



Structural and spectroscopic parameters of $C_nF_2^+$ ($n = 1-5$): Insights using MP2/CBS method



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ABSTRACT

The structural and spectroscopic parameters of the fluorine doped carbon isomers, $C_nF_2^+$ ($n = 1-5$) cations, were calculated using frozen core second order Møller-Plesset perturbation theory (MP2(fc)) at the complete basis set (CBS) limit with the aug-cc-pVXZ ($X = D, T, Q$) basis sets. The optimised geometries, rotational constants, dipole moments, and vibrational frequencies of the cations were computed to the CBS limit. The even-odd alternation effect was observed in the geometrical parameters, the dipole moments and the stabilities of the isomers. The carbon clusters containing even numbers of carbon atoms are linear with $D_{\infty h}$ symmetry, while those containing an odd number of carbon atoms adopt a bent structure with bond angle in the range $120-130^\circ$. Some of the calculated parameters show good agreement to those available in the literature. Therefore, the reported data of the isomers should be accurate and it is hoped that the data on the isomers will be useful in helping to detect these cations in the interstellar medium.

1. Introduction

The interstellar medium (ISM) is not empty, but is pervaded with molecules and ions, which cannot be detected by the eyes because they are at much lower temperatures compared to stars [1]. The quasi-collisionless condition prevalent in the ISM allows the habitation of heteroatom doped carbon clusters [2]. Several of these clusters have been subjected to theoretical investigations throughout the past years [3–19]. Out of these studies, the halogen doped carbon clusters have attracted attention [12–19]. An in-depth analysis of these studies, as detailed in the following paragraphs, has been helpful to set the objectives of our current research.

The dicarbides of the third row elements including C_2Br were studied by Rayøen and coworkers [13] using the QCISD/aug-cc-pVTZ method. They reported that the structures of C_2K , C_2Ca , and C_2Ga , display C_{2v} symmetry while the others favour a linear structure, with C_2Br being slightly bent. The tricarbides of the third row elements were investigated by Villaneuva et al. [14], using the B3LYP functional with

the aug-cc-pVTZ basis sets for C and Ga to Br atoms, and the CVTZ basis set for K and Ca atoms. This was followed by more reliable computations using the QCISD method. The linear isomers are stable with the Br counterpart being the only exception using both methods. The stable structure of C_3Br was bent with an angle of 145° .

The chlorine doped carbon clusters were studied by Li and Tang [15], along with the other carbon clusters doped with the second row elements. The linear structures were optimised using the B3LYP/6-311+G(d) method. All the clusters (neutral, anion and cation) are stable in the linear geometry, except for the chlorine doped clusters. However, some of the small chlorine clusters (CCl^+ , CCl^- , CCl , C_2Cl^- , C_2Cl , and C_3Cl^+) are linear. According to the computations of Largo et al. [16] using the B3LYP/6-311G(d) method, the clusters (C_nCl , C_nCl^+ , C_nCl^- ; $n = 1-7$) which are unstable in the linear form adopt slightly bent geometries. A controversy was reported between the experimental and theoretical structure of C_4Cl in terms of the CCC bond angle. Sumiyoshi et al. [17] reported a slightly bent structure of C_4Cl based on rotational spectroscopy. A similar structure was predicted by

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Largo et al. [16] using the B3LYP/6-311G(d) method. Sumiyoshi et al. [17] revisited the study of Largo et al. [16] and optimised C_4Cl using the B3LYP/cc-pVTZ method. They observed a change in the CCC bond angle from 171° [B3LYP/6-311G(d)] to 178° [B3LYP/cc-pVTZ]. They concluded that there should be a convergence to the linear structure. Arulmozhiraja and Ehara [18] settled these controversies using higher levels of theory and they reported that C_4Cl should be linear based on the more reliable SAC-Cl/cc-pVTZ method.

Chen and Wu [19] investigated the neutral and ionic forms of C_nF ($n = 1-7$), using the B3LYP/aug-cc-pVTZ method. The study was also complemented with RCCSD computations to validate those obtained using the B3LYP functional. They reported that the neutral clusters up to $n = 6$ are non-linear, while those containing longer carbon clusters ($n = 6, 7$) are linear. For the cations, all the structures are linear, except for C_2F^+ and C_4F^+ , which are slightly bent. The even-odd alternation effect is present in the structure of the anions and in the stabilities of the cations and anions, but not in the neutral clusters.

Hydrogen is the most abundant element in the ISM [1], and therefore several of the hydrogen doped cationic carbon clusters have been detected. These include the C_2H radical [20], the C_2H_2 [21], C_4H_2 and C_6H_2 [22] molecules. The nucleosynthesis of fluorine is an ongoing process in the ISM, particularly in type II supernovae, Wolf-Rayet stars and Asymptotic Giant Branch stars [23], and hence the fluorine doped counterparts also stand a very high chance of being present in the ISM. The presence of fluorine in the ISM has also been confirmed by the detection of fluorine containing molecules, namely the AlF [24] and HF [25] molecules, and the CF^+ cation [26]. The neutral and ionic forms of C_nF ($n = 1-7$) have already been studied by Chen and Wu [19]. In view of the above, and the prevailing conditions of the ISM leading to ionisation of molecules, the fluorine doped carbon clusters, $C_nF_2^+$ ($n = 1-5$) cations have been the target of the research work. Accurate data is required for astronomical detections [27] and thus the reliable frozen core second order Møller-Plesset perturbation theory (MP2(fc)) at the complete basis set (CBS) limit [28] method has been adopted.

2. Computational methods

All the computations were carried out with the Gaussian 09W suite of programs [29], implemented on the resources provided by GridChem Science Gateway [30,31]. GaussView 5.0 [32] was used for visualisation. Initially, the most stable geometries of the cations under investigation were determined by optimising the possible isomers using the same method [B3LYP/6-311G(d,p)] as reported by Qi and Zhu [12]. The very tight convergence with root mean square force criterion set to 1×10^{-6} was used for all computations. The nature of the stationary points was checked by frequency computation. The isomers having the lowest energies, and no imaginary frequencies were chosen as the most stable. Further optimisation using very tight convergence criteria and frequency computations were performed on the most stable counterpart at the MP2 level of theory with three successively improving quality basis sets, namely the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ as proposed by Kendall et al. [33]. However, the $C_5F_2^+$ cation was not successfully optimised with the aug-cc-pVQZ basis set with our available resources. All computed parameters were extrapolated to the CBS limit.

The use of basis sets with successively increasing indices exhibit systematic convergence to the CBS limit. Two extrapolations schemes were employed for the CBS extrapolation; the two and three parameter formulae:

$$A_n = A_{\infty 1} + Bn^{-3} \quad (1)$$

$$A_n = A_{\infty 2} + Be^{-(n-1)} + Ce^{-(n-1)^2} \quad (2)$$

where $A_{\infty 1}$, and $A_{\infty 2}$ represent the CBS values for each extrapolation scheme. The approach of Feller et al. [34] was adopted and the CBS value was calculated as an average of $A_{\infty 1}$, and $A_{\infty 2}$. However,

exceptionally for the $C_4F_2^+$ and $C_5F_2^+$ cations, the CBS value was computed using the two parameter formulae only, and the CBS value was taken as being equal to $A_{\infty 1}$. This is because, for the $C_4F_2^+$ cation, optimisation using the aug-cc-pVDZ basis set resulted in one imaginary frequency for the linear isomer. The uncertainty in the extrapolation was then taken as the spread between the values. $A_{\infty 1}$ was computed using the two highest indices (3 and 4), as recommended by Halkier et al. [35], and $A_{\infty 2}$ using all three indices (2, 3, and 4). Both equations were solved using the lsqcurvefit() implemented in Matlab[®] [36].

3. Results and discussion

3.1. Geometry optimisation

The optimisation using the B3LYP/6-311G(d,p) method results in several geometries, which are displayed in figure S11 (SI=Supplementary information). For all the cations under study, the most stable isomer possesses either a linear or bent geometry, containing a fluorine atom at each end of the chain. However, in the case of the $C_3F_2^+$ cation, the cyclic isomer is the most stable, followed by the bent isomer. In view of the small energy difference (1.3 kJ/mol) between the most stable isomer (cyclic) of the $C_3F_2^+$ cation and next higher energetic isomer (bent), both of them were chosen as being equally probable for interstellar detection. A computational study of the $C_3Cl_2^+$ cation performed by Redondo et al. using the B3LYP/6-311G(d) method [37] also shows that the cation favours both the cyclic and the bent isomer, with a difference of 149.0 kJ/mol between the two isomers.

The geometrical parameters of the most stable isomers including their electronic states, extrapolated to the CBS limit are displayed in Fig. 1, generated using CYLview [38]. The computed parameters using the MP2/aug-cc-pVXZ ($X = D, T, Q$) method have been listed in Tables S11–S19.

Due to lack of experimental data for CF_2^+ and $C_2F_2^+$, the predicted bond lengths have been compared with the experimental data for their neutral counterparts. The bond lengths of CF_2 (1.212 Å) and C_2F_2 (1.233 Å and 1.222 Å) compare satisfactorily with the experimental values of their neutral counterparts (CF_2 : 1.297 Å, C_2F_2 : 1.187 Å and 1.283 Å), as reported by Poutsma et al. [39]. The difference may be attributed to the delocalisation of charges in the cation, resulting in bond shortening of the C–C bonds [40]. The C–F bonds are longer in the cations because of nuclear repulsion arising due to the loss of σ -electrons [41]. The theoretical values for CF_2^+ , available on the NIST database [42] were extrapolated to the CBS limit. The calculated bond length and bond angle (1.212 Å and 124.9°) are in excellent agreement with those calculated at MP2/CBS level. The even-odd alternation effect is present in the optimised geometries. The carbon clusters containing even numbers of carbon atoms are linear, with $D_{\infty h}$ symmetry, while those containing an odd number of carbon atoms adopt a bent structure with bond angle $120-130^\circ$, as compared with the C_nF^+ clusters, where the C–C–F bond angle is 180° [19]. The degree of linearity increases as the number of carbon atoms in the clusters increases. The C–C–C bond angles and the C–C bond lengths of the $C_3F_2^+$ cation are similar to those of the $C_3Cl_2^+$ cation, computed at MP2 (full) level of theory, as reported by Redondo et al. [37].

3.2. Electric dipole moment and equilibrium rotational constants

A permanent electric dipole moment is a prerequisite for a cation to possess pure rotational spectra. The probability of photon absorption depends on the cation's electric dipole moment. The cations possessing a larger electric dipole moment can more easily be detected, by virtue of their more intense spectral lines [43]. The computed values for the electric dipole moments, the center of mass as the origin, using the MP2 method, and the aug-cc-pVXZ ($X = D, T, Q$) basis set are reported in Table S116, and the values extrapolated to the CBS limit are reported in

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