly evident that the *trans*-TFA(thiol) is thermodynamically the most dominating species among the conformers of isolated TFA.

The other tautomer, TFA(thione), also exhibits geometric isomerism but through transition state TS1 which involves rotation around C-O bond. However, geometric isomerisation in TFA(thione) is thermodynamically less favourable than that in the TFA(thiol) because as evident from Table 2, the standard Gibbs free energy change to reach the transition state (TS1) along the pathway of TFA(thione) is relatively higher than that required for TS0 along the pathway of TFA(thiol). This may be due to the presence of strong π-character of C-O bond in thione form than that of C-S bond in thiol form.The tautomerisation of *trans*-TFA(thiol) with *trans*-TFA(thione) proceeds through 1,3-hydrgen shift which is relatively less feasible than the geometric isomerisation previously discussed for thiol form though it is slightly more feasible than the geometric isomerisation of thione form as evident from standard Gibbs free-energy change during the pathways in Table 2. However, the tautomerisation between *cis*-TFA(thiol) and *cis*-TFA(thione) is not possible as acidic hydrogen lies away from O and S, respectively, though it can indirectly tautomerise through geometric isomerisation route: *cis*-TFA(thiol)→TS0→*trans*-TFA(thiol)→TS2→*trans*-TFA(thione)→TS1→*cis*-TFA(thione).

Table 1. Relative energies of identified isomers of TFA and interconnecting transition states, depicted in Figure 2, with respect to *trans*-TFA(thiol)[a] at *ZPE* corrected DFT/B3LYP/6-311++G(2d,2p) and CCSD(T)/6-311++G(2d,2p)//DFT/B3LYP/6-311++G(2d,2p) levels of theory. The values compared in parenthesis are from Ref.[8] computed at MP2/6-311++G(2d,2p) level of the theory.

S.No.	**Spieces**	B3LYP/6-311++G(2d,2p) (MP2/6-311++G(2d,2p))	CCSD(T)/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)
1	*trans*-TFA(thiol)	0.00 (0.00)	0.00
2	*cis*-TFA(thiol)	0.69 (0.81)	0.75
3	*trans*-TFA(thione)	4.52 (3.63)	0.75
4	*cis*-TFA(thione)	9.29 (8.31)	4.33
5	IM1	73.73	75.68
6	IM2	103.79	105.67
7	TS0	9.35 (8.90)	9.66
8	TS1	17.51 (16.39)	13.93
9	TS2	31.75 (30.33)	35.27
10	TS3	106.36	110.44
11	TS4	106.74	110.44
12	TS5	108.31	112.32

[a]The total energy including (*ZPE*) of *trans*-TFA(thiol) at DFT/B3LYP/6-311++G(2d,2p) and CCSD(T)/ 6-311++G(2d,2p)// DFT/B3LYP/6-311++G(2d,2p) levels of theory is -512.7580 (0.0277) and 512.0386(0.0277) a.u., respectively.

Table 2. Standard Gibbs free-energy change (ΔG) in kcal/mol (at 298.15K) for the reaction pathways depicted in Figure 2, at B3LYP/6-311++G(2d,2p) and CCSD(T)/6-311++G(2d,2p)//DFT/ B3LYP/6-311++G(2d,2p) levels of the theory. The value in parenthesis represents net free-energy change during the complete pathway.

Reaction pathways	B3LYP/6-311++G(2d,2p)	CCSD(T)/6-311++G(2d,2p)//DFT/B3LYP/6-311++G(2d,2p)
***Geometric* (Thiol)**		
trans-TFA(thiol) →TS0	9.35	8.16
TS0→ *cis*-TFA(thiol)	-8.66	-7.53
	(0.69)	**(0.63)**
trans-TFA(thiol) → TS5	108.31	107.05
TS5→ IM1	-35.64	-37.46
IM1 → TS4	34.14	36.14
TS4 → IM2	-2.95	-2.76
IM2 →TS3	2.57	3.39
TS3 → *cis*-TFA(thiol)	-105.74	-105.74
	(0.69)	**(0.62)**
***Geometric* (Thione)**		
trans-TFA(thione) → TS1	13.05	11.99
TS1→ *cis*-TFA(thione)	-8.28	-7.40
	(4.77)	**(4.59)**
Tautomeric		
trans-TFA(thiol) → TS2	31.94	32.57
TS2 →*trans*-TFA(thione)	-27.36	-28.36
	(4.58)	**(4.21)**

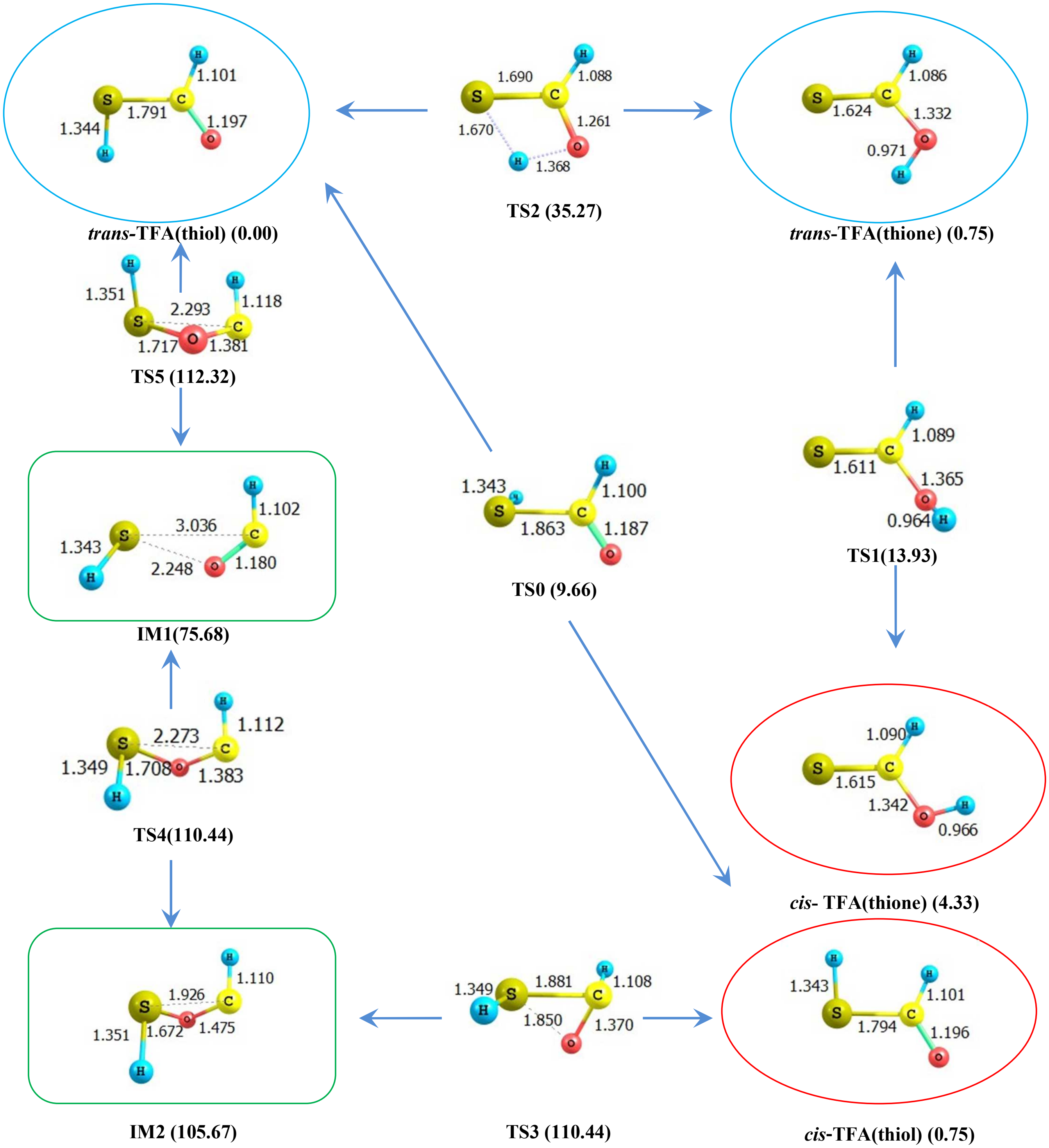


Figure 2. Isomerisation pathways between geometric and tautomeric forms of TFA connecting different isomers with TSs. The geometries (with bond length in Å) are optimized at DFT/B3LYP/6-311++G(2d,2p) level of theory. The values in parenthesis refers to *ZPE* corrected relative energies (in kcal/mol) with respect to *trans*-TFA(thiol) at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of the theory.

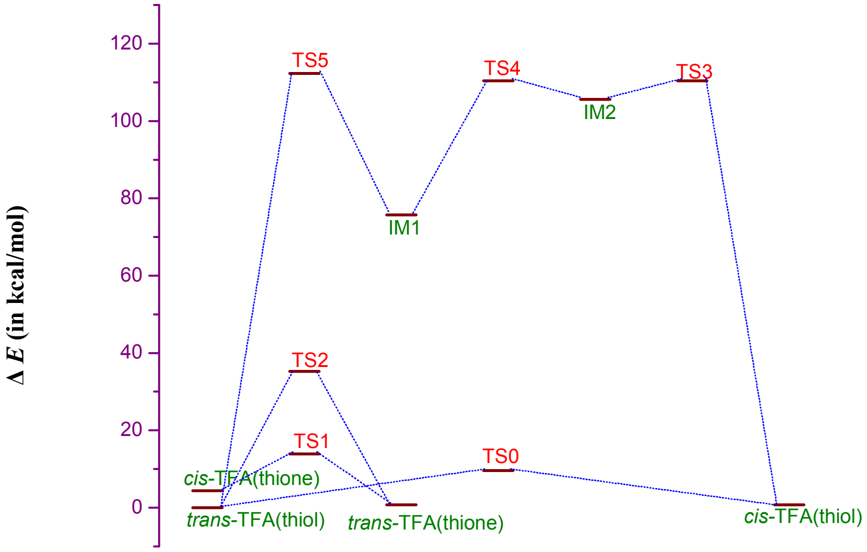


Figure 3. Potential energy profile (in kcal/mol) for the isomerisation pathways of TFA at *ZPE* corrected CCSD(T)/6-311++(2d,2p)//B3LYP/6-311++G(2d,2p) level of the theory. The relative energy (Δ*E*) depicted is with respect to the lowest-lying isomer *trans*-TFA(thiol).

3.2 Water migration and Isomerisation in TFA-water complexes

Though single-water molecule complexes of TFA have been investigated in a previous study on the hydrogen-bonding interactions in these complexes,[11] but to the best of our knowledge, the detailed mechanism of water migration and isomerisation in these complexes is being worked out for the first time here. The various possible reaction routes involving water migration and geometric isomerisation traced out using GRRM in the complexes of TFA with single water molecule are depicted in Figure 4 for TFA(thiol) and Figure 5 for TFA(thione), besides a water-catalysed dissociation pathway of TFA was also traced as depicted in Figure 6. The tautomeric routes and automeric (self-isomeric) transition states explored are further displayed in Figures 7 and 8, respectively. The relative energies of various structures, explored along the pathways, with respect to *trans*-(thiol)- H_2O [Complex1], and stabilization energy of relevant complexes are listed in Table 3. The overview of reaction routes and the relative energy profile are further provided in Figures 9 and 10, respectively. The standard Gibbs free-energy change (ΔG) along the pathways is provided in Table 4, while Table 5 depicts the Gibbs free-energy change relative to the isolated species at different temperatures for the dissociation reaction: TFA-water complex → TFA + H_2O.

The GRRM explored 12 potential complexes of TFA with single-water molecule and 17 interconversion states. The located complexes can be categorized into four classes, *viz*., (i) water-complexes of *trans* form of TFA (thiol): *trans*-TFA(thiol)-H_2O[Complex 1], *trans*-TFA(thiol)-H_2O[Complex 2] and *trans*-TFA(thiol)-H_2O[Complex 3], (ii) water-complexes of *cis* form of TFA(thiol): *cis*-TFA(thiol)-H_2O[Complex 4], *cis*-TFA(thiol)-H_2O[Complex 5] and *cis*-TFA(thiol)-H_2O[Complex 6], (iii) water-complexes of *trans* form of TFA(thione): *trans*-TFA(thione)-H_2O[Complex 7], *trans*-TFA(thione)-H_2O[Complex 8] and *trans*-TFA(thione)-H_2O[Complex 9], (iv) water-complexes of *cis* form of TFA(thione): *cis*-TFA(thione)-H_2O[Complex 10], *cis*-TFA(thione)-H_2O[Complex 11] and *cis*-TFA(thione)-

H_2O[Complex 12]. The relative energy of TFA(thione)-water Complex 7 is not only more than TFA(thiol)-water Complex 1 but the stablization energy of formation (i.e. relative to the sum of separated reactant) for Complex 7 is also more than that of Complex 1. In the present work,the PES is reported relative to TFA(thiol)-water Complex 1 as shown in Figure 10.

Table 3. Relative energies of TFA-water complexes, interconnecting transition states and dissociation channels with respect to *trans*-TFA(thiol)-H_2O[Complex1][a] depicted in Figures 4-7 at *ZPE* and BSSE corrected (1) DFT/B3LYP/6-311++G(2d,2p), and (2) CCSD(T)/ 6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p) levels of the theory. The stabilization energy of these complexes are represented in bold, and values compared in parenthesis are from Ref. [8] computed at MP2/6-311++G(2d,2p) level of the theory.

S.No	Spieces	DFT/B3LYP/6-311++G(2d,2p)			BSSE (1)	CCSD(T)/6-311++G(2d,2p// DFT/B3LYP/6-311++G(2d,2p)	BSSE (2)
1	Complex1	0.00	**6.28**	(6.40)	0.31	0.00	1.57
2	Complex2	1.26	**4.20**	(4.65)	0.25	0.69	1.00
3	Complex3	2.38	**2.32**	(2.88)	0.13	1.76	0.63
4	Complex4	1.69	**4.27**	(4.85)	0.25	1.13	1.00
5	Complex5	2.13	**3.51**	(4.03)	0.19	1.69	0.82
6	Complex6	2.32	**3.64**	(3.98)	0.13	2.01	0.88
7	Complex7	1.38	**10.17**	(9.44)	0.63	2.01	2.13
8	Complex8	6.15	**3.58**	(3.87)	0.19	5.46	1.07
9	Complex9	7.03	**2.26**	(2.99)	0.13	5.77	0.75
10	Complex10	6.65	**8.28**	(8.02)	0.38	6.40	1.38
11	Complex11	10.23	**4.39**	(4.66)	0.13	9.35	1.13
12	Complex12	11.30	**2.89**	(3.01)	0.13	10.60	0.75
13	Complex TS 1/2[c]	1.82			0.13	1.57	0.82
14	Complex TS 1/3[b]	3.51			0.06	3.14	0.56
15	Complex TS 4/5	2.82			0.13	2.45	0.63
16	Complex TS 1/5[b]	11.11			0.31	9.54	0.88
17	Complex TS 2/4[b]	11.04			0.25	9.16	0.94
18	Complex TS 7/8	7.84			0.25	7.03	0.75
19	Complex TS 8/9[b]	7.15			0.13	6.21	0.69
20	Complex TS 7/9[c]	7.47			0.19	5.77	0.75
21	Complex TS 10/11	11.17			0.13	10.23	0.75
22	Complex TS 10/12	11.30			0.13	10.17	0.69
23	Complex TS 7/10[b]	21.59			0.38	14.62	1.44
24	Complex TS 8/11[b]	19.26			0.13	17.57	1.07
25	Complex TS 1/7[c]	10.92[11.11][d]			0.88[1.13][d]	16.82[18.32][d]	4.77[6.34][d]
26	Complex TS 2/8	33.63 [33.82][e]			0.25[0.44][e]	33.76[36.14][e]	0.75[3.14][e]
27	Complex TS 7/7	1.69			0.44	2.07	1.82
28	Complex TS 7/7(2)	2.57			0.56	2.76	1.82
29	Complex TS 8/8	7.03			0.19	6.09	0.82
30	Complex TS3/DC	38.34[38.78][f]			0.82[1.26][f]	43.93[46.06][f]	4.58[6.78][f]
31	DC (Complex 3)	0.63			0.38	-6.90	1.38

[a] The total energy including BSSE correction and (*ZPE*) of Complex1 at DFT/B3LYP/6-311++G(2d,2p) and CCSD(T)/ 6-311++G(2d,2p)// DFT/B3LYP/6-311++G(2d,2p) level of theory is -589.2045(0.0527) and -588.2757(0.0527)a.u.

[b] TS obtained from saddle point optimization option in GRRM.

[c] TS obtained from double ended TS search option in GRRM.

[d] Using counterpoise computations w.r.t 4 fragments[H(3), H(2),O(2)H(4), HC(O)S]

[e] Using counterpoise computations w.r.t 3 fragments[H(2), H_2O, HC(O)S].

[f] Using counterpoise computations w.r.t 5 fragments[H(1),H(3), O(2)H(4), SH, CO]

* ComplexTS*m*/*n*(*i*) specifies *i*th transition state interconnecting *n*th TFA-water complex with *m*th complex. TS represented without any number in parenthesis indicates only identified TS.

Table 4. Standard Gibbs free-energy change (ΔG) in kcal/mol (at 298.15 K) for the reaction pathways depicted in Figures 4, 5, 7 and 8, at B3LYP/6-311++G(2d,2p) level of the theoy. The value in parenthesis represents net free-energy change during the complete pathway.

Reaction Pathways	B3LYP/6-311++G(2d,2p)
***Geometric* (*trans-cis* Thiol)**	
Complex 1→Complex TS1/2	-1.63
Complex TS1/2→ Complex 2	-0.19
Complex 2→Complex TS2/4	9.60
Complex TS2/4→ Complex 4	-8.28
	(-0.50)
Complex 1→Complex TS1/5	7.34
Complex TS1/5 →Complex 5	-8.91
	(-1.57)
***Geometric* (*trans-cis* Thione)**	
Complex 7→Complex TS7/10	14.37
Complex TS7/10→Complex 10	-8.66
	(5.71)
Complex 7→Complex TS7/8	6.40
Complex TS7/8 →Complex 8	-1.07
Complex 8→Complex TS8/11	13.11
Complex TS8/11→Complex 11	-9.10
	(9.34)
***Tautomeric* (Thiol-Thione)**	
Complex 1→Complex TS1/7	11.92
Complex TS1/7→Complex 7	-10.29
	(1.63)
Complex 2→Complex TS2/8	30.94
Complex TS2/8→Complex 2	-25.41
	(5.53)
Dissociation	
Complex 3 →Complex TS3/DC	38.47
Complex TS3/DC→DC	-41.48
	(-3.01)

Table 5. Gibbs free-energy change (ΔG) in kcal/mol for the dissociation: TFA-water complex → TFA + H_2O, at different temperatures (in K) for various complexes of TFA with single-water molecule depicted in Figures 4 and 5, using computations at B3LYP/6-311++G(2d,2p) level of the theory.

TFA-water Complex	Temperature (in K)						
	200	250	273.15	298.15	350	400	450
Complex1	-1.13	-2.51	-3.20	-5.65	-5.46	-6.90	-8.28
Complex2	-1.57	-2.64	-3.20	-3.83	-4.89	-5.96	-6.97
Complex3	-2.38	-3.33	-3.70	-4.08	-5.08	-5.90	-6.71
Complex4	-1.38	-2.51	-3.01	-4.46	-4.71	-5.77	-6.84
Complex5	-1.63	-2.64	-3.07	-3.39	-4.64	-5.52	-6.46
Complex6	-2.20	-3.45	-4.02	-4.58	-5.96	-7.15	-8.35
Complex7	**2.07**	**0.50**	-0.19	-1.00	-2.76	-4.20	-5.71
Complex8	-2.38	-3.58	-4.08	-4.77	-5.96	-7.09	-8.16
Complex9	-3.33	-4.58	-5.08	-5.71	-7.03	-8.28	-9.48
Complex10	**1.82**	**0.63**	**0.06**	-0.38	-1.82	-3.01	-4.27
Complex11	-1.82	-3.07	-3.64	-4.02	-5.52	-6.71	-7.91
Complex12	-2.26	-3.26	-3.70	-3.64	-5.21	-6.15	-7.09

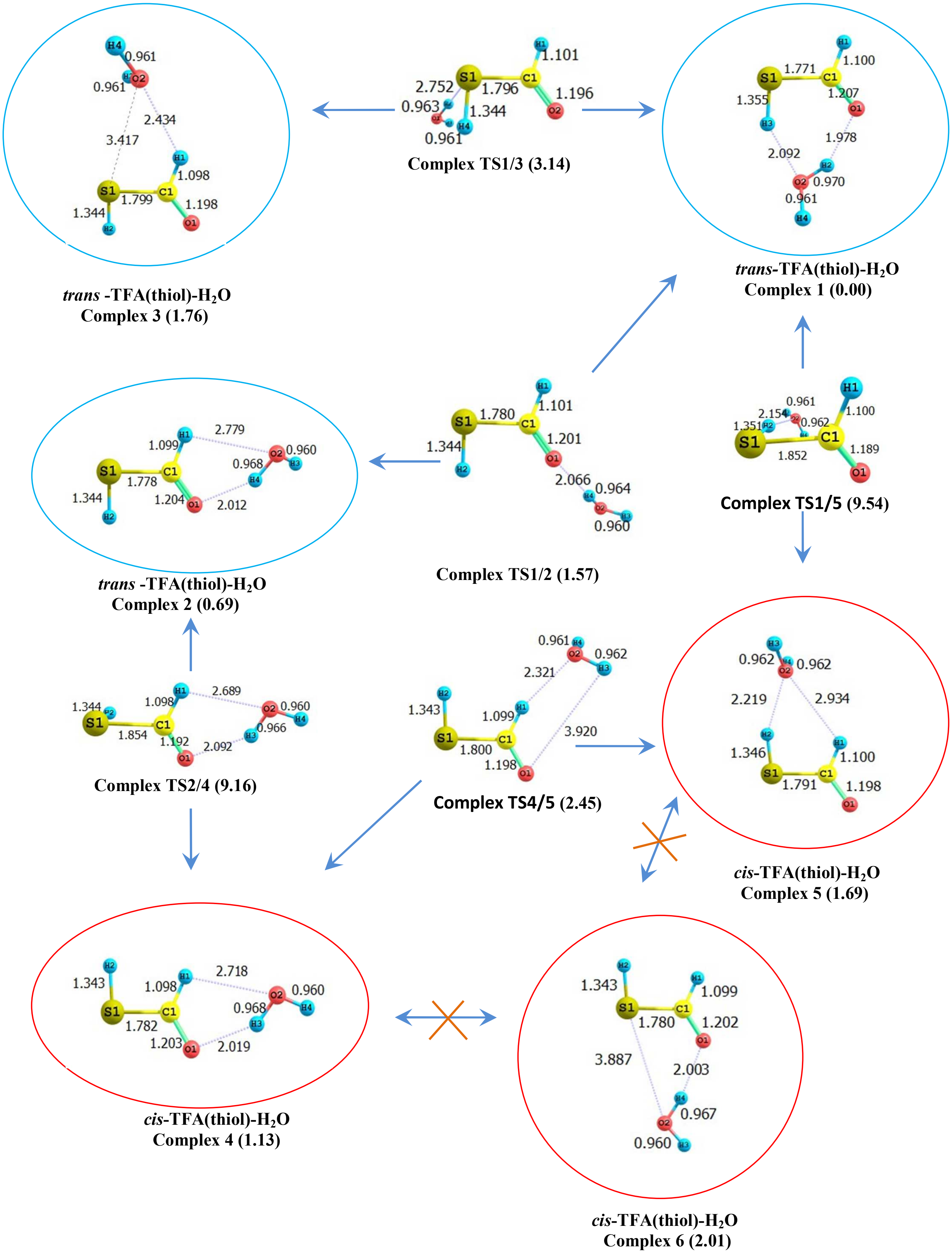


Figure 4. Pathways of water migration and *cis-trans* isomerisation in gas-phase complexes of TFA(thiol) with single-water molecule. The geometries (with bond length in Å) are optimized at DFT/B3LYP/6-311++G(2d,2p) level of theory. The values in parenthesis refer to *ZPE* and BSSE corrected relative energies (in kcal/mol) with respect to *trans*-TFA(thiol)-H$_2$O[Complex 1] obtained at the CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of the theory. ComplexTS*m*/*n* specifies *i*th transition state interconnecting *n*th TFA-water complex with *m*th complex.

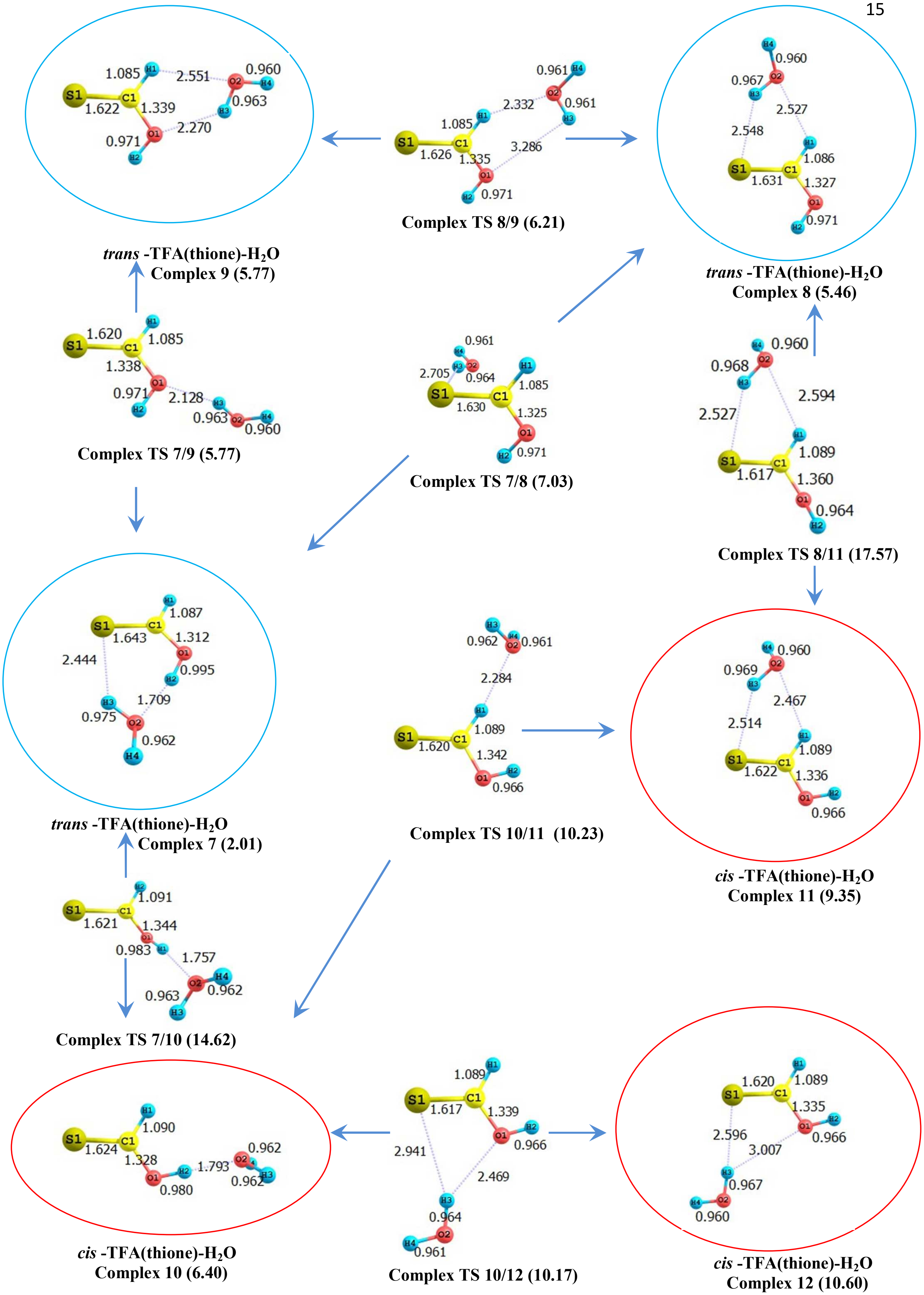
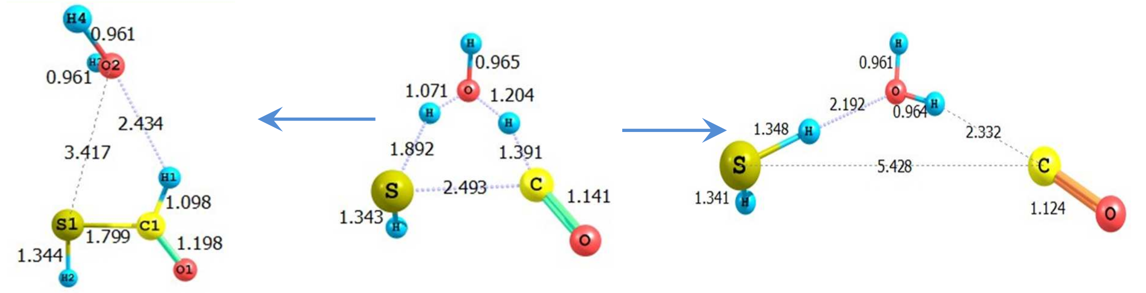


Figure 5. Same as Figure 4, but for complexes of TFA(thione) with single-water molecule.

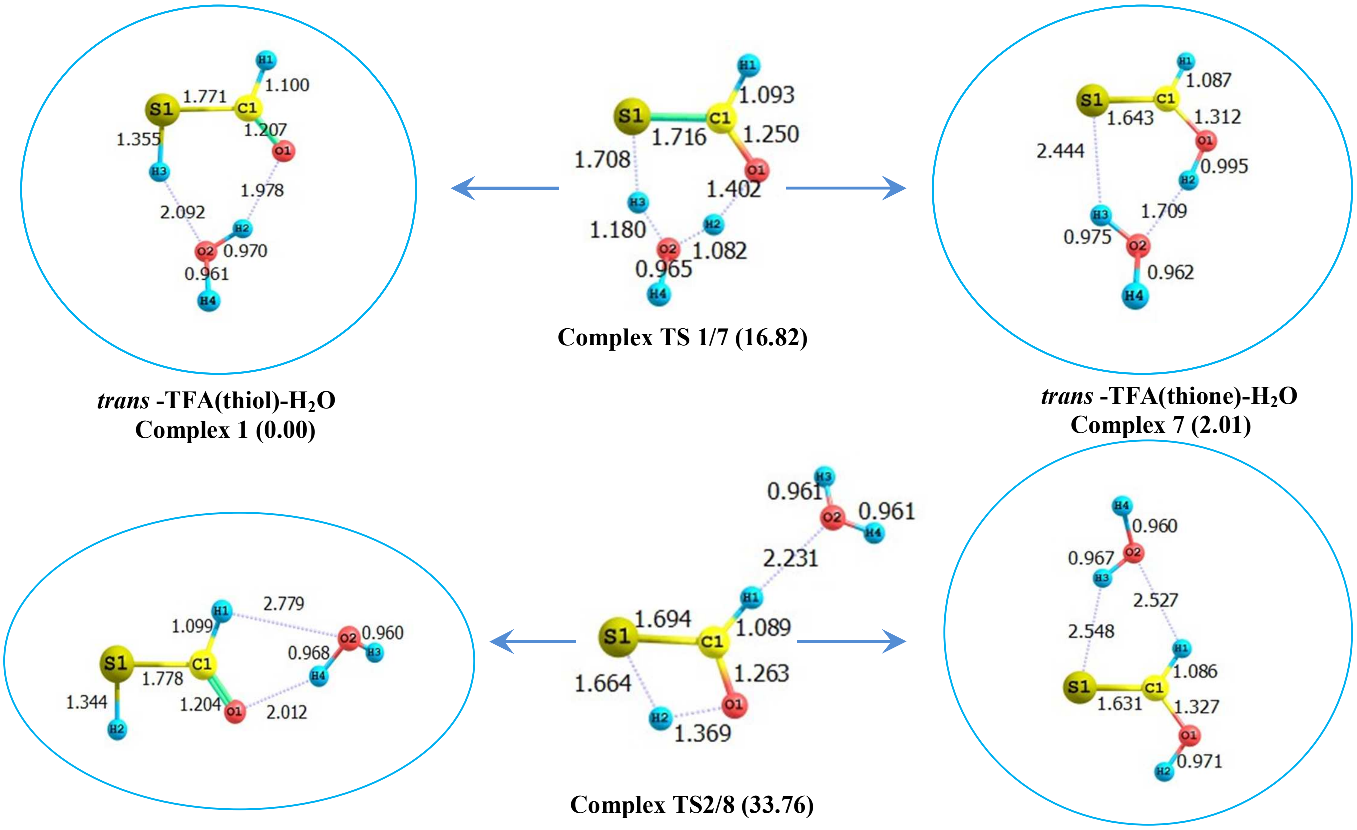


trans -TFA(thiol)-H_2O Complex 3 (1.76)

Complex TS3/DC (46.06)

DC (-6.90)

Figure 6. Same as Figure 4, but depicting water-catalysed dissociation pathway of TFA(thiol).



***trans* -TFA(thiol)-H_2O Complex 1 (0.00)**

Complex TS 1/7 (16.82)

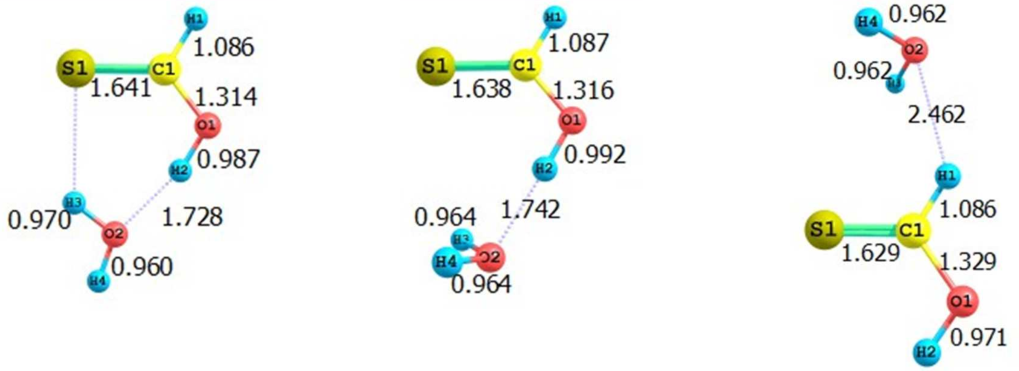
***trans* -TFA(thione)-H_2O Complex 7 (2.01)**

***trans* -TFA(thiol)-H_2O Complex 2 (0.69)**

Complex TS2/8 (33.76)

***trans* -TFA(thione)-H_2O Complex 8 (5.46)**

Figure 7. Same as Figure 4, but depicting water-catalysed tautomeristion pathways of TFA-water complexes.



Complex TS 7/7{1} (2.07) **Complex TS 7/7 {2} (2.76)** **Complex TS 8/8 (6.09)**

Figure 8. Transition states governing automerisation routes of TFA-water complexes at B3LYP/6-311++G(2d,2p) level of the theory. The values in parenthesis refer to *ZPE* and *BSSE* corrected relative energies (in kcal/mol) with respect to *trans*-TFA(thiol)-H_2O[Complex 1] obtained at the CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of the theory. ComplexTS*m*/*n*{*i*} specifies *i*th transition state interconnecting *n*th TFA-water complex with *m*th complex. TS represented without any number in braces indicates only identified TS.

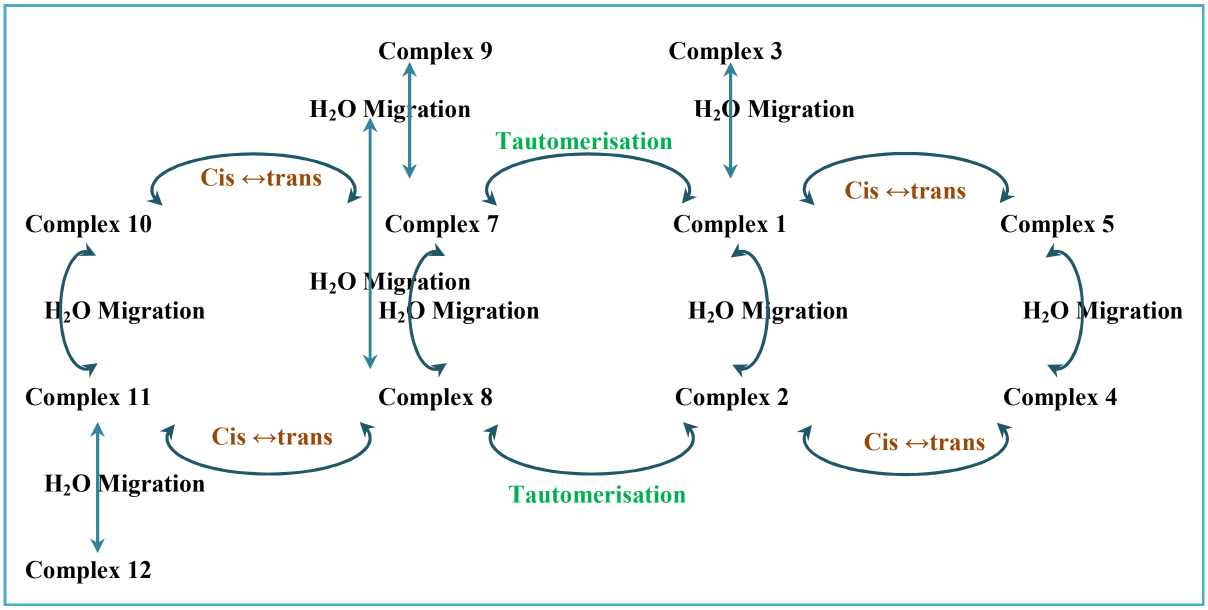


Figure 9. Overview of different pathways depicted in Figures 4-7 involving migration of water molecule and isomerisation (tautomerisation and geometric) in complexes of TFA with single-water molecule.

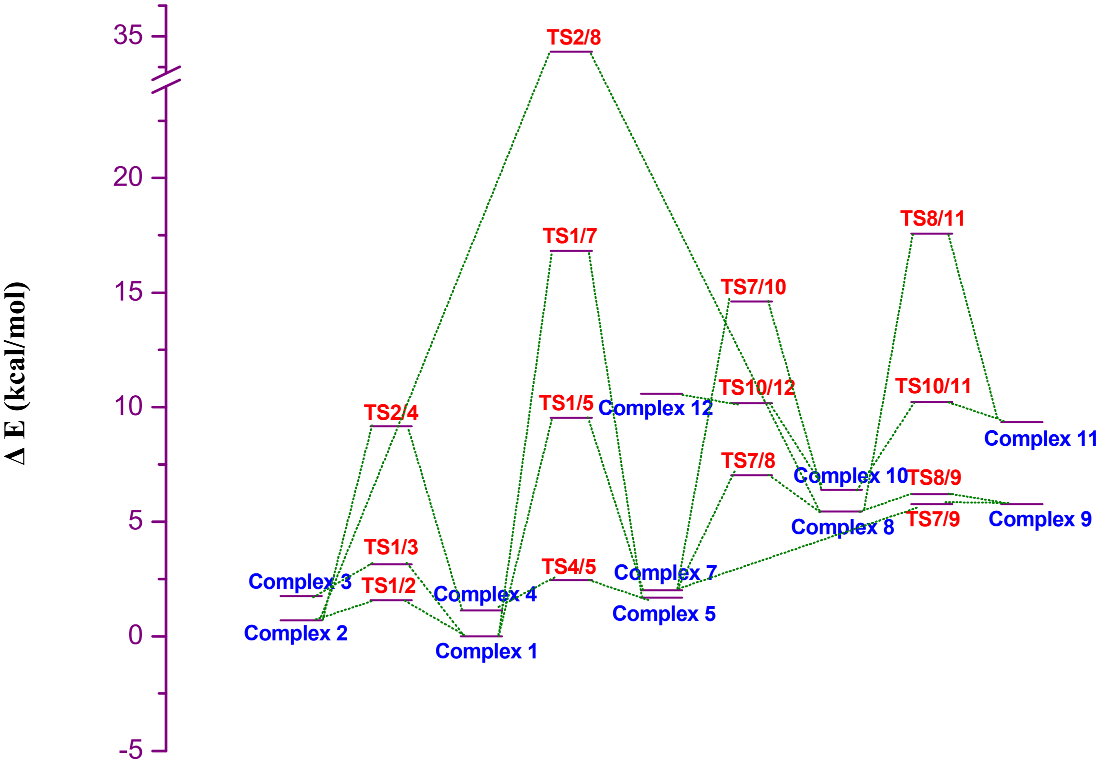


Figure 10. Potential energy profile (in kcal/mol) for the water migration and isomerisation pathways of TFA-water complexes at *ZPE* and BSSE corrected CCSD(T)/6-311++(2d,2p)//B3LYP/6-311++G(2d,2p) level of the theory. The relative energy (ΔE) depicted is with respect to *trans*-TFA(thiol)-H_2O[Complex1]. Complex TS*m*/*n* specifies *i*th transition state interconnecting *n*th TFA-water complex with *m*th complex.

3.2.1. *Pathways for Water-migration and geometric isomerisation in the complexes of TFA(thiol) with single-Water molecule*

TFA(thiol)-water Complex 1 is the lowest lying complex on singlet PES as depicted in Figure 10. The lowest activation energy for its coversion to TFA-water Complex 2 and Complex 3 is 1.82 an 3.51 kcal/mol, respectively, through governing transition states Complex TS1/2 and TS1/3 at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory. In moving from TFA-water Complex 1 to Complex 2, water migrates from bottom to sideway facing C=0 and formyl hydrogen of *trans*-TFA(thiol) through ComplexTS1/2 and this pathway for water migration readily feasible as evident from ΔG in Table 4. However, in transition state ComplexTS1/3, water molecule lies out of the plane of TFA due to large size of sulfur atom, leading to a top-to-bottom shift of water on the *trans*-TFA(thiol). TFA-water Complex 3, is relatively less stable due to stabilization by single H-bond as compared to two H-bonds in Complex 1 where *trans*-TFA(thiol) act as both H-bond acceptor and donor. However, Complex 3 can readily dissociate through a pathway, depicted in Figure 6, which actually reveals water assisted dissociation of *trans*-TFA(thiol).

In the case single-water molecule complexes of *cis*-TFA(thiol), only Complex 4 and Complex 5 can interconvert via Complex TS 4/5 lying at 2.45 kcal/mol involving the migration of water from one-side to the other of *cis*-TFA(thiol) in the same plane. However, TS involving the conversion between Complex 4 ↔ Complex 6, and Complex 5↔ Complex 6 could not be located. The water complexes of *trans*-TFA(thiol) can interconvert to those of *cis*-TFA(thiol) through rotational transition state involving geometric isomerisation. For example, the conversion between Complex 1(*cis*)↔ Complex 5(*trans*) via Complex TS 1/5 proceeds through H-bond formation between water and acidic hydrogen of TFA(thiol), which facilitaes the rotation of S-H bond by decreasing the rotational barrier by 0.12 kcal/mol as compared to isolated TFA. Further, in the conversion between Complex 2(*trans*) ↔

Complex 4, water indirectly participate by forming two H-bonds, one with C=O and another with formyl hydrogen causing stabilization of Complex TS 2/4 by 0.50 kcal/mol as compared to TS0 for TFA(thiol) in the absence of water. This is supported by the net standard Gibbs free-energy change along the geometric pathways as evident in Table 4, depicting the favourability for *cis* form over *trans* form of TFA(thiol) in the complexes of TFA with single-water molecule, which is in contrast to that observed for isolated TFA, however, net standard Gibbs free-energy change in the two cases is within 1 kcal/mol for the most feasible pathways.

3.2.2. *Pathways for Water-migration and geometric isomerisation in the complexes of TFA(thione) with single-Water molecule*

TFA(thione)-water Complex **7** can be excited to transition state ComplexTS7/8 in which water lie out of the plane of *trans*-TFA(thione), leading to Complex 8, with the reverse conversion being relatively much less energetic as evident in Figure 5 and Table 3. The conversion between Complex 7 ↔ Complex 9 can crop up via governing ComplexTS7/9 which lies at the same level of Complex 9 involving the movement of water molecule to opposite side of *trans*-TFA(thione). TFA-water Complex 8 ↔ Complex 9 conversion can crop up via ComplexTS8/9 which lays at 6.21 kcal/mol. It is worthnoting that ComplexTS8/9 lays only 0.69 kcal/mol above ComplexTS7/9 indicating that respective conversion routes are competing each other. TFA-water Complex 12 is the least stable among all TFA-water complexes. TFA-water Complex 10 can isomerise to Complex 12 through ComplexTS 10/12, however, reverse isomerisation is more feasible in this case since conversion barrier for TFA-water Complex 12→ Complex 10 is negative. Interconversion between Complex 10↔ Complex 11 can occur through Complex TS 10/11 with the conversion barrier of 3.83 kcal/mol. It should, however, be noted that dissociation of TFA-water complexes, except Complex 7 and Complex 10, towards separated speices (TFA and H_2O) at room temperature (298.15 K) is more favorable than the water migration as evident from ΔG values at different temperatures listed in Table 5. However, as the temperature decreases, the association between TFA and water seems to increase, though the dissociation still remains dominating at lower temperatures. Among single-water complexes of TFA(thione), gemetric interconversions between TFA-water Complex 7↔ 10, and Complex 8↔ Complex 11 require high activation energy as barrier height is 12.61 and 12.11 kcal/mol via rotational ComplexTS7/10 and TS8/11, respectively. As evident in Table 4, the net standard Gibbs free-energy change along these pathways favours *trans* form of TFA(thione) in the single-water molecule complexes of TFA(thione), in fact even more strongly than that observed in the case of isolated TFA(thione) indicating a catalytic effect of water. It should also be noted that in a previous study involving formamide,[19] similar water migration and tautomerism pathways were observed, however, without any geometric isomerism.

3.2.3. *Tautomerisation and automerisation (self isomerisation) in the complexes of TFA(thiol) with single-water molecule*

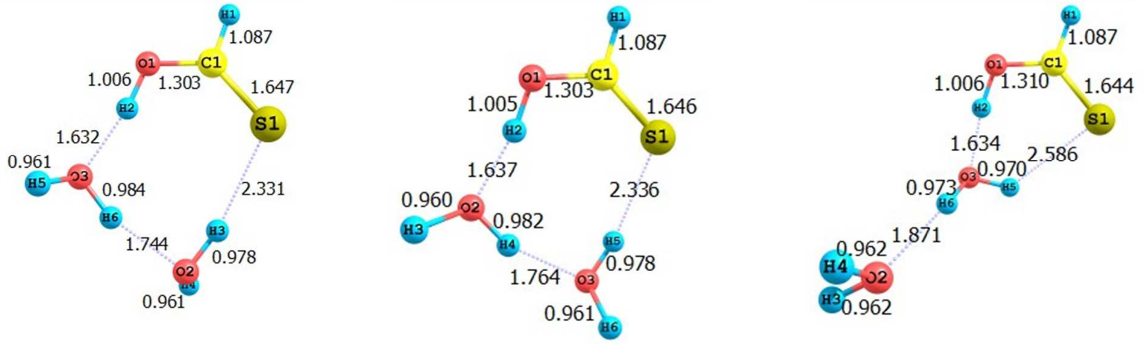
TFA-water Complex 1 can tautomerise to Complex 7 via six-membered cyclic high lying ComplexTS1/7 involving the direct participation of water as depicted in Figure 7. This pathway has been investigated earlier also.[17] Besides this, TFA-water Complex 2↔ Complex 8 interconversion can occur via a four-membered ComplexTS2/8 where there is indirect involment of water. It should be noted that transition state TS2, in case of tautomerization of isolated TFA, lies higher than ComplexTS1/7 and ComplexTS2/8 by 18.45 and 1.51 kcal/mol, respectively, at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) indicating the positive catalytic effect of water in the tautomerisation of TFA, however, the standard Gibbs free-energy change, as evident in Tables 2 and 4, favors thiol form of TFA in both the cases. Besides above isomerisation pathways, GRRM also traced few automerisation pathways via Complex TS7/7{1}, Complex TS7/7{2} and Complex TS 8/8 with the barrier height of 2.07, 2.76 and 6.09 kcal/mol, respectively, as depicted in Figure 8.

3.3. Complexes of TFA with two-Water molecules

As mentioned earlier that the *trans* conformer of TFA is more stable than *cis* conformer , therefore, we will analyze here only on the *trans* form. The GRRM traced out 22 complexes of TFA with two-water molecules: 11 of *trans*-TFA(thione) and 11 of *trans*-TFA(thiol). To the best of our knowledge, there is no experimental and theoretical study on the two-water molecule complexes of TFA, hereafter referred as "Bicomplexes". Since most of the Bicomplexes of *trans*-TFA(thione) have highest stabilization energy of formation than those of *trans*-TFA(thiol), so we decided to discuss them first. The geometries of these Bicomplexes are depicted in Figure 11 for *trans*-TFA(thione), and in Figure 12 for *trans*-TFA(thiol), while the relative energies and stabilization energy of formation with respect to Bicomplex 0 are listed in Table 6. Gibbs free-energy change for all the Bicomplexes relative to the isolated species, at various temperatures are further listed in Tables 7 and 8. The second order interaction energies, computed using NBO analysis, in these Bicomplexes are summarized in supporting information Table S1 and S2 for *trans*-TFA(thione) and *trans*-TFA(thiol), respectively. The vibrational frequencies with corresponding highest IR intensities are further provided in supporting information Tables S3 and S4.

Table 6. Same as Table 2, but for complexes of *trans*-TFA (thione) and TFA(thiol) with two-water molecules depicted in Figures 11 and 12, respectively.

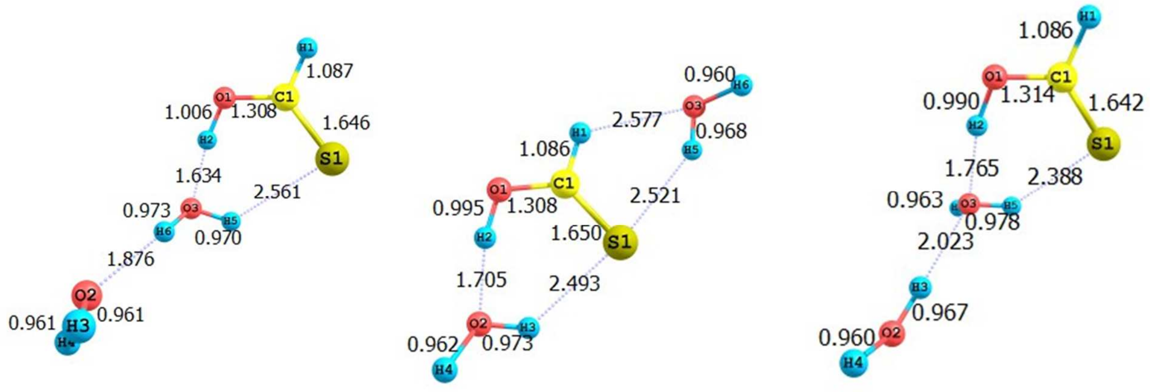
Spieces	TFA(thione)					TFA(thiol)				
	B3LYP/6-311++G(2d,2p)		BSSE (1)	CCSD(T)/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)	BSSE (2)	B3LYP/6-311++G(2d,2p)		BSSE (1)	CCSD(T)/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)	BSSE (2)
Bicomplex 0	0.00	**20.83**	1.13	0.00	3.89	0.00	**15.19**	1.00	0.00	3.45
Bicomplex 1	0.44	**20.21**	1.13	0.38	3.83	0.38	**14.68**	0.94	0.31	3.39
Bicomplex 2	2.38	**16.57**	1.07	1.57	3.33	1.44	**12.74**	0.75	0.44	2.76
Bicomplex 3	2.45	**16.50**	1.07	1.69	3.33	3.51	**10.48**	0.63	2.13	2.64
Bicomplex 4	4.58	**13.74**	0.88	3.14	3.14	3.14	**10.73**	0.69	2.13	2.57
Bicomplex 5	4.89	**13.37**	0.94	3.58	3.01	3.01	**10.73**	0.75	2.26	2.64
Bicomplex 6	5.46	**12.55**	0.88	3.64	3.07	4.39	**9.04**	0.63	2.76	2.26
Bicomplex 7	6.28	**11.55**	0.88	4.27	2.76	4.52	**8.41**	0.56	2.89	2.13
Bicomplex 8	8.16	**9.41**	0.82	5.33	2.64	4.58	**8.91**	0.69	3.14	2.26
Bicomplex 9	8.53	**8.41**	0.56	6.46	2.20	5.08	**8.03**	0.75	3.45	2.26
Bicomplex 10	9.85	**6.84**	0.63	7.03	2.01	5.65	**7.34**	0.63	3.89	1.95



Bicomplex 0 (0.00)

Bicomplex 1 (0.38)

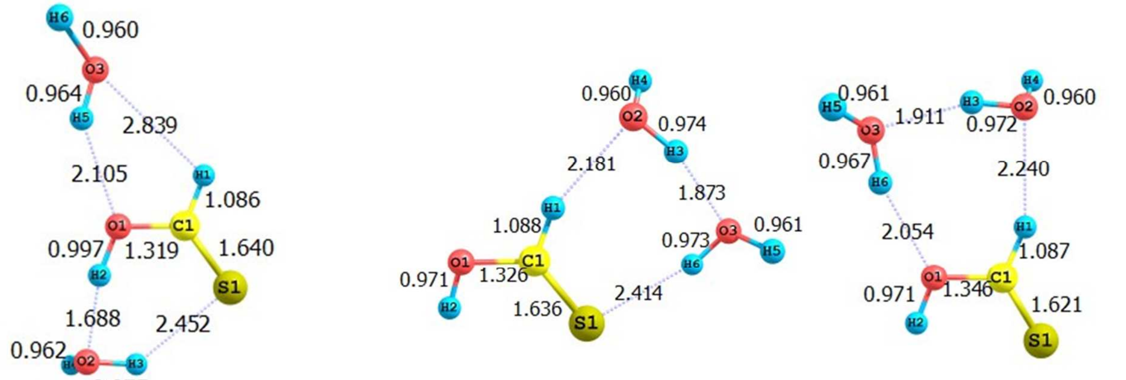
Bicomplex 2 (1.57)



Bicomplex 3 (1.69)

Bicomplex 4 (3.14)

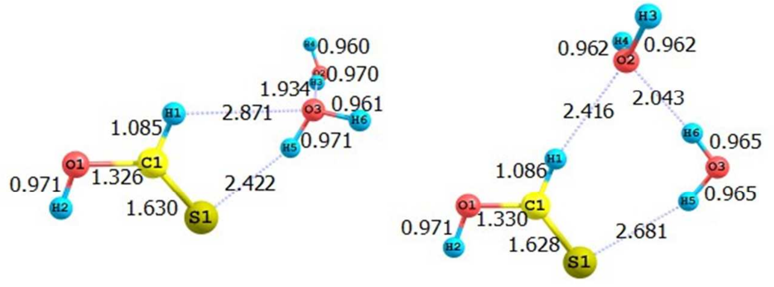
Bicomplex 5 (3.58)



Bicomplex 6 (3.64)

Bicomplex 7 (4.27)

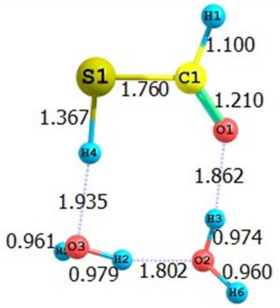
Bicomplex 8 (5.33)



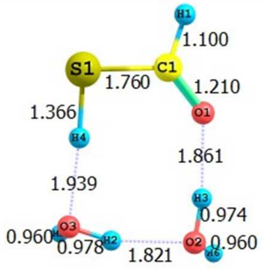
Bicomplex 9 (6.46)

Bicomplex 10 (7.03)

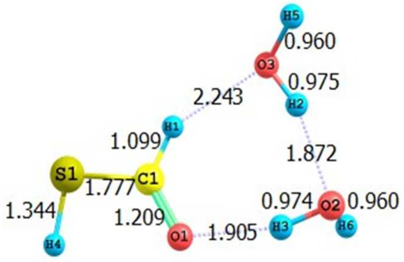
Figure 11. Gas-phase complexes of *trans*-TFA(thione) with two-water molecules. The geometries (with bond length in Å) are optimized at DFT/B3LYP/6-311++G(2d,2p) level of theory. The values in parenthesis refers to *ZPE* corrected relative energies (in kcal/mol) with respect to Bicomplex0 at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of the theory.



Bicomplex 0 (0.00)



Bicomplex 1 (0.31)



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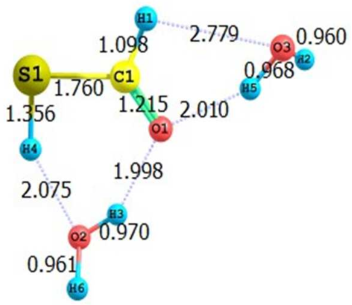

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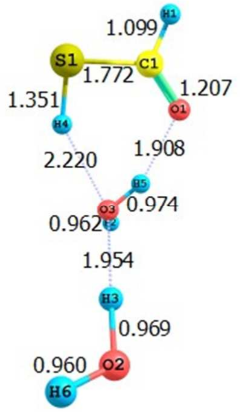
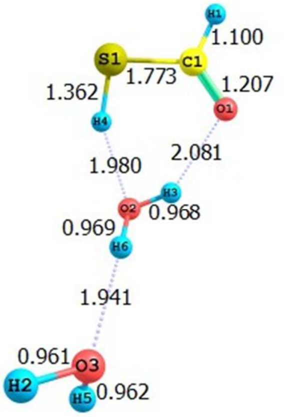
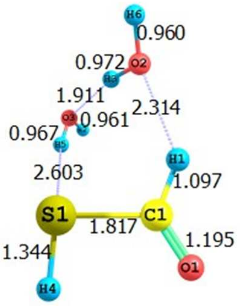


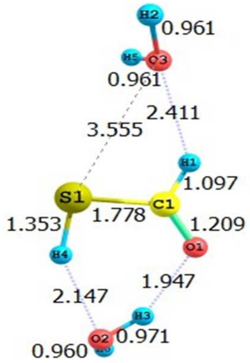
Bicomplex 4 (2.13)



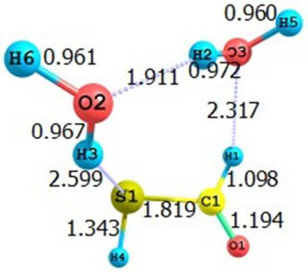
Bicomplex 5 (2.26)



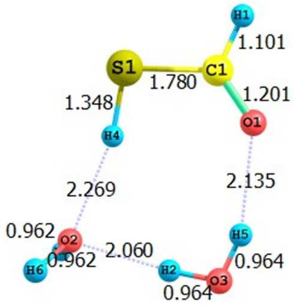
Bicomplex 6 (2.76)



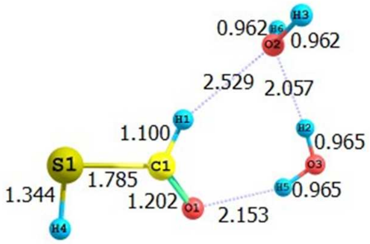
Bicomplex 7 (2.89)



Bicomplex 8 (3.14)



Bicomplex 9 (3.45)



Bicomplex 10 (3.89)

Figure 12. Same as Figure 11, but for complexes of *trans*-TFA(thiol) with two-water molecules.

Table 7. Same as Table 5 but for Bicomplexes of *trans*-TFA(thione) with two-water molecules depicted in Figure 11.

Bicomplex	Temperature (in K)						
	200	**250**	**273.15**	**298.15**	**350**	**400**	**450**
0	**3.83**	**0.75**	-0.63	-2.20	-5.40	-8.41	-11.42
1	**3.45**	**0.44**	-0.94	-2.51	-5.65	-8.66	-11.61
2	**2.26**	-0.44	-1.63	-3.07	-5.90	-8.53	-11.11
3	**2.26**	-0.44	-1.63	-3.01	-5.77	-8.41	-10.98
4	-0.25	-3.01	-4.20	-5.65	-8.41	-11.04	-13.68
5	-0.06	-2.70	-3.83	-5.21	-7.91	-10.48	-12.99
6	**0.50**	-2.01	-3.14	-5.84	-7.03	-9.41	-11.73
7	-2.07	-4.89	-6.09	-7.53	-10.42	-13.11	-15.75
8	-3.83	-6.53	-7.72	-9.10	-11.86	-14.43	-17.01
9	-2.89	-5.15	-6.15	-7.28	-9.60	-11.73	-13.81
10	-4.71	-7.09	-8.16	-9.35	-11.73	-13.93	-16.19

Table 8. Same as Table 5 but for Bicomplexes of *trans*-TFA(thiol) with two-water molecules depicted in Figure 12.

Bicomplex	Temperature (in K)						
	200	**250**	**273.15**	**298.15**	**350**	**400**	**450**
0	0.00	-2.95	-4.33	-5.84	-8.97	-11.86	-14.68
1	-0.38	-3.26	-4.64	-6.15	-9.16	-12.05	-14.87
2	-1.32	-4.08	-5.40	-6.78	-9.66	-12.36	-15.06
3	-3.20	-5.84	-7.03	-8.41	-11.17	-13.74	-16.25
4	-2.32	-4.89	-6.02	-7.34	-9.98	-12.42	-14.87
5	-2.07	-4.58	-5.71	-6.97	-9.60	-12.05	-14.43
6	-3.77	-6.34	-7.53	-8.79	-11.42	-13.87	-16.25
7	-3.33	-5.65	-6.65	-7.84	-10.23	-12.36	-14.50
8	-4.02	-6.53	-7.72	-9.04	-11.67	-14.12	-16.50
9	-4.02	-6.46	-7.53	-8.72	-11.30	-13.55	-15.81
10	-4.64	-7.03	-8.09	-9.29	-11.73	-13.99	-16.25

3.3.1. Complexes of *trans*-TFA(thione) with two–water molecules

Bicomplex 0 forms eight-membered cyclic structure where both water molecules lie on the same side and it has highest stabilization energy, even more than that of lowest-lying Bicomplex of TFA(thiol), due to presence of stronger hydrogen-bonding interaction in O-H---O complexes than that in S-H---O complexes as evident in Figure 11 and Tables 6. In the Bicomplex 0, TFA acts as an acceptor as well as H-bond donor forming two H-bonds with water besides one H-bond between the water molecules. The covalent component of O3---H2-O1 is stronger than that of O2---H6-O3 and S1---H3-O2 because the second-order NBO interaction energy in $n_{O3} \rightarrow \sigma^*_{O1\text{-}H2}$ orbital interaction is relatively much higher than that in $n_{O2} \rightarrow \sigma^*_{O3\text{-}H6}$ and $n_{S1(2)} \rightarrow \sigma^*_{O2\text{-}H3}$ interactions, as evident from Table S1. The comparison shows that O---H bond is stronger than S---H bond due to more electronegativity and smaller size of the oxygen atom as compared to those for the sulfur atom. Due to the formation H-bonds, O-H bond of *trans*-TFA(thione) is elongated by 0.035 Å which is about 3% longer than that present in the isolated TFA, and C=S bond is also extended by 1.4% (0.032 Å) further leading to shortening of C-O bond by 2%.

Bicomplex 1 is similar to Bicomplex 0, however, difference lies in the orientation of H(5)O(3)H(6) as O3---H6 lies above the plane of the complex and three H-bonds formed are slightly longer. It lays only 0.44 kcal/mol above than Bicomplex 0. In Bicomplex **2**, there are three H-bonds: O3---H2, S1---H5 and O2---H6 with bond lengths 1.634, 2.586 and 1.871 Å, respectively, where first two H-bonds form six-membered ring complex between TFA(thione) and two-water molecules. The covalent component (in parenthesis) and bond length gives the H-bond strength order as follows: O3---H2(31.53)> O2---H6(9.99)> S1---H5(3.16) indicating that on hydration, the O-H and C=S bond elongates and C-O bond shortens. Bicomplex **3** lays above Bicomplex 2 just by 0.07 kcal/mol because of similarity in the structure and it only differs mainly in the orientation of H(3)O(2)H(4) along with change in some bond-lengths. Bicomplex 5 also has similar structure but lays 2.51 kcal/mol higher in energy than Bicomplex 2, whereas Bicomplex 4 form bicyclic planar structure with five- and six-membered ring involving four H-bonds with bond lengths: 1.705 Å (O2---H2), 2.493 Å (S1---H3), 2.521 Å (S1---H5) and 2.577 Å (O3---H1). The H-bond between O2---H2 has more stronger covalent component as compared to other bonds as evident from Table S1. Here also, complex formation causes elongation of O-H and C=S bond by 2.4% and 1.5%, respectively and shortening of C-O bond by 1.8% compared to isolated TFA.

In Bicomplex 6, there are four H-bonds forming bicyclic structure with one five- and other six-membered ring with water molecules on the opposite side of TFA(thione). As a result of H-bond formation, C=S and O-H bonds extend by 0.016 Å and 0.026 Å, respectively, besides shortening of the C-O bond. There are three hydrogen bonds in Bicomplex **7** forming seven-membered ring structure with both water molecules lying on the same side facing C-H and C=S bonds of *trans*-TFA(thione). The shortest and strongest bond is formed between two water molecules with second-order interaction energy value of 10.50 kcal/mol for $n_{O3} \rightarrow \sigma^*_{O2\text{-}H3}$ orbital interaction. The complex formation results in slight decrease of C-O bond by 0.006 Å and increase of C-S bond by 0.012 Å as compared to the isolated TFA. The remaining Bicomplexes 8-10 have relatively low stabilization energy of formation, therefore, for the sake of brevity, the structural details of these Bicomplexes are not discussed.

The Bicomplexes of TFA-water were also characterised through vibrational frequency analysis as presented in supporting information Tables S3 and S4. For the sake of brevity, frequencies corresponding to three highest IR intensities are listed in the tables. It should be noted that O-H stretching frequency of *trans*-TFA(thione) decreases in all the two-water molecule complexes of TFA where O-H bond is involved in H-bond formation as compared to single-water molecule complexes of TFA. Infact, the maximum decrease was observed for Bicomplex 3. However, O-H stretching intensity increases in all the complexes with exceptionaly high increase observed in Bicomplex 0. The C-H stretching frequency and intensity also show slight change due to H-bonding. Besides these, C=S stretching frequency decreases slighty in all bicomplexes, except in Bicomplexes 6 and 8 while corresponding stretching intensity increase in all except in Bicomplex 6 and 9. It should be noted that the association of TFA with two-water molecules increases as the temperature decreases which is evident from the increasingly positive Gibbs free-energy change with decrease in temperature as evident in Table 7. Interestingly, Bicomplexes 0-3 of TFA(thione) seem to be thermodynamically more feasible than the single-water molecule complexes of TFA. This may be due to the fact that more number of hydrogen-bonds are involved in the complexes with two-water molecules than that in the complexes with single-water molecule.

3.3.2. Complexes of *trans*-TFA(thiol) with two-water molecules

The stabilization energy of formation for low lying bicomplexes of *trans*-TFA(thiol) with two-water molecules is even lower than Bicomplex 3 of *trans*-TFA(thiol) as evident in Table 6. In Bicomplex 0 of TFA(thiol), there is formation of eight-membered cyclic structure with three H-bonds having bond lengths 1.802, 1.862 and1.935 Å for O2---H2, O1---H3 and O3---H4 bonds, respectively, resulting in elongation of S-H and C=O bond lengths by 0.023 Å (1.7%) and 0.013 Å (1%) along with shortening of C-S bond by 0.031(1.7%) compared to those in isolated TFA. Bicomplex 1 lays only 0.31 kcal/mol above Bicomplex 0 and has similar structure. The only difference between Bicomplex 0 and 1 is the alignment of O2-H6 bond of one of the water molecule besides two H-bonds (O3---H4 and O2---H2) being longer than those in Bicomplex 0. However, the second-order interaction energy for these two H-bonds in Bicomplex 1 is relatively less than those in Bicomplex 0.

In the next higher lying Bicomplex **2**, there is formation of seven membered complex with water molecules lying on the same side facing C-H and C-O bond of *trans*-TFA(thiol) involving three H-bonds. The strongest H-bond is formed between water molecules, and covalent component for this bond (O2---H2) is 10.41 kcal/mol. This Bicomplex formation leads to reduction in C-S bond and extension in C=O bonds compared to isolated TFA due to their involvement in the H-bond formation. However, in Bicomplex 3, the two-water molecules are separated from each other as they lie on the different side of *trans*-TFA(thiol), thereby forming bicyclic structure containing six and five member rings formed by four H-bonds in the same plane. There is extension of C=O(1.215 Å) and S-H(1.356 Å) by 0.018 and 0.012 Å, respectively and shortening of C-S(1.760 Å) by 0.031 Å compared to isolated TFA.

Bicomplex **4** forms six membered complex involving *trans*-TFA(thiol) and H(2)O(3)H(5) containing three hydrogen bonds. Bicomplex **5** has similar structure and lies just 0.13 kcal/mol above Bicomplex 4. They differs in H-bond lengths, position as well as alignment of water molecules. Bicomplexes **6** and **8** contains two water molecules lying on the same side of TFA but in different planes. In Bicomplex 6, water molecules lie below the plane of *trans*-TFA(thiol) while in Bicomplex 8 they lie above the plane though the difference in bond lengths is negligible. The complexation with water-molecules leads to C-S bond elongation in these Bicomplexes. In Bicomplex **7**, the two water molecules lie on the opposite side of *trans*-TFA(thiol) forming three H-bonds with H(2)O(3)H(5) acting as only H-bond acceptor. For simplicity, the structural details of Bicomplexes 9 and 10 are not discussed.

In the case of complexes of TFAt(thiol) with two-water molecules, reduction in S-H stretching frequency and elevation in S-H stretching intensity is found to be maximum in Bicomplex 0 as evident in Table S4. There is slight increase in C-H stretching frequency in all the complexes with major change in Bicomplex 7. A red shift was observed for C=O strectching frequency except for Bicomplexes 6 and 8. Besides these, significant reduction of C=O strectching frequency was found in Bicomplex 3 as O atom of C=O bond forms two hydrogen bonds with water molecules resulting in a frequency shift of 72.38 cm^{-1} from that in isolated TFA. All the frequency shifts observed are consitent with changes observed in bond distances discussed above. For bicomplexes of TFA(thiol), the dissociation of water-complexes is more dominating, contrary to that observed for the Bicomplexes of TFA(thione), as indicated by Gibbs free-energy change relative to the isolated speices, at various temperatures in Table 8. The dissocation becomes even more dominating at higher temperatures.

4. Conclusion

In conclusion, the isomerisation (tautomeric and geometric) pathways of TFA were explored by the GRRM method, and a new pathway for *cis-trans* conversion of TFA(thiol) was traced though requiring high activation energy but equally feasible as already known pathway in the literature. Further, although the complexes of TFA with single water molecule are well studied, the mechanism for water migration and isomerisation in the water-complexes of TFA has been presented here for the first time except for one tautomeric pathway. From the present study, it is evident that the catalytic effect of water influences not only the tautomeric routes, but also *cis-trans* interconversions by stabilization of reactants and/or transition states. Though the *trans* form of isolated TFA(thiol) is known to be dominating species among the isomeric forms of TFA as also observed in the present study, however, *cis* form of TFA(thiol) in the gas-phase complexes of TFA with single-water molecule is found to be equally feasible as the *trans* form. Besides this, it is also observed that the migration of water molecule around TFA in gas phase may ultimately leads to catalytic isomerisation. Moreover, twenty-two complexes of *trans*-TFA with two-water molecules were explored for the first time to understand the hydrogen bonding interactions involved in these extensively hydrogen-bonded species.

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Notes

The authors declare no competing financial interests.

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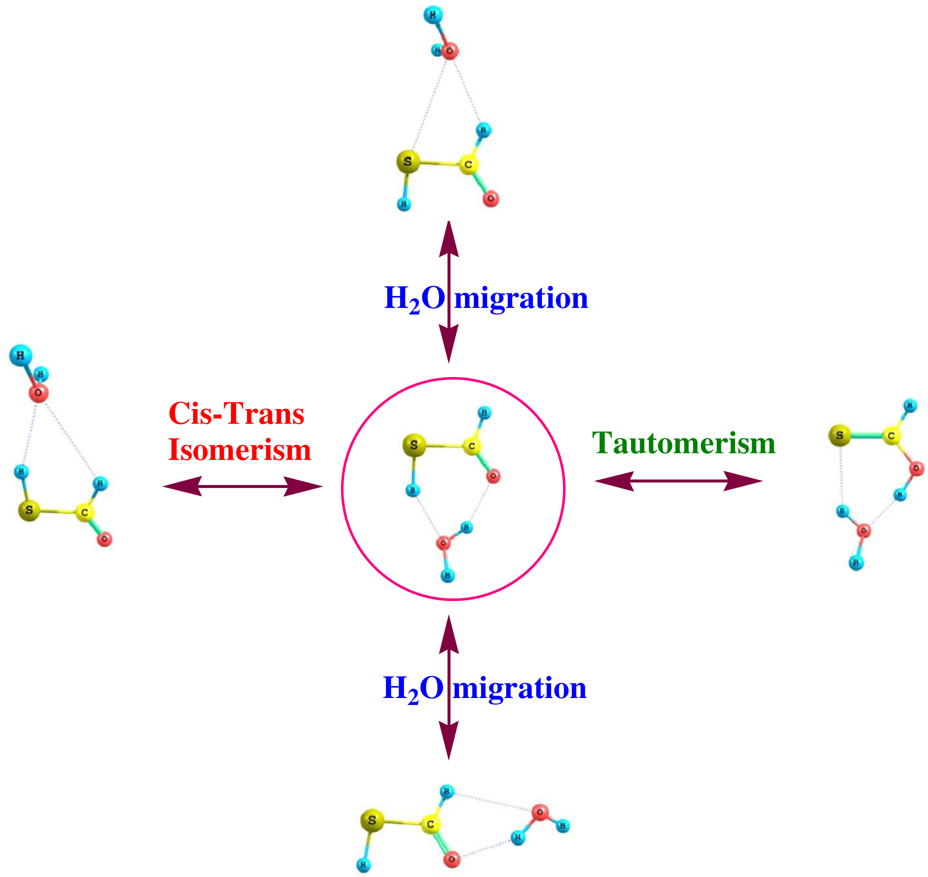

Supporting information

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

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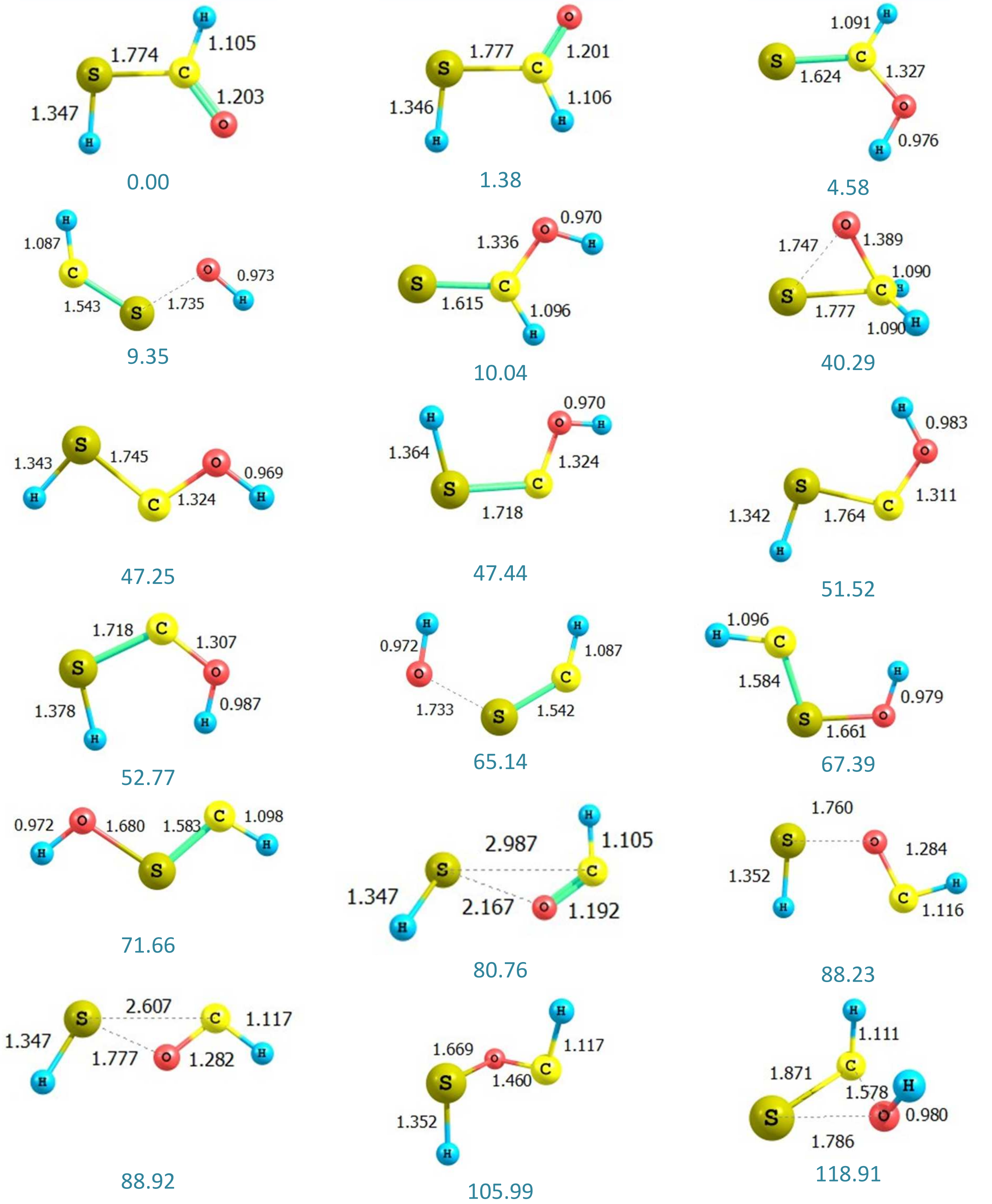

Figure 1. The geometries (with bond length in Å) of isomers of TFA and the values in parenthesis refer to *ZPE* corrected relative energies (in kcal/mol) with respect to *trans*-TFA(thiol) obtained at DFT/PBE1PBE/6-31+G(d) level.

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 TFA Acceptor H_2O	$E^{(2)}$	Donor H_2O Acceptor TFA	$E^{(2)}$	Donor H_2O Acceptor H_2O	$E^{(2)}$
0	$n_{S1(1)} \rightarrow \sigma^*_{O2\text{-}H3}$	1.63	$n_{O3(1)} \rightarrow \sigma^*_{O1\text{-}H2}$	0.70	$n_{O2(1)} \rightarrow \sigma^*_{O3\text{-}H6}$	0.31
	$n_{S1(2)} \rightarrow \sigma^*_{O2\text{-}H3}$	10.67	$n_{O3(2)} \rightarrow \sigma^*_{O1\text{-}H2}$	31.50	$n_{O2(2)} \rightarrow \sigma^*_{O3\text{-}H6}$	17.79
1	$n_{S1(1)} \rightarrow \sigma^*_{O3\text{-}H5}$	1.59	$n_{O2(1)} \rightarrow \sigma^*_{O1\text{-}H2}$	0.63	$n_{O3(1)} \rightarrow \sigma^*_{O2\text{-}H4}$	0.26
	$n_{S1(2)} \rightarrow \sigma^*_{O3\text{-}H5}$	10.38	$n_{O2(2)} \rightarrow \sigma^*_{O1\text{-}H2}$	30.67	$n_{O3(2)} \rightarrow \sigma^*_{O2\text{-}H4}$	15.95
2	$n_{S1(1)} \rightarrow \sigma^*_{O3\text{-}H5}$	0.22	$n_{O3(1)} \rightarrow \sigma^*_{O1\text{-}H2}$	0.80	$n_{O2(1)} \rightarrow \sigma^*_{O3\text{-}H6}$	0.11
	$n_{S1(2)} \rightarrow \sigma^*_{O3\text{-}H5}$	3.16	$n_{O3(2)} \rightarrow \sigma^*_{O1\text{-}H2}$	31.53	$n_{O2(2)} \rightarrow \sigma^*_{O3\text{-}H6}$	9.99
3	$n_{S1(1)} \rightarrow \sigma^*_{O3\text{-}H5}$	0.26	$n_{O3(1)} \rightarrow \sigma^*_{O1\text{-}H2}$	0.81	$n_{O2(1)} \rightarrow \sigma^*_{O3\text{-}H4}$	0.08
	$n_{S1(2)} \rightarrow \sigma^*_{O3\text{-}H5}$	3.57	$n_{O3(2)} \rightarrow \sigma^*_{O1\text{-}H2}$	31.54	$n_{O2(2)} \rightarrow \sigma^*_{O3\text{-}H4}$	9.44
4	$n_{S1(1)} \rightarrow \sigma^*_{O2\text{-}H3}$	0.41	$n_{O2(1)} \rightarrow \sigma^*_{O1\text{-}H2}$	0.58		
	$n_{S1(2)} \rightarrow \sigma^*_{O2\text{-}H3}$	4.62	$n_{O2(2)} \rightarrow \sigma^*_{O1\text{-}H2}$	23.48		
	$n_{S1(1)} \rightarrow \sigma^*_{O3\text{-}H5}$	0.13	$n_{O3(1)} \rightarrow \sigma^*_{C1\text{-}H1}$	0.07		
	$n_{S1(2)} \rightarrow \sigma^*_{O3\text{-}H5}$	3.69	$n_{O3(2)} \rightarrow \sigma^*_{C1\text{-}H1}$	0.46		
5	$n_{S1(1)} \rightarrow \sigma^*_{O3\text{-}H5}$	0.66	$n_{O3(1)} \rightarrow \sigma^*_{O1\text{-}H2}$	0.84	$n_{O3(1)} \rightarrow \sigma^*_{O2\text{-}H3}$	4.19
	$n_{S1(2)} \rightarrow \sigma^*_{O3\text{-}H5}$	7.94	$n_{O3(2)} \rightarrow \sigma^*_{O1\text{-}H2}$	18.62	$n_{O3(2)} \rightarrow \sigma^*_{O2\text{-}H3}$	0.64
6	$n_{S1(1)} \rightarrow \sigma^*_{O2\text{-}H3}$	0.46	$n_{O3(2)} \rightarrow \sigma^*_{C1\text{-}H1}$	0.12		
	$n_{S1(2)} \rightarrow \sigma^*_{O2\text{-}H3}$	5.86	$n_{O2(1)} \rightarrow \sigma^*_{O1\text{-}H2}$	0.62		
	$n_{O1(1)} \rightarrow \sigma^*_{O3\text{-}H5}$	1.90	$n_{O2(2)} \rightarrow \sigma^*_{O1\text{-}H2}$	24.92		
7	$n_{S1(1)} \rightarrow \sigma^*_{O3\text{-}H6}$	0.44	$n_{O2(1)} \rightarrow \sigma^*_{C1\text{-}H1}$	0.20	$n_{O3(1)} \rightarrow \sigma^*_{O2\text{-}H3}$	0.16
	$n_{S1(2)} \rightarrow \sigma^*_{O3\text{-}H6}$	7.51	$n_{O2(2)} \rightarrow \sigma^*_{C1\text{-}H1}$	4.09	$n_{O3(2)} \rightarrow \sigma^*_{O2\text{-}H3}$	10.50
8	$n_{O1(1)} \rightarrow \sigma^*_{O3\text{-}H6}$	2.94	$n_{O2(1)} \rightarrow \sigma^*_{C1\text{-}H1}$	0.19	$n_{O3(1)} \rightarrow \sigma^*_{O2\text{-}H3}$	0.12
			$n_{O2(2)} \rightarrow \sigma^*_{C1\text{-}H1}$	3.18	$n_{O3(2)} \rightarrow \sigma^*_{O2\text{-}H3}$	8.84
9	$n_{S1(1)} \rightarrow \sigma^*_{O3\text{-}H5}$	0.27	$n_{O3(1)} \rightarrow \sigma^*_{C1\text{-}H1}$	0.12	$n_{O3(1)} \rightarrow \sigma^*_{O2\text{-}H3}$	0.14
	$n_{S1(2)} \rightarrow \sigma^*_{O3\text{-}H5}$	6.23			$n_{O3(2)} \rightarrow \sigma^*_{O2\text{-}H3}$	8.18
10	$n_{S1(1)} \rightarrow \sigma^*_{O3\text{-}H5}$	0.09	$n_{O2(1)} \rightarrow \sigma^*_{C1\text{-}H1}$	1.71		
	$n_{S1(2)} \rightarrow \sigma^*_{O3\text{-}H5}$	2.29	$n_{O2(2)} \rightarrow \sigma^*_{C1\text{-}H1}$	0.27	$n_{O2(2)} \rightarrow \sigma^*_{O3\text{-}H6}$	5.07

where n denotes the donation of lone pair from lewis structure to σ^* 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 TFA → Acceptor H_2O	$E^{(2)}$	Donor H_2O → Acceptor TFA	$E^{(2)}$	Donor H_2O → Acceptor H_2O	$E^{(2)}$
0	$n_{O1(1)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	5.18	$n_{O3(1)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	0.60	$n_{O2(1)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	0.20
	$n_{O1(2)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	3.86	$n_{O3(2)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	13.45	$n_{O2(2)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	13.91
1	$n_{O1(1)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	5.10	$n_{O3(1)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	0.58	$n_{O2(1)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	0.15
	$n_{O1(2)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	3.90	$n_{O3(2)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	13.22	$n_{O2(2)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	12.14
2	$n_{O1(1)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	1.67	$n_{O3(1)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	0.20	$n_{O2(1)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	0.14
	$n_{O1(2)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	7.05	$n_{O3(2)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	3.23	$n_{O2(2)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	10.41
3	$n_{O1(1)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	1.75	$n_{O2(1)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	0.30		
	$n_{O1(2)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	3.47	$n_{O2(2)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	7.08		
	$n_{O1(1)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	0.57	$n_{O3(2)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	0.10		
	$n_{O1(2)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	4.22				
4	$n_{O1(1)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	2.82	$n_{O3(1)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	1.70	$n_{O3(1)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	2.34
	$n_{O1(2)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	5.40	$n_{O3(2)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	2.24	$n_{O3(2)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	5.54
5	$n_{O1(1)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	1.03	$n_{O2(1)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	0.47	$n_{O3(1)} \rightarrow \sigma^{*}_{O2\text{-}H6}$	0.09
	$n_{O1(2)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	2.72	$n_{O2(2)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	10.54	$n_{O3(2)} \rightarrow \sigma^{*}_{O2\text{-}H6}$	7.53
6	$n_{S1(1)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	0.42	$n_{O2(1)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	0.42	$n_{O3(1)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	0.14
	$n_{S1(2)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	2.34	$n_{O2(2)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	1.94	$n_{O3(2)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	8.69
			$n_{O2(2)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	0.18		
7	$n_{O1(1)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	2.25	$n_{O2(1)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	0.21		
	$n_{O1(2)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	4.67	$n_{O2(2)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	5.25		
			$n_{O3(1)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	0.45		
			$n_{O3(2)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	1.26		
8	$n_{S1(1)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	0.46	$n_{O3(1)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	0.19	$n_{O2(1)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	0.14
	$n_{S1(2)} \rightarrow \sigma^{*}_{O2\text{-}H3}$	2.39	$n_{O3(2)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	2.65	$n_{O2(2)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	8.79
					$n_{O2(2)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	0.05
9	$n_{O1(1)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	1.25	$n_{O2(1)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	2.04	$n_{O2(1)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	0.99
	$n_{O1(2)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	1.04	$n_{O2(2)} \rightarrow \sigma^{*}_{S1\text{-}H4}$	1.78	$n_{O2(2)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	3.36
10	$n_{O1(1)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	0.33	$n_{O2(1)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	1.24		
	$n_{O1(2)} \rightarrow \sigma^{*}_{O3\text{-}H5}$	2.42	$n_{O2(2)} \rightarrow \sigma^{*}_{C1\text{-}H1}$	0.22	$n_{O2(2)} \rightarrow \sigma^{*}_{O3\text{-}H2}$	4.90

where *n* denotes the donation of lone pair from lewis structure to σ^{*} antibond of non-lewis structure

Table S3. Vibrational frequencies (in cm^{-1}) corresponding to three highest intensities (in 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	ν(O-H) in TFA
	3535.33	858.119	ν_{asym}(O-H) in water
	3415.59	635.748	ν(O-H) in TFA.
1	3034.13	1239.06	ν (O-H) in TFA
	3542.58	850.724	ν_{asym}(O-H) in water
	3443.89	576.170	ν_{asym}(O-H) in water
2	3010.49	1236.92	ν_{sym}(O-H) and ν_{sym}(C-H) in TFA
	3719.63	506.078	ν_{asym}(O-H) in H(5)O(3)H(6)
	3623.28	331.001	ν_{sym}(O-H) in H(5)O(3)H(6)
3	3001.98	1221.75	ν(O-H) in TFA
	3713.11	548.120	ν_{asym}(O-H) in H(5)O(3)H(6)
	3629.95	277.438	ν_{sym}(O-H) in H(5)O(3)H(6)
4	3213.17	758.517	ν (O-H) and ν (C-H) in TFA
	3642.8	341.475	ν_{asym}(O-H) in H(3)O(2)H(4)
	1308.23	308.591	ν (C=O) with ϖ (H1) and ϖ(H2) in TFA
5	3541.76	682.442	ν (O-H) in TFA and ν_{asym}(O-H) in water
	3309.14	500.876	ν (O-H) in TFA and ν(O-H) in H(5)O(3)H(6)
	1291.82	297.652	ν (C=O) with ϖ (H1) and ϖ(H2) in TFA
6	3174.00	598.164	ν (O-H) and ν (C-H) in TFA
	1287.13	378.141	ν (C=O) with ϖ (H1) and ϖ (H2) in TFA
	3604.57	376.367	ν_{sym}(O-H) in H(3)O(2)H(4)
7	3630.95	573.839	ν_{asym} in water
	1249.74	419.118	ν (C=O) with ϖ (H1) and ϖ (H2) in TFA
	3585.09	360.591	ν_{asym} in water
8	1209.27	442.799	ν (C=O) in TFA
	3641.32	324.122	ν_{asym} in H(3)O(2)H(4)
	3747.79	274.437	ν_{asym} in H(5)O(3)H(6)
9	3643.31	651.648	ν_{asym} in H(5)O(3)H(6)
	1236.05	329.964	ν (C=O) with ϖ (H1) and ϖ (H2) in TFA
	3685.61	231.755	ν_{asym} in H(3)O(2)H(4)
10	1236.16	384.954	ν (C=O) with ϖ (H1) and ϖ (H2) in TFA
	220.363	217.887	ϖ(O-H) in Water
	1467.85	174.211	ϖ (H1) and ϖ (H2) and ν (C=O) and (C=S) in TFA

* ν_{sym} for symmetric stretch, ν_{asym} for asymmetric stretch, ϖ for wagging.

Table S4. Same as Table S3, but for bicomplexes of *trans*-TFA(thiol) with two-water molecules depicted in Figure 12.

Bicomplex	Frequency	IR intensity	Assignment
0	3627.66	633.309	v_{asym}(O-H) in H(3)O(2)H(6)
	2390.93	576.619	v(S-H) in TFA
	3508.69	441.723	v_{asym}(O-H) in H(2)O(3)H(5)
1	3630.05	645.466	v_{asym}(O-H) in H(3)O(2)H(6)
	2398.17	563.623	v(S-H) in TFA
	3536.30	384.986	v_{asym}(O-H) in H(2)O(3)H(5)
2	3634.54	688.054	v_{asym}(O-H) in H(3)O(2)H(6)
	1711.27	382.886	v (C=O) in TFA and δ(OH) in water
	3581.44	342.385	v_{asym}(O-H) in H(2)O(3)H(5)
3	3726.81	234.727	v_{asym}(O-H) in H(2)O(3)H(5)
	1695.05	233.241	v (C=O) and ϖ (H4) in TFA and δ(OH) in water
	3693.89	230.970	v_{asym}(O-H) in H(3)O(2)H(6)
4	3618.25	448.402	v_{asym}(O-H) in H(2)O(3)H(5)
	1722.19	335.817	v (C=O) in TFA and δ(OH) in water
	3696.90	289.200	v_{asym}(O-H) in H(3)O(2)H(6)
5	3769.96	475.728	v_{asym}(O-H) in H(3)O(2)H(6)
	2448.87	411.217	v_{asym}(O-H) in H(2)O(3)H(5)
	1725.28	304.288	v (C=O) in TFA and δ(OH) in water
6	1771.83	402.874	v (C=O) in TFA
	3644.60	302.831	v_{asym}(O-H) in H(3)O(2)H(6)
	3740.15	209.222	v_{asym}(O-H) in H(2)O(3)H(5)
7	1716.50	330.606	v (C=O) TFA and δ(OH) in H(3)O(2)H(6)
	3658.82	258.819	v_{asym}(O-H) in in H(3)O(2)H(6)
	135.428	210.496	ϖ(O-H) in Water and ϖ in TFA
8	1774.26	400.225	v (C=O) in TFA
	3641.90	308.003	v_{asym}(O-H) in H(3)O(2)H(6)
9	1750.65	350.256	v (C=O) in TFA and δ(OH) in H(2)O(3)H(5)
	216.735	223.429	ϖ(O-H) in Water
	564.120	178.369	ϖ (H4) in TFA and ϖ(O-H) in Water
10	1744.62	335.601	v (C=O) in TFA and δ(OH) in H(2)O(3)H(5)
	229.967	245.223	ϖ(O-H) in Water
	1686.70	193.296	δ(OH) in water

* v_{sym} for symmetric stretch, v_{asym} for asymmetric stretch, ϖ for wagging, δ 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 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 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 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^{-1}

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^{-1}

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^{-1}

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_2O (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_2O (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_2O (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_2O (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_2O (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_2O (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_2O (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_2O (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_2O (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_2O (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_2O (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_2O (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^{-1}

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^{-1}

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^{-1}

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 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 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^{-1}

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^{-1}

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 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 a.u.

ZPE= 0.0543 a.u.

One imaginary frequency = -41.6435 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 a.u.

ZPE= 0.0540 a.u.

One imaginary frequency = -83.9158 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

BSSE corrected energy = -589.2235 a.u.

ZPE= 0.0534 a.u.

One imaginary frequency = -429.6389 cm^{-1}

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

BSSE corrected energy = -589.2270 a.u.

ZPE= 0.0532 a.u.

One imaginary frequency = -681.6726 cm^{-1}

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^{-1}

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^{-1}

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^{-1}

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^{-1}

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^{-1}

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^{-1}

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