BLUE-SHIFTING HYDROGEN BONDS AND SECONDARY INTERACTIONS IN THE $C_3H_6 \cdots HCF_3$, $C_2H_4O \cdots HCF_3$ AND $C_2H_4S \cdots HCF_3$ CYCLIC COMPLEXES

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ABSTRACT

In this article, a theoretical study of molecular properties of small cyclic systems is presented. Through the calculations performed at the B3LYP/6-311++G(d,p) level of theory, the optimized geometries of the $C_3H_6 \cdots HCF_3$, $C_2H_4O \cdots HCF_3$ and $C_2H_4S \cdots HCF_3$ hydrogen-bonded complexes were determined. By analyzing the structural parameters, it was observed a contraction of the C–H bond length of the fluoroform (HCF_3). As such, the examination of the harmonic infrared spectrum accused the existence of a blue-shift effect in this bond, once its stretch frequency is displaced to upward values accompanied by a significant diminishing on the absorption intensity. In the purpose to comprehend this vibrational phenomenon, topological parameters computed at the light of the Quantum Theory of Atoms in Molecules (QTAIM) were also used. An interesting aspect is the non-linearity deviation on the hydrogen bonds ($O \cdots H$) and ($S \cdots H$) due to the formation of a secondary interaction ($H^a \cdots F^a$) between the fluoride (F^a) of fluoroform and the axial hydrogen atoms (H^a) of the heterocyclic structures.

Keywords: Blue-shifting; homocyclic, heterocyclic, complexes, B3LYP, QTAIM.

1. INTRODUCTION

In all fields of chemistry, physics and biology, it is well established that several molecular systems are formed by non-covalent interactions, in special, the hydrogen bonds¹. In fact, the importance of the hydrogen bonds is due to a large number of phenomena originated from the contact between a rich charge density and a proton donor², such as those routinely observed in organic reaction mechanisms³, functionality of agonist biomolecules⁴, as well as in projection and development of pharmacologic action drugs⁵.

In physical-chemistry, the hydrogen bond is analyzed in conformity with the electrostatic potential, polarizability effect, spin-exchange and repulsion terms, as well as the charge transfer⁶. Well, the contribution of these parameters for quantifying the total energy is quite relative⁷, although is well known that often the electrostatic potential is the most important term⁸. However, by means of an *ab initio* study of structural and spectroscopic parameters of clusters formed by hydrogen cyanide⁹, King and Weinhold informed how much the charge transfer was decisive for determination of total energy and molecular stabilization of these systems. In other words, the charge transfer was considered the dominant term, more than electrostatic or any other one. In hydrogen-bonded complexes, it is well established that the charge transfer provokes changes on their proton donors ($H-X = Cl, F$ and CN groups)¹⁰⁻¹¹, where normally are verified drastic enhancements on their bond lengths¹²⁻¹³.

In spectroscopy, the deformation scenery in the $H-X$ bond length can be observed when the stretch frequencies are shifted to downward values followed of an intense increase on the absorption intensity¹⁴, phenomenon known as red-shift effect. In heterocyclic hydrogen-bonded complexes, such as $C_2H_4O \cdots H-X$ with $X = F, Cl$ and CN ¹⁵⁻¹⁸, besides the formation of the primary hydrogen bond ($O \cdots HX$), these systems reveal other interesting structural parameter, the non-linearity on the ($O \cdots HX$) hydrogen bond¹⁹. Such distortion occurs due to a secondary interaction between the halogen or cyanide groups of monoprotic acids and the axial hydrogen atoms of the heterocyclic structure. This is not analyzed uniquely in theoretical viewpoint, but experimental assays also have demonstrated the existence of secondary interactions in heterocyclic complexes²⁰⁻²¹.

Nevertheless, some time ago Hobza *et al*²² have studied a new intermolecular interaction type, so-called anti-hydrogen bonds because instead of a red-shift, a blue-shift on the proton donor molecule is observed²³. Thus, in opposition to the traditional aspects of the hydrogen-bonded systems wherein the red-shift effect is one of the most important characteristics, in regards to the hydrogen-bonded complexes with blue-shift effects, a strengthening of the proton donor bond is considered the investigation cornerstone for these systems²⁴, and thereby their stretch frequencies are shifted to upward values²⁵⁻²⁸. About the complex $C_2H_4O \cdots HCF_3$, the C–H bond of the fluoroform (HCF_3) was characterized theoretically by sophisticated *ab initio* calculations²⁹. In such case, the results revealed the existence of the blue-shift on the C–H oscillator. Properly, it is interesting to evaluate whether there is the possibility

to form the non-linearity deviation³⁰ in the hydrogen bonds ($O \cdots H$) and ($S \cdots H$) of the respective heterocyclic complexes $C_2H_4O \cdots HCF_3$ and $C_2H_4S \cdots HCF_3$, but also in regards to the homocyclic complex $C_3H_6 \cdots HCF_3$. By this context, it is expected a direct relationship among the hydrogen bond strength, blue-shift effect and the non-linearity deviation of these systems.

There are theoretical methods³¹ whose focus is the investigation of electronic structure and related phenomena³²⁻³³. Using *ab initio*³⁴⁻³⁵ or Density Functional Theory (DFT) calculations³⁶⁻³⁷, semiempirical methods³⁸, molecular dynamics simulations³⁹, or even discrete analysis of the solvent effect⁴⁰, the nature of the chemical bond and hydrogen bonds, in particular, is still an essentially unresolved question⁴¹. The specialized literature reports a large number of studies about hydrogen-bonded complexes where is proved the DFT efficiency⁴²⁻⁴³ through the application of exchange-correlation functionals⁴⁴⁻⁴⁶. Very recently, Sherrill and co-workers⁴⁷ performed a robust test of theoretical methods, of which DFT and Post-Hartree Fock approaches were included in this study, although previously all of them were considered able to describe the structure of hydrogen-bonded complexes, and in the end, fails and success about these methods were reported. Before this occurrence, Xu *et al*⁴⁸ also investigated the efficiency of density functionals on evaluating hydrogen bonds, wherein it was observed that B3LYP dispose results with small errors for hydrogen bond energies. It is by this sense and other investigations⁴⁹⁻⁵² that B3LYP was the hybrid functional chosen to be used in this work.

It is not in recent years that the charge transfer has been viewed as one of the most important parameters in hydrogen bond studies⁵³⁻⁵⁵. The interaction between the HOMO-LUMO molecular orbitals, which represent the proton acceptor and proton donor respectively, bring a qualitative electronic idea by which the hydrogen bond is formed. Albeit there are many methods routinely used in charge transfer examinations⁵⁶, the ChelpG algorithm was chosen because it has been applied successfully in many intermolecular investigation types⁵⁷. In addition, by taking into the account the referential work of Koch and Popelier⁵, intermolecular and/or intramolecular hydrogen bonds can be well interpreted by means of the topological parameters derived from Bader's Quantum Theory of Atoms in Molecules (QTAIM)⁵⁸. Thus, the QTAIM calculations also will be applied in this work with the purpose to characterize the hydrogen bonds ($O \cdots H$), ($S \cdots H$) and ($p-\pi \cdots H$), and if possible, the secondary interactions.

2. Computational details

The optimized geometries of the $C_3H_6 \cdots HCF_3$, $C_2H_4O \cdots HCF_3$ and $C_2H_4S \cdots HCF_3$ cyclic complexes were obtained at the B3LYP/6-311++G(d,p) theoretical level, where all calculations were performed by the GAUSSIAN 98W program⁵⁹, including also the ChelpG charges computations⁶⁰. The values of the hydrogen bond energies were determined in according to the supermolecule approach², as well as the corrections were performed by means of the Zero Point Energy (ZPE)⁶¹ and Basis Sets Superposition Error (BSSE)⁶² calculations. The QTAIM calculations were processed using the GAUSSIAN

98W and AIM 2000 1.0 programs⁶³.

3. RESULTS AND DISCUSSION

3.1 Geometry

The optimized geometries of the $\text{C}_3\text{H}_6\cdots\text{HCF}_3$ (a), $\text{C}_2\text{H}_4\text{O}\cdots\text{HCF}_3$ (b) and $\text{C}_2\text{H}_4\text{S}\cdots\text{HCF}_3$ (c) complexes are presented in Figure 1. The results of the structural analysis of these complexes are listed in Table 1. Initially, the characterization of these systems as blue-shifting hydrogen-bonded complexes concerns to the reduction of the bond length of $r(\text{C}-\text{H})$, whose calculated values are -0.0007 Å, -0.0001 Å and -0.0014 Å for (a), (b) and (c) complexes, respectively. In terms of intermolecular distances, the (b) complex presented the shortest hydrogen bond ($\text{O}\cdots\text{H}$). Although is well-known that intermolecular heterocyclic systems are strongly bound than homocyclic ones, the results reveals that the distance value of ($\text{p}-\pi\cdots\text{H}$) in $\text{C}_3\text{H}_6\cdots\text{HCF}_3$ (a) is shorter in comparison with ($\text{S}\cdots\text{H}$) of $\text{C}_2\text{H}_4\text{S}\cdots\text{HCF}_3$ (c).

Fig. 1. Optimized geometries of the $\text{C}_3\text{H}_6\cdots\text{HCF}_3$ (a), $\text{C}_2\text{H}_4\text{O}\cdots\text{HCF}_3$ (b) and $\text{C}_2\text{H}_4\text{S}\cdots\text{HCF}_3$ (c) blue-shifting hydrogen complexes using B3LYP/6-311++G(d,p) calculations.

Table 1. Structural parameters of the $\text{C}_3\text{H}_6\cdots\text{HCF}_3$ (a), $\text{C}_2\text{H}_4\text{O}\cdots\text{HCF}_3$ (b) and $\text{C}_2\text{H}_4\text{S}\cdots\text{HCF}_3$ (c) blue-shifting hydrogen complexes using B3LYP/6-311++G(d,p) calculations.

Parameters	Blue-shifting hydrogen complexes		
	(a)	(b)	(c)
$R(\text{p}-\pi\cdots\text{H})$	2.6377	—	—
$R(\text{O}\cdots\text{H})$	—	2.163	—
$R(\text{S}\cdots\text{H})$	—	—	3.0239
$R(\text{H}^a\cdots\text{F}^b)$	—	4.441	2.7044
$r(\text{C}-\text{H})$	1.0892	1.0895	1.0885
$\Delta r(\text{C}-\text{H})$	-0.0007	-0.0001	-0.0014
θ	—	53.0	56.0

* Values of R and r are given in Å;

* Values of θ are given in degrees;

* Value of the $\text{C}-\text{H}$ bond length in HCF_3 monomer is 1.0899 Å.

About the secondary interactions, namely as ($\text{H}^a\cdots\text{F}^b$), the value of 4.441 Å in (b) is very long, whereas in (c) the result of 2.7044 Å is shorter. By taking into account the fixed van der Waals radii whose values for hydrogen, oxygen and sulphur are respectively 1.20 Å, 1.52 Å and 1.80 Å⁶⁴, the secondary interaction ($\text{H}^a\cdots\text{F}^b$) is possible to be formed only in (c). In (a), indeed, there is no structural condition to exist an interaction between the fluorine atoms of the fluoroform and the axial hydrogen atoms of the cyclopropane. Due to this, a natural consequence in the hydrogen bonds ($\text{O}\cdots\text{H}$) and ($\text{S}\cdots\text{H}$) is the arising of a linear deviation (θ) in their structures, whose values for (b) and (c) complexes are 53.0° and 56.0°, respectively. Note that, the θ value in (c) complex is larger than in (b), once the secondary interaction is more evident in (c), and thereby the linearity deviation is greater.

3.2 Analysis of the infrared harmonic spectrum

The vibrational harmonic modes (a), (b) and (c) complexes were also analyzed through the application of the B3LYP/6-311++G(d,p) calculations. In Table 2 are listed the values of hydrogen bond stretch frequencies (ν) and their absorption intensities (I). It can be seen that the stretch frequency of 46.4 cm^{-1} of the ($\text{p}-\pi\cdots\text{H}$) hydrogen bond is the weakest intermolecular mode, as well as the absorption of 0.27 km mol^{-1} is the lowest intensity in comparison to those calculated for the complexes (b) and (c). For these last ones, mainly in (b), besides its $\nu(\text{O}\cdots\text{H})$ of 94.7 cm^{-1} be the strongest, its intensity of 5.2 km mol^{-1} is the highest among the three complexes studied in this current work. However, the vibrational mode of the secondary interaction in (c) was also identified through the B3LYP/6-311++G(d,p) level of theory, whose results of the stretch frequency and absorption intensities are 77.2 cm^{-1} and 4.8 km mol^{-1} , respectively. It is interesting to observe that the stretch frequency of the primary hydrogen bond $\nu(\text{S}\cdots\text{H})$ is weaker than the secondary interaction $\nu(\text{H}^a\cdots\text{F}^b)$, what lead us to an ambiguous question: the thiirane is proton donor or acceptor? Well, recent studies show that this question cannot be easily answered⁶⁵.

Table 2. Main vibrational modes of the $\text{C}_3\text{H}_6\cdots\text{HCF}_3$ (a), $\text{C}_2\text{H}_4\text{O}\cdots\text{HCF}_3$ (b) and $\text{C}_2\text{H}_4\text{S}\cdots\text{HCF}_3$ (c) blue-shifting hydrogen complexes using B3LYP/6-311++G(d,p) calculations.

Parameters	Blue-shifting hydrogen complexes		
	(a)	(b)	(c)
$\nu(\text{p}-\pi\cdots\text{H})$	46.4 (0.27)	—	—
$\nu(\text{O}\cdots\text{H})$	—	94.7 (5.2)	—
$\nu(\text{S}\cdots\text{H})$	—	—	59.9 (0.4)
$\nu(\text{H}^a\cdots\text{F}^b)$	—	—	77.2 (4.8)
$\nu(\text{C}-\text{H})$	3150	3156.9	3157.1
$I(\text{C}-\text{H})$	4.0	9.0	11.0
$\Delta\nu(\text{C}-\text{H})$	+7.8	+15.7	+15.9
$I(\text{C}-\text{H})_c/I(\text{C}-\text{H})_m$	0.12	0.17	0.33

* Values of ν and I are given in cm^{-1} and km mol^{-1} , respectively;

* Absorption intensities (I) of the $(\text{p}-\pi\cdots\text{H})$, $(\text{O}\cdots\text{H})$, $(\text{S}\cdots\text{H})$ and $(\text{H}^{\text{a}}\cdots\text{F}^{\text{b}})$ hydrogen bonds are gathered in parenthesis.

* Values of ν and I of the C–H bond of HCF_3 are 3141.2 cm^{-1} and 32.8 km mol^{-1} , respectively.

3.3 Intermolecular energies

Through the B3LYP/6-311++G(d,p) calculations, the Table 4 list the values of the intermolecular energies, either uncorrected (ΔE) or corrected (ΔE^{c}), as well as the values of ΔZPE and BSSE for the complexes (a), (b) and (c). Initially, it can be perceived that small BSSE amounts were computed, of course due to the application of the complete basis set 6-311++G(d,p). By taking into account the ΔE^{c} values, the (b) complex is twice more stable than (c). In conformity with recent studies about the formation of heterocyclic and homocyclic complexes⁶⁶, as expected the (a) complex presented the lower intermolecular energy, whose value is 2.23 kJ mol^{-1} .

Table 3. Electronic parameters of the $\text{C}_3\text{H}_6\cdots\text{HCF}_3$ (a), $\text{C}_2\text{H}_4\text{O}\cdots\text{HCF}_3$ (b) and $\text{C}_2\text{H}_4\text{S}\cdots\text{HCF}_3$ (c) blue-shifting hydrogen complexes using B3LYP/6-311++G(d,p) calculations.

Parameters	Blue-shifting hydrogen complexes		
	(a)	(b)	(c)
ΔE	4.62	16.24	10.81
ΔZPE	1.53	2.11	2.20
BSSE	0.86	1.74	2.12
ΔE^{c}	2.23	12.40	6.49
$\delta q(\text{C}-\text{C})$	+0.22	—	—
$\delta q\text{O}$	—	+0.052	—
$\delta q\text{S}$	—	—	+0.014
$\delta q\text{H}$	-0.16	-0.14	-0.05

* Values of ΔE , ΔZPE , BSSE and ΔE^{c} are given in kJ mol^{-1} ;

* Values of δq are given in electrostatic units (e.u.).

Not only in terms of intermolecular energies, but the importance of the transference of charge density between the HOMO-LUMO frontier molecular orbital pairs led the necessity for quantifying the charge transfer amount, namely as δq . As is well-known, even though the pseudo- π bond of the cyclopropane is the proton acceptor center, the result of +0.22 e.u. in (a) indicates a loss of charge in the C–C bond. Although is not cooperative⁶⁷, the value of -0.016 e.u. shows a receiving of charge in H. For (b) and (c) complexes, the diminutions of charge of +0.052 e.u. and +0.014 e.u. are evidences of the charge transfer from the n lone-electron pairs of oxygen and sulphur to the hydrogen atoms (HCF_3), in which, the charge transfer receiving is demonstrated by means of the results of -0.14 e.u. and -0.05 e.u. on (b) and (c) complexes, respectively.

3.4 QTAIM calculations

Created by Bader and co-workers⁶⁸, the QTAIM algorithm was developed to describe the electronic structure based on quantum mechanic formalisms⁶⁹. In an overview, QTAIM describes the molecular topology through the determination of Bond Critical Points (BCP) between two neighboring atoms⁷⁰. The BCP is a source to develop a numeric integration of the electronic density. Thereby, some observable topological parameters can be obtained, such as the electronic density (ρ) and Laplacian field ($\nabla^2\rho$)⁷¹. These parameters describes the molecular stability through the identification of charge density centers within the chemical bond and, so, the internuclear pathways are classified as shared (covalent) or closed-shell (hydrogen bonds) whether the electronic density is concentrated or depleted⁷², respectively. From this insight, the results of the topological analysis for the (a), (b) and (c) complexes are presented in Table 4. The QTAIM topological parameters have not only characterized the $(\text{p}-\pi\cdots\text{H})$, $(\text{O}\cdots\text{H})$ and $(\text{S}\cdots\text{H})$ hydrogen bonds with small ρ amounts and positive Laplacians $\nabla^2\rho$, but two important results deserve attention: identification and characterization of the secondary interaction in (c), but not in (b). Even though the values of the van der Waals radii permitted the existence of the secondary interaction ($\text{H}^{\text{a}}\cdots\text{F}^{\text{b}}$), BCP between the H^{a} and F^{b} atoms were localized only in (c), as can be seen in Figure 2. This result corroborates with vibrational

analysis wherein the intermolecular stretch frequency and absorption intensity for ($\text{H}^{\text{a}}\cdots\text{F}^{\text{b}}$) were characterized. Well, one direct conclusion about (c) is that the value of the hydrogen bond energy of 6.49 kJ mol^{-1} cannot be fully dedicated to $(\text{S}\cdots\text{H})$, but ΔE^{c} is also distributed partially in $(\text{H}^{\text{a}}\cdots\text{F}^{\text{b}})$ ⁷³.

Table 4. QTAIM topological parameters (ρ and $\nabla^2\rho$) of the $\text{C}_3\text{H}_6\cdots\text{HCF}_3$ (a), $\text{C}_2\text{H}_4\text{O}\cdots\text{HCF}_3$ (b) and $\text{C}_2\text{H}_4\text{S}\cdots\text{HCF}_3$ (c) blue-shifting hydrogen complexes at the B3LYP/6-311++G(d,p) theoretical level.

Parameters	Blue-shifting hydrogen complexes		
	(a)	(b)	(c)
$(\text{p}-\pi\cdots\text{H})$	0.006 (0.043)	—	—
$(\text{O}\cdots\text{H})$	—	0.016 (0.056)	—
$(\text{S}\cdots\text{H})$	—	—	0.006 (0.018)
$(\text{H}^{\text{a}}\cdots\text{F}^{\text{b}})$	—	—	0.004 (0.018)
C–H	0.302 (-1.12)	0.304 (-1.162)	0.303 (-1.147)

* All values are given in electronic units, e.u.;

* Values of $\nabla^2\rho$ are given in parenthesis;

* Values of ρ and $\nabla^2\rho$ for the HCF_3 monomer are 0.30 e.u. and -1.124 e.u., respectively.

Fig. 2. BCP in $\text{C}_3\text{H}_6\cdots\text{HCF}_3$ (a), $\text{C}_2\text{H}_4\text{O}\cdots\text{HCF}_3$ (b) and $\text{C}_2\text{H}_4\text{S}\cdots\text{HCF}_3$ (c) blue-shifting hydrogen complexes.

Regarding to the accumulation of electronic density and indirectly to the charge transfer, the high concentration of ρ indicates that C–H yields an shared interaction profile, as well as in comparison with HCF_3 monomer ($\rho = 0.30 \text{ e.u.}$), it can be seen an increase of ρ in all complexes (a), (b) and (c), whose values are 0.302 e.u., 0.304 e.u. and 0.303 e.u., respectively. Corroborating with vibrational spectrum, these amplifications of ρ are an explanation for blue-shift on C–H, i.e., the decreasing of C–H bond length and its stretch frequency displacing to downward values in infrared spectrum is explained through the increasing of electronic density, which occurs due to the charge transfer from

n lone pairs of oxygen and sulphur, as well as from the pseudo- π bond to the HCF_3 molecule.

4. CONCLUSIONS

In this work a theoretical study about vibrational blue-shift effect and formation of non-linearity in anti-hydrogen bonds of the $\text{C}_3\text{H}_6\cdots\text{HCF}_3$, $\text{C}_2\text{H}_4\text{O}\cdots\text{HCF}_3$ and $\text{C}_2\text{H}_4\text{S}\cdots\text{HCF}_3$ complexes was presented through the analysis of molecular parameters computed at the B3LYP/6-311++G(d,p) level of theory. To formulate an explanation about the blue-shift effect in the (C–H) of the fluoroform, theoretical approaches used in this work characterized the formation of the (p- π -H), (O $\cdots$ H) and (S $\cdots$ H) hydrogen bonds by means of structural, vibrational and electronic parameters, in which the QTAIM theory was essential because the topology of the (C–H) bond was deciphered. In other words, the higher charge density values computed indicate that (C–H) is strengthened after complexation. Moreover, the QTAIM topography revealed the existence of the secondary interaction formed between the fluoride ($\text{F}^\ominus$) of HCF_3 and axial hydrogen ($\text{H}^\oplus$) of the $\text{C}_2\text{H}_4\text{S}$ heteroring. This is very seriously, once that the hydrogen bond strength should be divided between (O $\cdots$ H) and ($\text{H}^\oplus\cdots\text{F}^\ominus$), what also implicates in a non-consensus about the capacity of the $\text{C}_2\text{H}_4\text{S}$ to function as donor or receptor of protons. On the other hand, no BCP was found between the $\text{H}^\oplus$ and $\text{F}^\ominus$ atoms of $\text{C}_2\text{H}_4\text{O}\cdots\text{HCF}_3$, indicating that (O $\cdots$ H) is the only hydrogen bond verified in this complex.

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Support information

Cartesian coordinates of the optimized geometries of the $C_3H_6 \cdots HCF_3$, $C_2H_2O \cdots HCF_3$ and $C_2H_4S \cdots HCF_3$ cyclic complexes using the B3LYP/6-311++G(d,p) theoretical level are placed below:

$C_3H_6 \cdots HCF_3$	$C_2H_2O \cdots HCF_3$	$C_2H_4S \cdots HCF_3$
C -3.524844		
0.002734 0.012404		
C -2.212729	O 1.768994 -0.018105	C 2.064820 0.373030
0.743784 -0.014619	0.446156	0.969240
C -2.231327	C 2.855321 0.737239	C 2.103382 0.960350
-0.770533 -0.018694	-0.111703	-0.386159
H -4.091062	C 2.887951 -0.729276	H 2.982630 0.338418
0.007159 0.935727	-0.104879	1.544192
H -4.132134	H 3.444830 1.290209	H 1.157581 0.482752
0.012641 -0.884400	0.613672	1.551659
H -1.899159	H 2.621733 1.264095	H 1.224122 1.481274
1.250218 0.890892	-1.032475	-0.746405
H -1.939138	H 3.501349 -1.248617	F -1.454575 0.959106
1.255551 -0.929968	0.625545	-0.749119
H -1.930918	H 2.678696 -1.274621	F -1.488917 0.033039
-1.289627 0.884137	-1.020748	1.223535
H -1.971083	F -1.757792 -0.973949	F -3.003597 -0.493063
-1.284058 -0.936998	-0.848646	-0.253748
H 0.444331	F -1.787412 1.179857	C -1.706471 -0.188699
-0.062718 -0.039636	-0.506791	-0.088279
C 1.531821	F -2.207582 -0.191093	H -1.058726 -0.984803
-0.010941 -0.005949	1.136241	-0.450922
F 2.077593	C -1.449177 -0.006168	S 1.962444 -0.875841
-1.058697 -0.649417	0.039051	-0.380856
F 1.967385	H -0.388056 -0.030338	H 3.048705 1.335990
-0.023876 1.266923	0.282708	-0.759648
F 1.970760 1.118192		
-0.590686		