

Protonation in Noble Gas Containing Molecular Systems: Observing Periodic Trends in CF_3Cl , CF_3Br , CH_3F , CH_3Cl

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Abstract: Protonation of molecular systems containing noble gases have been studied and compared for CF_3Cl , CF_3Br , CH_3F , and CH_3Cl with the aim of pointing out and defining the periodic trends existing in such molecules. This was achieved by calculating the proton affinities (PA) of the molecules using high level Ab-initio methods. This studies reveals that CF_3Cl and CF_3Br follows the same trend while CH_3F and CH_3Cl follows a different trend; For CF_3Cl and CF_3Br the most stable site of protonation differs from the site which corresponds to the experimentally determined PA value while for CH_3F and CH_3Cl , the most stable site of protonation is the same as the site which corresponds with the experimentally determined PA. These findings have uncovered the paucity of information available in literature on noble gas containing molecular systems and have provided a good rationale for exploiting the interstellar mediums (ISM).

1. INTRODUCTION

One of the most significant reaction in chemistry and biology is protonation reaction as it applies to many stoichiometric, catalytic and enzymatic processes, such a reaction is commonly depicted by the general equation $\text{A} + \text{H}^+ \rightarrow \text{AH}^+$ [1,2]. During a protonation reaction, a proton is added to the molecule, atom or ion leading to a change in charge and mass of the molecule, atom or ion and release of energy. The released energy is termed proton affinity [3]. The proton affinity of molecules can be determined using experimental approaches but this method poses great difficulties and prompted the advent of the advanced computational methods which have have stand the taste of time in modern chemistry [4,5,6,7,8]

The application of Proton affinity (PA) is of significance owing to its use in exploring the interstellar mediums (ISM) [9,10,11,12]. According to Crosswell [13], noble gases containing molecular systems do not form naturally on earth but in the interstellar medium due to their completely filled outer orbital and scientist are using their presence in the interstellar medium to probe the history of the universe. Owing to the high temperature and density in the ISM, noble gases tend to things ordinarily they would not undergo here on earth. The presence of noble gases and noble gas containing molecular species in the ISM has been reported by many scientists [15,16,17] the presence of hydrogen in abundance in the ISM contributes to the interactions and reactions leading to the formation of noble gas containing molecular systems such as the once under study.

Having verified the presence of noble gass containing molecular systems in the ISM, it is worthy of note that **F**, **Cl** and **Br** are all noble gases anad all in the same group, the question of whether there is or not a trend amongst CF_3Cl , CF_3Br , CH_3F , and CH_3Cl triggered the present study, thus the aim of this research is; (i) to observe and define the periodic trend in CF_3Cl , CF_3Br , CH_3F , and CH_3Cl (ii) To use the high level Ab-initio computational methods in calculating their proton affinities (iii)To bridge the gap between currently existing in literature on noble gas containing molecular systems.

2. METHODOLOGY

We employed the high level Gaussian 09 suit of programs in calculating the PAs of the molecular species as described by Frisch and his co-workers [18]. Six (6) Ab-initio computational methods which include: Gaussian 04 (G4) compound method, Hartree-Fock (HF) method, Becke, three-parameter, Lee-Yang-Parr (B3LYP) method, Coupled Cluster Single Double CCSD/6-311++G**, Moller-Plesset perturbation theory (MP2) at 6-311++G** basis set and Moller-Plesset perturbation theory (MP2) at cc-pVDZ basis set were used in carrying out the calculations

These methods were chosen based on experience from our previous studies [9, 10, 11, 12, 19] in which these methods were applied and accurate results were obtained. Also, the use of these methods is essential in monitoring how consistent or coherent the results are which will aid in determining the best method. The proton affinity (PA) is calculated as the difference in energy (Electronic Energy) between a neutral specie and its protonated analogue.

3. RESULTS AND DISCUSSION

The results obtained for the quantum chemical calculations are presented and discussed below;

1. CF_3Cl (Chlorotrifluoromethane)

There are 3 possible sites for protonation in this molecule, however, when a proton is attached to the central carbon atom, it optimizes to the one in which the proton is attached to any of the fluorine atoms, thus leaving us with only two protonated analogues instead of 3. Table 1a and 1b shows the PA of the protonated molecular species formed from CF_3Cl and their Sum of electronic and zero-point Energies respectively

Table1. PA values for CF_3Cl (Chlorotrifluoromethane)

Method	Proton attached to F atom		Proton attached to Cl atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	141.3358	-4.83584	133.7875	2.712471
B3LYP/6-311++G**	142.3298	-5.82982	133.7687	2.731296
MP2/6-311++G**	145.9286	-9.42858	132.4836	4.016436
MP2/cc-pVDZ	144.5412	-8.14116	138.6696	-2.16955
CCSD/6-311++G**	145.5339	-9.03388	140.3205	-3.82053
G4	144.8279	-8.32793	145.3619	-8.86194
Expt	136.5	NA	136.5	NA

The experimentally measured PA value for CF_3Cl corresponds to the protonated analogue in which the proton is attached to the Cl-atom. However, the protonated analogue in which the proton is attached to the F-atom is found to be the most stable as shown by the energy value from the different quantum chemical calculation methods in table 1b. The structures are shown in Fig. 1a-c

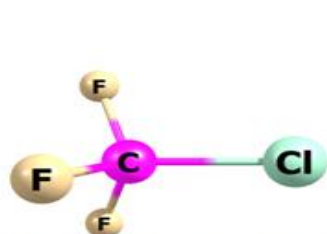


Fig. 1a Optimized geometry for CF_3Cl

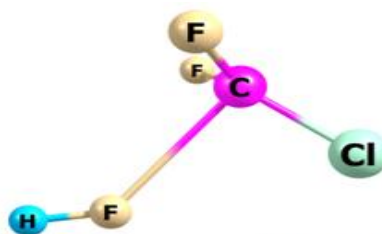


Fig. 1b Geometry for protonation at F



Fig. 1c Geometry for protonation at Cl

Table1b. Sum of electronic and zero-point Energies for protonated molecular species

Method	Energy (Hartree/Particle)*	
	F	Cl
HF/6-311++G**	-795.997	-795.985
B3LYP/6-311++G**	-798.176	-798.162
MP2/6-311++G**	-796.899	-796.878
MP2/cc-pVDZ	-796.739	-796.729
CCSD/ 6-311++G**	-796.758	-796.75
G4	-798.057	-798.058

2. CF_3Br (Bromine Trifluoromethane)

There are 3 possible sites (Br, C and any of the identical F-atoms) for protonation in this molecule, however, when a proton is attached to the central carbon atom, it optimizes to the one in which the proton is attached to any of the fluorine atoms, thus leaving us with only two protonated analogues instead of 3. The optimized geometries are as shown in Fig 2a-c

Table 2a. PA values for CF_3Br (Bromine Trifluoromethane)

Method	Proton attached to F atom		Proton attached to Br atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	144.8913	-6.29131	134.4163	4.183707
B3LYP/6-311++G**	146.3233	-7.72329	139.875	-1.275
MP2/6-311++G**	149.014	-10.414	137.9906	0.609413
MP2/cc-pVDZ	147.5877	-8.98772	142.7176	-4.11762
CCSD/6-311++G**	148.9651	-10.3651	144.1013	-5.50127
G4	147.7264	-9.1264	148.967	-10.367
Expt	138.6	NA	138.6	NA

In Table 2a, The MP2 method with the 6-311++G** basis set accurately predicts the PA value of CF_3Br with an error of 0.609 kcal/mol. The experimentally measured PA value for CF_3Br corresponds to the protonated analogue in which the proton is attached to the Br-atom. However, the protonated analogue in which the proton is attached to the F-atom is found to be the most stable as shown by the energy value from the different quantum chemical calculation methods presented in table 2b.

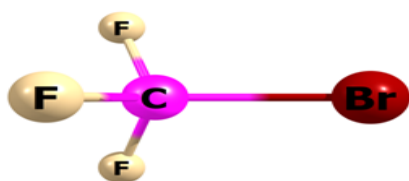


Fig. 2a Optimized geometry for CF_3Br

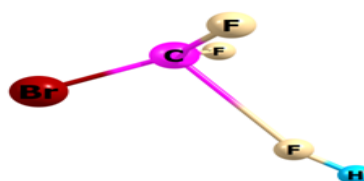


Fig. 2b Geometry for protonation at F

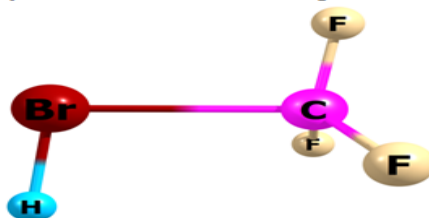


Fig. 2c Geometry for protonation at Br

Table 2b. Sum of electronic and zero-point Energies for protonated molecular species

Method	Energy (Hartree/Particle)*	
	F	Br
HF/6-311++G**	-2908.86	-2908.84
B3LYP/6-311++G**	-2912.1	-2912.09
MP2/6-311++G**	-2909.75	-2909.73
MP2/cc-pVDZ	-2909.61	-2909.61
CCSD/6-311++G**	-2909.63	-2909.62
G4	-2911.73	-2911.74

3. CH_3F (Fluoroform)

Table 3a. PA values for CH_3F (Fluoroform)

Method	Proton attached to F atom		Proton attached to C atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	148.9143	-5.81427	117.6762	25.42378
B3LYP/6-311++G**	141.2154	1.884642	112.1692	30.9308
MP2/6-311++G**	142.1334	0.966595	110.4467	32.65331

MP2/cc-pVDZ	146.4099	-3.30988	114.6774	28.42264
CCSD/6-311++G**	148.3508	-5.25077	115.6425	27.45753
G4	147.9805	-4.88054	121.1765	21.92353
Expt	143.1	NA	143.1	NA

As observed in the previous case, the MP2 method with the 6-311++G** basis set excellently predicts the PA value of CH_3F with an error of 0.966 kcal/mol. The experimentally measured PA value for CH_3F corresponds to the protonated analogue in which the proton is attached to the F-atom. Unlike in the cases of CF_3Cl and CF_3Br , the protonated analogue in CH_3F in which the proton is attached to the F-atom is also found to be the most stable protonated analogue. Table 3a-b depicts the proton PA and Sum of electronic and zero-point Energies for protonated molecular species respectively and their geometries as shown in fig. 3a-c

Table3b. Sum of electronic and zero-point Energies for protonated molecular species

Method	Energy (Hartree/Particle)*	
	F	C
HF/6-311++G**	-139.279	-139.229
B3LYP/6-311++G**	-139.977	-139.931
MP2/6-311++G**	-139.634	-139.583
MP2/cc-pVDZ	-139.573	-139.522
CCSD/ 6-311++G**	-139.598	-139.546
G4	-139.942	-139.899

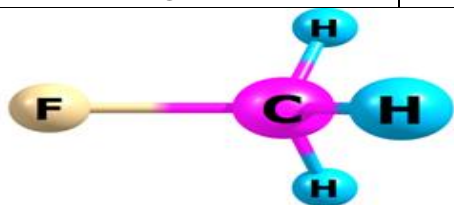


Fig. 3a Optimized geometry for CH_3F

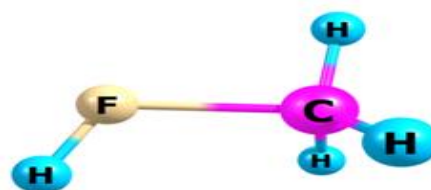


Fig.3b Geometry for the protonation at F



Fig. 3c Geometry for protonation at C

4. CH_3Cl (Chloromethane)

Table4a. PA values for CH_3Cl (Chloromethane)

Method	Proton attached to Cl atom		Proton attached to C atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	133.9739	-20.7261	109.0825	-45.6175
B3LYP/6-311++G**	118.9833	-35.7167	114.2939	-40.4061
MP2/6-311++G**	115.3318	-39.3682	114.3517	-40.3483
MP2/cc-pVDZ	117.4133	-37.2867	114.2814	-40.4186
CCSD/6-311++G**	123.0352	-31.6648	114.9591	-39.7409
G4	120.7429	-33.9571	116.6226	-38.0774
Expt	154.7	NA	154.7	NA

As observed in previous cases, the different quantum chemical calculation methods employed in this study are able to predict the PA values to a very good accuracy. Thus, we suspect error in the experimentally reported PA value for CH_3Cl in which the least error in all the methods is 20.726 kcal/mol obtained at the Hartree Fock level with the 6-311++G** basis set in table 4a. Be it as it may, going with the least error, the experimentally measured PA value for CH_3Cl corresponds to the protonated analogue in which the proton is attached to the Cl-atom. This protonated analogue is also found to be the most stable as shown in the table 4b. the geometries are shown in Fig. 4a-c.

Table 4b. Sum of electronic and zero-point Energies for protonated molecular species

Method	Energy (Hartree/Particle)*	
	Cl	C
HF/6-311++G**	-499.306	-499.266
B3LYP/6-311++G**	-500.304	-500.296
MP2/6-311++G**	-499.574	-499.573
MP2/cc-pVDZ	-499.552	-499.547
CCSD/ 6-311++G**	-499.591	-499.578
G4	-500.27	-500.264

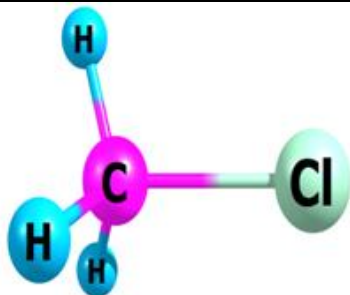


Fig. 4a Optimized geometry for CH_3Cl

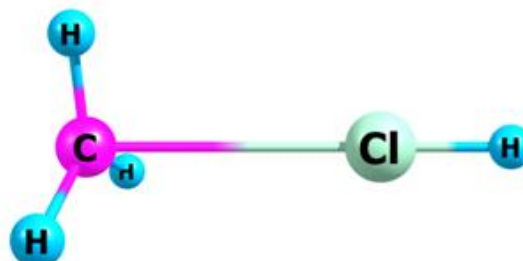


Fig. 4b Geometry for protonation at Cl

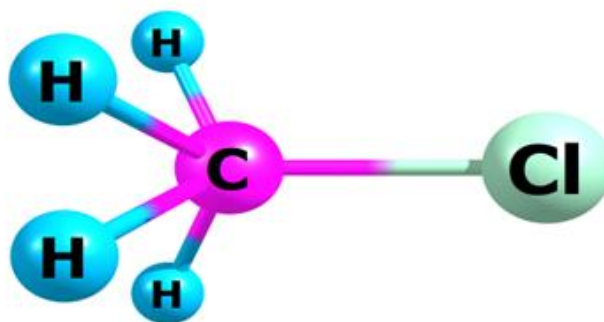


Fig. 4c Geometry for protonation at C

5. Factors that could influence the best site of protonation

From the foregoing studies, the following have been observed as factors which could influence the best site of protonation;

- (i) Bonding Nature
- (ii) Stability of the protonated analogue
- (iii) Electron density/electronegativity

4. CONCLUSION

The protonation in noble gas containing molecular systems have been studied and elucidated by employing six high definition Ab-initio quantum chemical calculation methods with the aim of observing whether or not there exist a periodic trend amongst CF_3Cl , CF_3Br , CH_3F , CH_3Cl . The best site of protonation i.e the site that corresponds with the experimentally measured proton affinity for each molecule were recorded and the most stable analogue were also pointed out which all aided in observing the periodic trend. From the results obtained, it reveals that CF_3Cl and CF_3Br follow the same trend while both CH_3F and CH_3Cl follow a different trend. For CF_3Cl and CF_3Br ; the most stable site of protonation and the site which corresponds to the experimentally determined proton affinity are quite different sites while for CH_3F and CH_3Cl ; the most stable site of protonation and the site which corresponds to the experimentally determined proton affinity are the same sites. These observations obviously are due to electron density/electronegativity, nature of bonding or stability of protonated analogue.

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