Protonation in Noble Gas Containing Molecular Systems: Observing Periodic Trends in CF$_3$Cl, CF$_3$Br, CH$_3$F, CH$_3$Cl

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Abstract: Protonation of molecular systems containing noble gases have been studied and compared for CF$_3$Cl, CF$_3$Br, CH$_3$F, and CH$_3$Cl 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$_3$Cl and CF$_3$Br follows the same trend while CH$_3$F and CH$_3$Cl follows a different trend: For CF$_3$Cl and CF$_3$Br the most stable site of protonation differs from the site which corresponds to the experimentally determined PA value while for CH$_3$F and CH$_3$Cl, 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 A + H$^+$ $\rightarrow$ AH$^+$. 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 Croswell [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 gas 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$_3$Cl, CF$_3$Br, CH$_3$F, and CH$_3$Cl triggered the present study, thus the aim of this research is: (i) to observe and define the periodic trend in CF$_3$Cl, CF$_3$Br, CH$_3$F, and CH$_3$Cl (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$_3$Cl (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$_3$Cl and their Sum of electronic and zero-point Energies respectively

Table 1a. PA values for CF$_3$Cl (Chlorotrifluoromethane)

<table>
<thead>
<tr>
<th>Method</th>
<th>Proton attached to F atom</th>
<th>Proton attached to Cl atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PA (kcal/mol)</td>
<td>Error</td>
</tr>
<tr>
<td>HF/6-311++G**</td>
<td>141.3358</td>
<td>-4.83584</td>
</tr>
<tr>
<td>B3LYP/6-311++G**</td>
<td>142.3298</td>
<td>-5.82982</td>
</tr>
<tr>
<td>MP2/6-311++G**</td>
<td>145.9286</td>
<td>-9.42858</td>
</tr>
<tr>
<td>MP2/cc-pVDZ</td>
<td>144.5412</td>
<td>-8.14116</td>
</tr>
<tr>
<td>CCSD/6-311++G**</td>
<td>145.5339</td>
<td>-9.03388</td>
</tr>
<tr>
<td>G4</td>
<td>144.8279</td>
<td>-8.32793</td>
</tr>
<tr>
<td>Expt</td>
<td>136.5</td>
<td>NA</td>
</tr>
</tbody>
</table>

The experimentally measured PA value for CF$_3$Cl 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

Table 1b. Sum of electronic and zero-point Energies for protonated molecular species

<table>
<thead>
<tr>
<th>Method</th>
<th>F</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy (Hartree/Particle)*</td>
<td></td>
</tr>
<tr>
<td>HF/6-311++G**</td>
<td>-795.997</td>
<td>-795.985</td>
</tr>
<tr>
<td>B3LYP/6-311++G**</td>
<td>-798.176</td>
<td>-798.162</td>
</tr>
<tr>
<td>MP2/6-311++G**</td>
<td>-796.899</td>
<td>-796.878</td>
</tr>
<tr>
<td>MP2/cc-pVDZ</td>
<td>-796.739</td>
<td>-796.729</td>
</tr>
<tr>
<td>CCSD/6-311++G**</td>
<td>-796.758</td>
<td>-796.75</td>
</tr>
<tr>
<td>G4</td>
<td>-798.057</td>
<td>-798.058</td>
</tr>
</tbody>
</table>
2. \( \text{CF}_3\text{Br} \) (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 \( \text{CF}_3\text{Br} \) (Bromine Trifluoromethane)**

<table>
<thead>
<tr>
<th>Method</th>
<th>Proton attached to F atom</th>
<th>Proton attached to Br atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PA (kcal/mol)</td>
<td>Error</td>
</tr>
<tr>
<td>HF/6-311++G**</td>
<td>144.8913</td>
<td>-6.29131</td>
</tr>
<tr>
<td>B3LYP/6-311++G**</td>
<td>146.3233</td>
<td>-7.72329</td>
</tr>
<tr>
<td>MP2/6-311++G**</td>
<td>149.014</td>
<td>-10.414</td>
</tr>
<tr>
<td>MP2/cc-pVDZ</td>
<td>147.5877</td>
<td>-8.98772</td>
</tr>
<tr>
<td>CCSD/6-311++G**</td>
<td>148.9651</td>
<td>-10.3651</td>
</tr>
<tr>
<td>G4</td>
<td>147.7264</td>
<td>-9.1264</td>
</tr>
<tr>
<td>Expt</td>
<td>138.6</td>
<td>NA</td>
</tr>
</tbody>
</table>

In Table 2a, The MP2 method with the 6-311++G** basis set accurately predicts the PA value of \( \text{CF}_3\text{Br} \) with an error of 0.609 kcal/mol. The experimentally measured PA value for \( \text{CF}_3\text{Br} \) 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.

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

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy (Hartree/Particle)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
</tr>
<tr>
<td>HF/6-311++G**</td>
<td>-2908.86</td>
</tr>
<tr>
<td>B3LYP/6-311++G**</td>
<td>-2912.1</td>
</tr>
<tr>
<td>MP2/6-311++G**</td>
<td>-2909.75</td>
</tr>
<tr>
<td>MP2/cc-pVDZ</td>
<td>-2909.61</td>
</tr>
<tr>
<td>CCSD/6-311++G**</td>
<td>-2909.63</td>
</tr>
<tr>
<td>G4</td>
<td>-2911.73</td>
</tr>
</tbody>
</table>

3. \( \text{CH}_3\text{F} \) (Fluoroform)

**Table 3a. PA values for \( \text{CH}_3\text{F} \) (Fluoroform)**

<table>
<thead>
<tr>
<th>Method</th>
<th>Proton attached to F atom</th>
<th>Proton attached to C atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PA (kcal/mol)</td>
<td>Error</td>
</tr>
<tr>
<td>HF/6-311++G**</td>
<td>148.9143</td>
<td>-5.81427</td>
</tr>
<tr>
<td>B3LYP/6-311++G**</td>
<td>141.2154</td>
<td>1.884642</td>
</tr>
<tr>
<td>MP2/6-311++G**</td>
<td>142.1334</td>
<td>0.966595</td>
</tr>
</tbody>
</table>
Protonation in Noble Gas Containing Molecular Systems: Observing Periodic Trends in CF$_3$Cl, CF$_3$Br, CH$_3$F, CH$_3$Cl

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy (Hartree/Particle)</th>
<th>Error PA</th>
<th>Error C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2/cc-pVDZ</td>
<td>146.4099</td>
<td>-3.30988</td>
<td>114.6774</td>
</tr>
<tr>
<td>CCSD/6-311++G**</td>
<td>148.3508</td>
<td>-5.25077</td>
<td>115.6425</td>
</tr>
<tr>
<td>G4</td>
<td>147.9805</td>
<td>-4.88054</td>
<td>121.1765</td>
</tr>
<tr>
<td>Expt</td>
<td>143.1</td>
<td>NA</td>
<td>143.1</td>
</tr>
</tbody>
</table>

As observed in the previous case, the MP2 method with the 6-311++G** basis set excellently predicts the PA value of CH$_3$F with an error of 0.966 kcal/mol. The experimentally measured PA value for CH$_3$F corresponds to the protonated analogue in which the proton is attached to the F-atom. Unlike in the cases of CF$_3$Cl and CF$_3$Br, the protonated analogue in CH$_3$F 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.

**Table 3b. Sum of electronic and zero-point Energies for protonated molecular species**

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy (Hartree/Particle)</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-311++G**</td>
<td>-139.279</td>
<td>-139.229</td>
</tr>
<tr>
<td>B3LYP/6-311++G**</td>
<td>-139.977</td>
<td>-139.931</td>
</tr>
<tr>
<td>MP2/6-311++G**</td>
<td>-139.634</td>
<td>-139.583</td>
</tr>
<tr>
<td>MP2/cc-pVDZ</td>
<td>-139.573</td>
<td>-139.522</td>
</tr>
<tr>
<td>CCSD/6-311++G**</td>
<td>-139.598</td>
<td>-139.546</td>
</tr>
<tr>
<td>G4</td>
<td>-139.942</td>
<td>-139.899</td>
</tr>
</tbody>
</table>

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$_3$Cl 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$_3$Cl 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 4a. PA values for CH$_3$Cl (Chloromethane)**

<table>
<thead>
<tr>
<th>Method</th>
<th>Proton attached to Cl atom</th>
<th>Proton attached to C atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PA (kcal/mol)</td>
<td>Error</td>
</tr>
<tr>
<td>HF/6-311++G**</td>
<td>133.9739</td>
<td>-20.7261</td>
</tr>
<tr>
<td>B3LYP/6-311++G**</td>
<td>118.9833</td>
<td>-35.7167</td>
</tr>
<tr>
<td>MP2/6-311++G**</td>
<td>115.3318</td>
<td>-39.3682</td>
</tr>
<tr>
<td>MP2/cc-pVDZ</td>
<td>117.4133</td>
<td>-37.2867</td>
</tr>
<tr>
<td>CCSD/6-311++G**</td>
<td>123.0352</td>
<td>-31.6648</td>
</tr>
<tr>
<td>G4</td>
<td>120.7429</td>
<td>-33.9571</td>
</tr>
<tr>
<td>Expt</td>
<td>154.7</td>
<td>NA</td>
</tr>
</tbody>
</table>

4. CH$_3$Cl (Chloromethane)
Protonation in Noble Gas Containing Molecular Systems: Observing Periodic Trends in CF₃Cl, CF₃Br, CH₃F, CH₃Cl

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

<table>
<thead>
<tr>
<th>Method</th>
<th>Cl</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-311++G**</td>
<td>-499.306</td>
<td>-499.266</td>
</tr>
<tr>
<td>B3LYP/6-311++G**</td>
<td>-500.04</td>
<td>-500.296</td>
</tr>
<tr>
<td>MP2/6-311++G**</td>
<td>-499.574</td>
<td>-499.573</td>
</tr>
<tr>
<td>MP2/cc-pVDZ</td>
<td>-499.552</td>
<td>-499.547</td>
</tr>
<tr>
<td>CCSD/6-311++G**</td>
<td>-499.591</td>
<td>-499.578</td>
</tr>
<tr>
<td>G4</td>
<td>-500.27</td>
<td>-500.264</td>
</tr>
</tbody>
</table>

Fig. 4a Optimized geometry for CH₃Cl  
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 CF₃Cl, CF₃Br, CH₃F, CH₃Cl. 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 CF₃Cl and CF₃Br follow the same trend while both CH₃F and CH₃Cl follow a different trend. For CF₃Cl and CF₃Br; the most stable site of protonation and the site which corresponds to the experimentally determined proton affinity are quite different sites while for CH₃F and CH₃Cl; the most stable site of protonation and the site which corresponds to the experimentally determined proton affinity are the same sites. These observation was obviously are due to electron density/electronegativity, nature of bonding or stability of protonated analogue.
REFERENCES