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C_4Cl revisited in a SAC-CI general-*R* light

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$C_{2n}H$ carbon-chain series radicals have attracted much attention experimentally and theoretically, partially due to the interesting energy separation feature between the ground and the first excited states, $^2\Sigma$ and $^2\Pi$: the energy separation and the order of these states vary with the number of carbon atoms. Attention has also been paid on chlorinated carbon-chain series, $C_{2n}Cl$, to investigate the substitution effects on the energy separation and the nature of the ground state structures. After a few contradictory reports, a combined experimental and theoretical study[1] has concluded that the C_2Cl, the first member of the $C_{2n}Cl$ carbon-chain series, has a bent structure due to a strong vibronic coupling between the two nearby states. However, such a consistent conclusion has not been arrived in a similar combined study on the next member of the $C_{2n}Cl$ series, C_4Cl.[2] A recent study[2] concluded that while experimental results, the rotational transitions and hyperfine coupling constant observed by Fourier-transform microwave (FTMW) spectroscope, support that the C_4Cl radical has the ground state corresponding to $^2\Pi$ and the molecular structure is bent due to the vibronic coupling, none of the high-level ab initio calculations support the bent structure. We carried out the present study to solve the existing contradiction between the theory and the experiment by obtaining the accurate ground state structure.

At first, the C_4Cl radical structure was optimized by using BLYP, BPW91, and B3LYP density functionals to clear a few earlier doubts. Many different basis sets, 6-311G(d), Dunning's correlation-consistent polarized valence triple-zeta (cc-pVTZ), augmented valence triple-zeta (aug-cc-pVTZ), quadruple-zeta (aug-cc-pVQZ), and quintuple-zeta (aug-cc-pV5Z) basis sets, were utilized for this purpose. Finally, we used high-level ab initio symmetry-adapted cluster (SAC) General-*R* method[3] which includes up to quadruple excitations for the optimization of the radical structure.

The results obtained using density functionals, especially using pure functionals, show that the radical has a bent structure. The results derived using BLYP functionals were presented in the Table 1. The bent structure is well pronounced: the $\theta(C_1C_2C_3)$ bond angle is calculated to be 166.2^o at BLYP/Aug-cc-pV5Z level. The linear structure has an imaginary frequency. The reliability of the results obtained using density functionals were verified by studying related radicals whose experimental/reliable values are available in the literature.

Finally, the C_4Cl ground state structure was optimized using SAC general-*R* theory with cc-pVTZ basis set and the results were tabulated in Table 2. The table clearly shows the non-linear nature of the radical structure. It has been confirmed that the results derived for

C_2Cl radical using the same level of theory agree very well with the established reliable results. The foregoing results clearly support the conclusions arrived in the earlier experimental study[1] that the C_4Cl has the ground state correlating $^2\Pi$ with a bent molecular structure. The next nearby lowest state, with $^2\Sigma$ symmetry, has also been optimized using SAC (SD-R) theory. It is shown to be linear in nature. The vertical transition energies of a few other excited states have also been calculated.

However, an earlier study[2] using MRCI and CCSD(T) predicted a linear C_4Cl radical structure with $^2\Sigma$ and $^2\Pi$ symmetry, respectively. We thoroughly investigated this problem. We also studied the structure using CCSD/cc-pVTZ level. The CCSD results show that the C_4Cl has a linear structure and it is shown to be global minima. The $<S^2>$ value (the degree of spin contamination) was calculated to be 1.14 in contrast to 0.75 for a pure doublet. Inclusion of triples through CCSD(T) was unable to rectify the spin contamination problem. So it is possible that the calculated state may not be a pure doublet state and in this context we believe that earlier CCSD(T) results may not be trusted. It is worth to mention here that the quartet state obtained using SAC(SD-R) theory is shown to have a linear structure.

Table 1. C_4Cl structures using BLYP functional with different basis sets. R in Å; θ in degrees.

Parameter	6-311G(d)	cc-pVTZ	Aug-cc-pVTZ	Aug-cc-pVQZ	Aug-cc-pV5Z
$R(C_1C_2)$	1.285	1.282	1.283	1.282	1.282
$R(C_2C_3)$	1.336	1.333	1.332	1.332	1.332
$R(C_3C_4)$	1.238	1.237	1.237	1.237	1.237
$R(C_4Cl)$	1.636	1.630	1.629	1.625	1.622
$\theta(C_1C_2C_3)$	164.7	166.0	166.1	166.2	166.2
$\theta(C_2C_3C_4)$	178.1	178.8	178.8	178.8	178.8
$\theta(C_3C_4Cl)$	179.6	179.6	179.7	179.8	179.8

Table 2. C_4Cl structure at SAC-CI(General-R)/cc-pVTZ level. R in Å; θ in degrees.

Parameter	General-R/cc-pVTZ
$R(C_1C_2)$	1.293
$R(C_2C_3)$	1.341
$R(C_3C_4)$	1.223
$R(C_4Cl)$	1.639
$\theta(C_1C_2C_3)$	172.6
$\theta(C_2C_3C_4)$	179.6
$\theta(C_3C_4Cl)$	179.3

The present study using DFT with large basis sets up to Aug-cc-pV5Z basis set and the high-level ab initio through the SAC General-R theory which includes up to quadruple excitations provide a bent ground state structure for the C_4Cl radical. The results overcome the earlier contradiction between the theory and experiment and clearly support the experimental conclusion that the C_4Cl radical has the ground state corresponding to $^2\Pi$ symmetry but the molecular structure is bent.

References:
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2. Sumiyoshi, Y.; Katoh, K.; Endo, Y. Chem. Phys. Lett. 2005, 414, 82.
3. Nakatsuji, H. Chem. Phys. Lett. 1991, 177, 331; and also the references therein.