

C₄Cl: Bent or linear?

Sundaram Arulmozhiraja and Masahiro Ehara

*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyoku-ku, Kyoto 615-8510, Japan*Hiroshi Nakatsuji^{a)}*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyoku-ku, Kyoto 615-8510, Japan and Fukui Institute for Fundamental Chemistry, Kyoto University, 34-4 Takano, Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103, Japan*

(Received 15 August 2006; accepted 17 October 2006; published online 17 November 2006)

The ground state structure for the C₄Cl radical was computed by using symmetry-adapted cluster configuration-interaction (SAC-CI) theory along with density functional theory to overcome the differences raised in the recently published paper [Y. Sumiyoshi *et al.*, Chem. Phys. Lett. **414**, 82 (2005)] between the theory and the experiment. SAC-CI results clearly support the earlier experimental conclusion that the radical has the bent ground state structure corresponding to ²Π symmetry. Contrarily, probably due to spin contamination, mixing of a bent doublet ground state with the quartet components of a linear structure, coupled-cluster singles and doubles (CCSD) calculations were unable to provide reliable results. Results obtained using density functional theory also show that the radical has a bent structure. Some low-lying doublet excited states were also studied using the SAC-CI theory. The energy difference between the ground Π state and the nearby Σ state is around 0.2 eV. The excitation energy for the transition with the largest oscillator strength agrees with the strongest absorption peak. © 2006 American Institute of Physics.
[DOI: 10.1063/1.2393224]

I. INTRODUCTION

A recent experimental work combined with theoretical investigations by Sumiyoshi *et al.*¹ made the following conflicting conclusion regarding the ground state structure of C₄Cl radical. While experimental results, the rotational transitions and the hyperfine coupling constant observed by Fourier-transform microwave (FTMW) spectroscopy, support that the C₄Cl radical has the ground state corresponding to ²Π but the molecular structure is bent due to the vibronic coupling, none of the high-level *ab initio* calculations support the bent structure. So the authors concluded that more reliable high-level calculations considering configuration interactions using a larger active space and a larger basis set are required to explain the experimental observation. This motivated us to take up this study to solve the existing contradictions.

In recent years attention has been paid on chlorinated carbon-chain series radicals, C_{2n}Cl, to understand their structure and nature of electronic states.¹⁻⁶ It is well known that the counterpart series, C_{2n}H carbon-chain series, got much attention experimentally and theoretically, due to the interesting energy separation feature between their ground and the first excited states, ²Σ and ²Π. The energy separation and the order of these states vary with the number of carbon atoms.⁷⁻¹⁶ So the studies on C_{2n}Cl radicals become important in understanding the substitution effects on the energy separation and the nature of the ground state structures. Addition-

ally, several carbon-chain molecules of the type C_nH (*n*=1-6) have been detected toward various astronomical sources.¹⁷ Therefore chlorinated carbon chains could also be detected in space. All these facts made the C_{2n}Cl compounds interesting for experimental as well as theoretical studies.

Earlier theoretical studies on C₂Cl radical^{18,19} have shown that the radical is linear in its ground state. The ²Π and ²Σ states are close in energy. Though the ²Π state is higher in energy than the ²Σ state at the Hartree-Fock (HF) level, correlation effects through Møller-Plesset (MP) theory favor the ²Π ground state.¹⁸ Largo *et al.*³ studied ground state electronic structures, vibrational frequencies, and dipole moments of C_nCl, C_nCl⁺, and C_nCl⁻ (*n*=1-7) by using density functional theory (DFT). Their results, obtained using B3LYP functional with 6-311G(*d*) and 6-311+G(*d*) basis sets, showed that most of the C_nCl radicals including C₂Cl radical have nonlinear structures with ²A' ground states.³ An even-odd parity effect (*n*-even clusters more stable than *n*-odd ones) has also been found in that study. Additionally, it was found that as *n* increases there is a higher tendency toward linearity, especially for *n*-even clusters. Meanwhile, Li and Tang studied the ground state structures of second-row-atom-doped linear carbon clusters C_nX, C_nX⁺, and C_nX⁻ (*n*=1-10) by using B3LYP/6-311+G(*d*) level.⁶ In all the cases including C_nCl series, only linear chain structures were considered in that study to simplify the computations. Almost all the C_nCl radicals in linear form were found to be saddle points on the corresponding potential energy surfaces because of their imaginary frequencies. However, some small C_nCl linear clusters including C₂Cl radical did not

^{a)} Author to whom correspondence should be addressed. Electronic mail: hiroshi@sbchem.kyoto-u.ac.jp

show any imaginary frequency. Later, a combined study of the FTMW spectroscopy and the multireference configuration-interaction (MRCI) calculations by Sumiyoshi *et al.*⁴ concluded that the ground state of the C₂Cl radical has a bent structure due to a strong vibronic coupling between the two nearby states. In the limit of linearity, the energy separation between the ground ²Σ state and the first excited ²Π state is just 200 cm⁻¹ (0.03 eV).

The next member of C_{2n}Cl series, C₄Cl, is expected to have a strong vibronic coupling as in the case of its C₄H counterpart. The first study on C₄Cl using B3LYP functional with 6-311G(*d*) and 6-311+G(*d*) basis sets by Largo *et al.*³ concluded a bent structure correlating ²Π state for the ground state of this radical. The C–C bond distances in C_nCl (*n*=1–7) radicals were predicted to be moderately strong double bonds suggesting that the most important valence structure is a cumulene-type structure. At the same time, observation of bond length alternation suggests that some polyacetylenic characters also contribute, particularly for the *n*-even chains.³ Li and Tang⁶ studied C_nX carbon clusters including C_nCl radicals using DFT by keeping the radical structures linear. Their calculations revealed that the linear C₄Cl radical has an imaginary frequency.

Van Wijngaarden *et al.*² recently studied the absorption spectra of C₃Cl, C₄Cl, and their ions in the Ne matrix. They also calculated the ground state geometries of both radicals using coupled-cluster singles and doubles with noniterative triples [CCSD(T)] theory and the vertical excitation energies of several excited states of both radicals at complete active space self-consistent field [CASSCF] theory with cc-pVTZ basis set. While their given optimized C₄Cl structure is a complete linear one with ²Π symmetry, it has also been mentioned in their report² that the ground state of C₄Cl is predicted to be quasilinear (²A') (correlating with the ²Π state), and the barrier to linearity is extremely small (0.17 kcal/mol). However, that ground state structure is not given in that report. They concluded that the C₄Cl radical is linear and its band origin has been assigned to 2 ²Π ← X ²Π electronic transition.² However, the recent calculations¹ using CCSD(T) and multireference averaged coupled-pair functional method (MR-ACPF) resulted in a linear structure with ²Π and ²Σ states, respectively, as the ground state of C₄Cl. Sumiyoshi *et al.*¹ have also calculated the C₄Cl radical structure using B3LYP functional with two different basis sets: the calculations with 6-311G(*d*) basis set predicted a bent structure [$\theta(\text{C}_1\text{C}_2\text{C}_3)=171^\circ$] correlating to the ²Π state, like the one predicted by Largo *et al.*,³ however, the same bond angle, $\theta(\text{C}_1\text{C}_2\text{C}_3)$, obtained with cc-pVQZ basis set is 178°. After seeing this trend, Sumiyoshi *et al.*¹ concluded that the calculations using B3LYP functional seem to converge to a linear structure with ²Π symmetry. Contrarily, as mentioned above, their experimental studies¹ concluded otherwise that the C₄Cl radical has the ground state correlating to ²Π but the molecular structure is bent due to the vibronic coupling.

The foregoing facts encouraged us to go for this present investigation. The main aim of the present work is to solve

the existing contradiction between the theory and the experiment by obtaining the accurate ground state structure of the C₄Cl radical by using high-level theories.

II. COMPUTATIONAL DETAILS

All the calculations were performed with GAUSSIAN 03 suite of programs.²⁰ The C₄Cl radical structure was optimized by using BLYP,^{21,22} BPW91,^{21,23} and B3LYP (Refs. 22 and 24) density functionals. Many different basis sets, 6-311G(*d*),^{25,26} Dunning's²⁷ 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. High-level *ab initio* SAC-CI singles and doubles (SD)-*R* method^{28–30} was used to obtain the radical structure. The C₄Cl neutral doublet radical was studied by the SAC-CI method as a cationic state of closed-shell anion and also as an anionic state of closed-shell cation.³¹ The LevelThree accuracy was adapted for these calculations. Finally, we used SAC-CI general-*R* method³² which includes up to quadruple excitations for the optimization of the structure of the C₄Cl radical. In this method, the doublet ground state of the C₄Cl radical was calculated by the ionization of the closed-shell C₄Cl⁻ molecule. In order to reduce the computational cost, perturbation selection was carried out.³³ The LevelTwo accuracy was adapted as follows: The threshold of the linked terms for the closed-shell C₄Cl⁻ was set to $\lambda_g=5 \times 10^{-6}$. (The unlinked terms were described as the products of the important linked terms whose SD-CI coefficients were larger than 0.005.) For the doublet states, the threshold of the linked doubles to quadruples was set to $\lambda_e=5 \times 10^{-7}$. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method were 0.05 and 0.0 for the *R* and *S* operators, respectively. Dunning's cc-pVTZ basis set was utilized for all the SAC-CI calculations unless or otherwise mentioned.

III. RESULTS AND DISCUSSIONS

A. Density functional theory: Reliability of pure functionals over hybrid ones

Sumiyoshi *et al.*¹ concluded that the calculations using the B3LYP functional seem to converge to a linear structure for the C₄Cl radical with the increase in the size of the basis set. So it is our interest and it is necessary to check whether the B3LYP functional really results into a linear structure. For this purpose, calculations were made by consistently increasing the size of the basis set by using Dunning's correlation-consistent basis set series up to aug-cc-pV5Z basis set. The optimized structural parameters for the C₄Cl radical were presented in Table I. Two points are worth noting down here. One, calculations show that the linear structure has an imaginary frequency preferring for a bent structure. For example, an imaginary frequency of 69i was obtained with the cc-pVTZ basis set which shows a loose confinement of motion. Two, even with the largest basis set, aug-cc-pV5Z, used in the present study, the calculations did not converge to a linear structure for the C₄Cl radical.

TABLE I. C₄Cl structures using three different density functionals with five different basis sets. *R* in Å; *θ* in degrees.

Parameter	6-311G(<i>d</i>)	cc-pVTZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z
B3LYP					
<i>R</i> (C ₁ C ₂)	1.283	1.281	1.280	1.280	1.280
<i>R</i> (C ₂ C ₃)	1.329	1.325	1.325	1.324	1.324
<i>R</i> (C ₃ C ₄)	1.227	1.226	1.226	1.226	1.226
<i>R</i> (C ₄ Cl)	1.624	1.619	1.618	1.615	1.611
<i>θ</i> (C ₁ C ₂ C ₃)	171.0	175.2	176.0	176.2	177.6
<i>θ</i> (C ₂ C ₃ C ₄)	178.8	179.7	179.7	179.7	179.8
<i>θ</i> (C ₃ C ₄ Cl)	179.5	179.9	180.0	180.0	179.7
BLYP					
<i>R</i> (C ₁ C ₂)	1.285	1.282	1.283	1.282	1.282
<i>R</i> (C ₂ C ₃)	1.336	1.333	1.332	1.332	1.332
<i>R</i> (C ₃ C ₄)	1.238	1.237	1.237	1.237	1.237
<i>R</i> (C ₄ Cl)	1.636	1.630	1.629	1.625	1.622
<i>θ</i> (C ₁ C ₂ C ₃)	164.7	166.0	166.1	166.2	166.2
<i>θ</i> (C ₂ C ₃ C ₄)	178.1	178.8	178.8	178.8	178.8
<i>θ</i> (C ₃ C ₄ Cl)	179.6	179.6	179.7	179.8	179.8
BPW91					
<i>R</i> (C ₁ C ₂)	1.283	1.280	1.281	1.280	1.280
<i>R</i> (C ₂ C ₃)	1.336	1.333	1.333	1.332	1.332
<i>R</i> (C ₃ C ₄)	1.237	1.236	1.236	1.236	1.236
<i>R</i> (C ₄ Cl)	1.623	1.619	1.619	1.615	1.612
<i>θ</i> (C ₁ C ₂ C ₃)	163.5	164.3	164.3	164.4	164.5
<i>θ</i> (C ₂ C ₃ C ₄)	178.0	178.6	178.6	178.6	178.6
<i>θ</i> (C ₃ C ₄ Cl)	179.7	179.8	179.5	179.7	179.7

Although the hybrid density functionals, especially the B3LYP functional, performed well for many chemical systems, it has been known that pure density functionals are more suitable to study radicals and biradicals.^{34–37} It may be because the HF character in the hybrid density functionals decreases the quality of the Kohn-Sham orbitals. High spin contamination at the unrestricted HF (UHF) leads to unreliable results for open-shell systems. Note that expectation values of S^2 which reflects the amount of spin contamination are sensitive to the amount of HF exchange in the hybrid density functional and on the other hand a pure functional always shows very small spin contamination. By considering these facts, two gradient-corrected pure density functionals, BLYP and BPW91, were employed to obtain the C₄Cl radical geometry. Again, different basis sets up to aug-cc-pV5Z were used for these calculations to make sure that the results are properly converged. This would also enable us to find the minimum-required basis set to study this kind of radicals using DFT. The two pure functionals, BLYP and BPW91, provided reliable geometry and energetics even for critical radicals and biradicals in the past.^{34–36}

The results obtained using BLYP and BPW91 functionals were also given in Table I. The highlight of the results calculated using these pure functionals is that the bent nature of the ground state structure is well pronounced. The important bond angle $\theta(\text{C}_1\text{C}_2\text{C}_3)$ is calculated to be 166.2° and 164.3° using BLYP and BPW91 functionals, respectively, with aug-cc-pV5Z basis set. As in the case with the hybrid functional, the linear structure has an imaginary frequency showing that it is a first-order saddle point. These results

support the experimental conclusion that the C₄Cl radical has a bent ground state structure. Table I clearly shows that all the structural parameters, including $\theta(\text{C}_1\text{C}_2\text{C}_3)$ bond angle, are almost converged with the aug-cc-pVTZ basis set.

The bond angle $\theta(\text{C}_1\text{C}_2\text{C}_3)$ obtained using B3LYP functional is around 10° larger than those obtained using BLYP and BPW91 functionals. The reliability of these DFT results should be checked before making any conclusion. It could be done by as follows: One vibrational mode has been experimentally observed in the IR spectrum for the ground state of C₄Cl radical that could be used to compare the DFT results.² This transition, 2022.1 cm⁻¹, is assigned to be the C–C stretching mode. The calculated vibrational frequencies (intensities) at BLYP/cc-pVTZ level of theory close to the observed frequency are 1764 cm⁻¹ (47) and 2078 cm⁻¹ (403). The more intense mode (in fact, this is the most intense one at this level of theory), 2078 cm⁻¹, agrees well with the observed mode, 2022.1 cm⁻¹. The same two vibrational modes derived using the BPW91 functional with the cc-pVTZ basis set, 1762 cm⁻¹ (123) and 2097 cm⁻¹ (500), are very similar to those derived using BLYP functional with the same basis set and again the more intense mode with 2097 cm⁻¹ wave number agrees well with the observed value. On the other hand, the corresponding two vibrational modes calculated at B3LYP/cc-pVTZ level of theory, 1904 cm⁻¹ (238) and 2167 cm⁻¹ (111), differ reasonably from the experimental value. A difference of about 145 cm⁻¹ wave number is obtained between the observed (2022.1 cm⁻¹) and the B3LYP (2167 cm⁻¹) values. The in-

TABLE II. C₂Cl structure at different levels of theories. *R* in Å; *θ* in degrees.

Parameter	Present study				
	B3LYP/ aug-cc-pV5Z	BLYP/ aug-cc-pV5Z	CCSD/ cc-pVTZ	SAC-CI general- <i>R</i> / cc-pVTZ	MRCI/ cc-pVTZ ^a
<i>R</i> (C ₁ C ₂)	1.270	1.276	1.275	1.269	1.269
<i>R</i> (C ₂ Cl)	1.621	1.637	1.634	1.642	1.645
<i>θ</i> (C ₁ C ₂ Cl)	163.9	159.9	162.9	157.1	156.9

^aReference 4.

tensity for this B3LYP mode, however, is not the strongest one unlike for the corresponding pure functional vibrational modes. Byrd *et al.*³⁸ made a systematic study of the accuracy of the structures and vibrational frequencies of 33 molecular radical species by using different levels of theories including B3LYP functional. The derived mean deviation and mean absolute deviation in the B3LYP/cc-pVTZ calculated vibrational frequencies relative to the experimental values are 46 and 71 cm⁻¹, respectively. Comparing with these values, the difference of 145 cm⁻¹ obtained in the present study on C₄Cl radical between the experimental value and the value calculated using the same B3LYP functional with the same cc-pVTZ basis set is very large. These facts reflect that the results derived for C₄Cl radical through B3LYP functional have some kind of flaw and on the other hand the BLYP and BPW91 results seem very reliable.

To further check the applicability of pure functionals to study the C_{2n}Cl series, we optimized the C₂Cl radical structure using both B3LYP and BLYP functionals. It is described in the Introduction that the earlier studies^{18,19} on this radical failed to find its correct ground state structure, however, the B3LYP functional correctly predicted the bent nature of the C₂Cl radical.³ Finally, Sumiyoshi *et al.*⁴ concluded a bent structure for the ground state of the C₂Cl through their combined experimental and MRCI results. The *θ*(C₁C₂Cl) bond angles calculated for the C₂Cl radical in the present study using B3LYP and BLYP functionals with aug-cc-pV5Z basis set (Table II) are 163.9° and 159.9°, respectively, while the same bond angle obtained using MRCI is 156.9°.⁴ The BLYP value agrees better with the MRCI value than the B3LYP value does. This again suggests that the results obtained using pure functionals seem more reliable than those obtained using hybrid functionals for C_{2n}Cl radicals. So we assume that the C₄Cl geometry calculated using pure density functionals is reliable. Nonetheless, the B3LYP results also show a nonlinear C₄Cl structure and the linear one has an imaginary frequency. Hence our DFT results support the experimental conclusion.

B. Coupled-cluster theories: Problem with spin contaminations

The CCSD(T) calculations by Sumiyoshi *et al.*¹ predicted a linear structure with ²Π symmetry for the C₄Cl radical and the ²Σ state was found to be very close in energy with the ground ²Π state. The energy difference was calculated to be 448 cm⁻¹ (0.06 eV) at CCSD(T)/cc-pVQZ level of theory. The MR-ACPF calculation with the reference con-

figuration obtained by CASSCF theory, however, resulted in the ²Σ ground state.¹ The energy difference between the ²Σ state and the nearby ²Π state was calculated to be 104 cm⁻¹ (0.01 eV) with the cc-pVQZ basis set. The authors¹ also tried to optimize the structure with C_s symmetry; however, they were unable to obtain a converged structure, probably due to a problem that the order of the molecular orbitals in the active space changes during the optimization. But at the same time, importantly, this cannot rule out the existence of a bent C₄Cl structure. In this sense the results derived¹ using MR-ACPF are not necessarily the conclusive one, but the CCSD(T) results need further examination.

To examine the coupled-cluster results, we optimized the C₄Cl radical structure at CCSD/cc-pVTZ level of theory starting with both linear and nonlinear structures. From the results, two points are worth to be noticed. The optimization started with the C_s symmetry converged into a linear structure. The structure optimized with the linear constraints is the global minima—the vibrational frequencies obtained for this optimized structure did not show any imaginary frequency. Thus the CCSD theory results to a linear C₄Cl radical. Most significantly, however, the $\langle S^2 \rangle$ value for the underlying UHF wave function was calculated to be 1.14. It is known that the CCSD procedure brings the spin contamination into the final wave function and the fundamental molecular orbitals derived from the UHF are spin contaminated. By considering the fact that the $\langle S^2 \rangle$ values for a pure doublet and a quartet are 0.75 and 3.75, respectively, the wave function of C₄Cl has only 87% doublet nature!! So the CCSD results obtained here for the C₄Cl radical may not be trusted. The inclusion of triples in the CCSD wave function, CCSD(T), should rectify this spin contamination problem somehow; however, it is known that perturbative methods and truncated coupled-cluster theories cannot obtain accurate results when the HF reference is poor one, as it is often the case for radicals.^{38,39} So we firmly believe that the CCSD results obtained in the present study should not be trusted. To check the CCSD performance on the C₂Cl radical, we optimized its geometry at the CCSD/cc-pVTZ level. Though the optimized geometry correctly shows the bent nature for the C₂Cl radical (Table II), the calculated *θ*(C₁C₂Cl) bond angle is larger by 6° than the value obtained using MRCI theory. The $\langle S^2 \rangle$ value in this case was calculated to be 0.86. All these results reveal that the linear structure resulted for the C₄Cl radical in the coupled-cluster based calculations might be due to the spin

TABLE III. C₄Cl structure at SAC-CI SD-*R* and general-*R* theories with cc-pVDZ and cc-pVTZ basis sets. *R* in Å; θ in degrees.

Parameter	SD- <i>R</i> ^a		SD- <i>R</i> ^b		General- <i>R</i>	
	cc-pVDZ	cc-pVTZ	cc-pVDZ	cc-pVTZ	cc-pVDZ	cc-pVTZ
$R(C_1C_2)$	1.289	1.290	1.300	1.293	1.291	1.293
$R(C_2C_3)$	1.345	1.340	1.345	1.340	1.345	1.341
$R(C_3C_4)$	1.225	1.220	1.225	1.222	1.226	1.223
$R(C_4Cl)$	1.638	1.633	1.636	1.637	1.636	1.639
$\theta(C_1C_2C_3)$	173.0	172.7	172.7	172.6	172.9	172.6
$\theta(C_2C_3C_4)$	179.5	179.5	179.6	179.6	179.5	179.6
$\theta(C_3C_4Cl)$	179.5	179.4	179.3	179.3	179.4	179.3

^aRadical considered as a cationic state of closed-shell anion.^bRadical considered as an anionic state of closed-shell cation.

contamination. Additionally, it is worth to mention here that due to the single reference nature, the CCSD(T) method was unable to provide reliable results for C₂Cl radical in which the ground and the first excited states lie closely.⁴

C. SAC-CI SD-*R* and general-*R* theories: Conclusive results

The C₄Cl radical geometry optimized using SAC-CI SD-*R* theory was tabulated in Table III. Since the excitation operators in the SAC-CI are spin symmetry adapted, the SAC-CI method is free from spin contamination problem.^{28–30} Thus, it should be suitable for the present study on the C₄Cl radical. The bent nature of the radical structure is well documented from the results: the calculated $\theta(C_1C_2C_3)$ bond angle is around 172°. Significantly, the results derived using two schemes, calculations on radical as a cationic state of closed-shell anion and as an anionic state of closed-shell cation, show a similar trend. The important bond angles, $\theta(C_1C_2C_3)$, calculated through these two schemes are almost same: 172.7° and 172.6°.

Finally, we used SAC-CI general-*R* theory to calculate the C₄Cl radical structure. Before going for the calculation on the target C₄Cl radical, we calculated the C₂Cl radical structure to show the reliability of general-*R* results. The results obtained for the C₂Cl radical were tabulated in Table II. Expectedly, the results display an excellent agreement with the MRCI results. We employed the same SAC-CI general-*R*/cc-pVTZ theory to calculate the C₄Cl radical geometry and the results were given in Table III. The table clearly shows the nonlinear nature of the C₄Cl structure. The geometrical parameters, including the $\theta(C_1C_2C_3)$ bond angle, obtained using general-*R* theory are mostly the same of those obtained using SD-*R* theory. So the inclusion of triples or higher excitation terms has no influence on the ground state structure of the C₄Cl radical. This result indirectly makes us to strongly consider that the spin contamination might be the reason for the linear structure resulted in the coupled-cluster theory calculations. It is worth to mention here that though the lowest-lying quartet state (⁴A'') has a bent structure [$\theta(C_1C_2C_3)=172.6^\circ$, $\theta(C_2C_3C_4)=144.9^\circ$, and $\theta(C_3C_4Cl)=131.5^\circ$], the lowest-lying quartet state with the same symmetry (A') as that of the doublet ground state has a linear structure [$\theta(C_1C_2C_3)=180.0^\circ$, $\theta(C_2C_3C_4)$

=179.2°, and $\theta(C_3C_4Cl)=178.3^\circ$] according to our preliminary DFT calculations. This quartet state (⁴A') obtained using SAC-CI SD-*R* theory is also shown to have a linear structure [$R(C_1C_2)=1.400$ Å, $R(C_2C_3)=1.269$ Å, $R(C_3C_4)=1.295$ Å, and $R(C_4Cl)=1.627$ Å; $\theta(C_1C_2C_3)=179.7^\circ$, $\theta(C_2C_3C_4)=179.5^\circ$, and $\theta(C_3C_4Cl)=180.0^\circ$ in the limit of C_s symmetry]. Though the crucial bond angle, $\theta(C_1C_2C_3)$, for the doublet ground state of C₄Cl radical resulted through the SAC-CI calculations is larger than the value resulted through BLYP calculations, its bent nature is clearly noticed.

The foregoing results and arguments clearly support the conclusions arrived in the earlier experimental study¹ that the CCCCCl radical has the ground state correlating ²Π symmetry with a bent molecular structure.

D. Excited states through SAC-CI theory

We also calculated some low-lying doublet excited states of C₄Cl radical by using the SAC-CI general-*R* at the ground state geometry obtained using the general-*R* theory. Table IV shows the vertical excitation energies and oscillator strengths, along with the available experimental value. Understandably, the transition energy due to the transition between the highest occupied and the singly occupied molecular orbitals with *a*'' and *a*' symmetries, respectively, is very small, 0.11 eV. A schematic diagram of molecular orbitals with the symmetries was given in Fig. 1. The vertical excitation energy for the next transition, formation of the Σ state, is 0.69 eV. Our preliminary calculations using SAC-CI

TABLE IV. Calculated vertical excitation energies of some low-lying doublets of C₄Cl. (π_{out} and π_{in} represents out-of-plane π and in-plane π orbitals, respectively.)

State	Nature	SAC-CI general- <i>R</i> /cc-pVTZ		Expt. ^a
		ΔE (eV)	<i>f</i>	
X ² A' (II)	Ground state	
1 ² A'' (II)	4 π_{out} -4 π_{in}	0.11	0.0000	
2 ² A' (Σ)	13 σ -4 π_{in}	0.69	0.0180	
3 ² A' (II)	3 π_{in} -4 π_{in}	3.34	0.1351	2.90 ^b
2 ² A'' (II)	3 π_{out} -4 π_{in}	3.34	0.0000	
3 ² A'' (II)	2 π_{out} -4 π_{in}	6.70	0.0000	

^aReference 2.^bAdiabatic excitation energy.

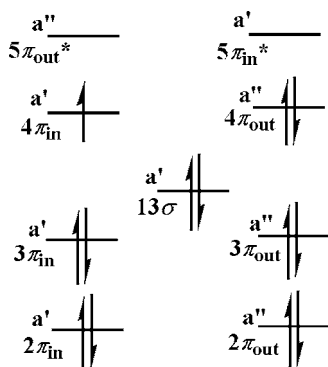


FIG. 1. Schematic diagram of orbital energy levels of the ${}^2\Pi$ state in the C_4Cl radical.

SD-*R* LevelTwo with D95(*d*) basis set show that the adiabatic excitation energy for this transition is a mere 0.18 eV. These results clearly reveal that these two states, Π and Σ , are existing very close to each other. Additionally, the geometry calculated for the Σ state using the SAC-CI SD-*R* theory is very close to linear: $R(\text{C}_1\text{C}_2)=1.241 \text{ \AA}$, $R(\text{C}_2\text{C}_3)=1.367 \text{ \AA}$, $R(\text{C}_3\text{C}_4)=1.212 \text{ \AA}$, and $R(\text{C}_4\text{Cl})=1.650 \text{ \AA}$; $\theta(\text{C}_1\text{C}_2\text{C}_3)=179.6^\circ$, $\theta(\text{C}_2\text{C}_3\text{C}_4)=179.1^\circ$, and $\theta(\text{C}_3\text{C}_4\text{Cl})=179.5^\circ$. The small energy difference between the Π and Σ states along with the linear nature of the Σ state makes a room to believe that strong vibronic coupling exists between these two states.

The main excitation comes from $\pi_{\text{in-plane}} \rightarrow \pi_{\text{in-plane}}$ transition. The excitation energy, 3.34 eV, obtained for this optically bright state is close to the experimental value, 2.90 eV.² It should be noticed here that the experimental value is an adiabatic one. Adiabatic excitation energy for this transition calculated using the SAC-CI SD-*R* is 3.15 eV. The existence of the Π ground state and the nearby Σ state within 0.18 eV energy separation might be a reason for the observed broadening in the experimental spectra.² Excitation energies for two other excited states were also tabulated in Table IV.

IV. CONCLUDING REMARKS

The computations using high-level *ab initio* through the SAC-CI 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 contradiction¹ 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, possibly due to the vibronic coupling. The present calculations using DFT with large basis sets up to augmented quintuple-zeta (aug-cc-pV5Z) basis set also result a bent ground state structure.

Unfortunately, the results derived through coupled-cluster based theories suffer a setback due to their in-bound spin contamination problem. The fundamental UHF wave function upon which these coupled-cluster calculations were made does not represent for a pure C_4Cl doublet ground state

rather it is mixed with the quartet state wave function. Due to the spin contamination, the C_4Cl structure calculated using these theories has a linear nature.

The vertical excitation energies of some excited states were calculated using the SAC-CI general-*R* theory. The ${}^2\Sigma$ state exists just around 0.2 eV above the ground ${}^2\Pi$ state. The excitation energy for the main transition calculated in the present study compared well with the experimental value.

Unlike the C_{2n}H carbon-chain series radicals, the C_{2n}Cl radicals studied so far, C_2Cl and C_4Cl , show nonlinear ground state structures. The C_{2n}H radicals have been extensively studied in the past. Electronic absorption spectra of C_{2n}H , $n \leq 8$, have been measured. The C_{2n}H radicals up to $n=4$ have also been studied using theoretical methods. These show that all the studied C_{2n}H radicals have linear ground state structures. The studies also reveal two closely lying ${}^2\Sigma$ and ${}^2\Pi$ electronic states, the latter being the lowest for $n \geq 3$. For example, the ${}^2\Sigma$ ground state of C_2H exists 0.46 eV below the first excited ${}^2\Pi$ state. In C_4H , the ${}^2\Sigma$ and ${}^2\Pi$ states are nearly degenerate and the energy difference between the ${}^2\Sigma$ ground and the nearby ${}^2\Pi$ states is just 0.01 eV. In C_6H the ${}^2\Pi$ state is the ground state; the nearby ${}^2\Sigma$ state is lying 0.18 eV above the ground state. Again in the C_8H case, ${}^2\Pi$ state is the ground state and the energy difference between this ground and the ${}^2\Sigma$ states is 0.25 eV. Because of these small energy differences between the ground and the first excited states, these two electronic states interact strongly which makes the vibrational and electronic spectroscopy of these radicals complicated and challenging for both experimentalists and theoreticians.

Only a few members of the C_{2n}Cl carbon-chain series, on the contrary, have been studied so far. Among them, the symmetry of the ground state, ${}^2\Sigma$ and ${}^2\Pi$, respectively, the energy difference between these two states is now known for C_2Cl and C_4Cl radicals only. But the results show some interesting signs: contrary with their C_{2n}H counterparts, these two radicals have bent ground state structures. While the C_2Cl has a ${}^2\Sigma$ ground state as the C_2H radical has, the C_4Cl has a ${}^2\Pi$ ground state contrary from the situation in its C_4H counterpart. On the other hand, as in C_{2n}H radicals, these states lie very closely. In C_2Cl , the ${}^2\Sigma$ state is lying just 0.03 eV below the ${}^2\Pi$ state and in C_4Cl , the energy difference between the ${}^2\Pi$ ground state and the nearby ${}^2\Sigma$ state is 0.18 eV according to the present study. Studies on C_{2n}Cl carbon series are promising by considering the following facts: (1) Many linear C_nH radicals with $n < 9$ have been detected in space, and in both molecular cloud cores and certain circumstellar shells, they are among the most abundant reactive molecules known. (2) Chains as long as C_{16}H have now been detected in the laboratory. In this sense, the results obtained in the present study are valuable in many aspects.

ACKNOWLEDGMENT

This study has been supported by the Grant for Creative Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

- ¹Y. Sumiyoshi, K. Katoh, and Y. Endo, *Chem. Phys. Lett.* **414**, 82 (2005).
- ²J. van Wijngaarden, I. Shnitko, A. Batalov, P. Kolek, J. Fulara, and J. P. Maier, *J. Phys. Chem. A* **109**, 5553 (2005).
- ³A. Largo, A. Cimas, P. Redondo, and C. Barrientos, *Int. J. Quantum Chem.* **84**, 127 (2001).
- ⁴Y. Sumiyoshi, T. Ueno, and Y. Endo, *J. Chem. Phys.* **119**, 1426 (2003).
- ⁵J. van Wijngaarden, A. Batalov, I. Shnitko, J. Fulara, and J. P. Maier, *J. Phys. Chem. A* **108**, 4219 (2004).
- ⁶G. Li and Z. Tang, *J. Phys. Chem. A* **107**, 5317 (2003).
- ⁷R. F. Curl, P. G. Carrick, and A. J. Merer, *J. Chem. Phys.* **82**, 3479 (1985).
- ⁸W. B. Yan, J. L. Hall, J. W. Stephens, M. L. Richnow, and R. F. Curl, *J. Chem. Phys.* **86**, 1657 (1987).
- ⁹H. Kanamori, K. Seki, and E. Hirota, *J. Chem. Phys.* **87**, 73 (1987).
- ¹⁰H. Kanamori and E. Hirota, *J. Chem. Phys.* **88**, 6699 (1988).
- ¹¹K. Kawaguchi, T. Amano, and E. Hirota, *J. Mol. Spectrosc.* **131**, 58 (1988).
- ¹²W.-B. Yan, H. E. Warner, and T. Amano, *J. Chem. Phys.* **94**, 1712 (1991).
- ¹³W.-B. Yan and T. Amano, *J. Chem. Phys.* **99**, 4312 (1993).
- ¹⁴M. C. McCarthy, C. A. Gottlieb, P. Thaddeus, M. Horn, and P. Botschwina, *J. Chem. Phys.* **103**, 7820 (1995).
- ¹⁵H. Suzuki, M. Ohishi, N. Kaifu, S. Ishikawa, T. Kasuga, S. Saito, and K. Kawaguchi, *Publ. Astron. Soc. Jpn.* **38**, 911 (1986).
- ¹⁶M. C. McCarthy, W. Chen, A. J. Apponi, C. A. Gottlieb, and P. Thaddeus, *Astrophys. J.* **520**, 158 (1999).
- ¹⁷E. Herbst, *Annu. Rev. Phys. Chem.* **46**, 27 (1995).
- ¹⁸A. Largo and C. Barrientos, *Chem. Phys.* **138**, 291 (1989).
- ¹⁹A. Largo-Cabrerizo and C. Barrientos, *Chem. Phys. Lett.* **155**, 550 (1989).
- ²⁰M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision B.01, Gaussian, Inc., Pittsburgh, PA, 2003.
- ²¹A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ²²C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ²³J. P. Perdew, K. Burke, and Y. Wang, *Phys. Rev. B* **54**, 16533 (1996).
- ²⁴A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ²⁵R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).
- ²⁶A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **72**, 5639 (1980).
- ²⁷D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **98**, 1358 (1993) and references therein.
- ²⁸H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978).
- ²⁹H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, 2053 (1978).
- ³⁰H. Nakatsuji, *Chem. Phys. Lett.* **67**, 329 (1979).
- ³¹H. Nakatsuji, K. Ohta, and T. Yonezawa, *J. Phys. Chem.* **87**, 3068 (1983).
- ³²H. Nakatsuji, *Chem. Phys. Lett.* **177**, 331 (1991).
- ³³H. Nakatsuji, *J. Chem. Phys.* **83**, 713 (1985).
- ³⁴W.-C. Chen, N.-Y. Chang, and C.-H. Yu, *J. Phys. Chem. A* **102**, 2584 (1998).
- ³⁵P. R. Schreiner, *J. Am. Chem. Soc.* **120**, 4184 (1998).
- ³⁶C. J. Cramer, *J. Am. Chem. Soc.* **120**, 6261 (1998).
- ³⁷C. J. Cramer, *Essentials of Computational Chemistry Theories and Models* (Wiley, England, 2002).
- ³⁸E. F. C. Byrd, C. D. Sherrill, and M. Head-Gordon, *J. Phys. Chem. A* **105**, 9736 (2001).
- ³⁹G. J. O. Beran, S. R. Gwaltney, and M. Head-Gordon, *Phys. Chem. Chem. Phys.* **5**, 2488 (2003).