Formation mechanism of CCl_4^- anion in condensed phase: a direct ab initio dynamics study

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Abstract

The structures and electronic states of the CCl_4^- anion in the condensed phase have been studied by direct ab initio dynamics calculation. The calculation showed that two stationary points were obtained as stable forms of CCl_4^-, which correspond to elongated and compressed forms of CCl_4^-. The elongated form has an elongated C–Cl bond, whereas the compressed form has a shorter C–Cl bond in CCl_4^-. The MP4SDQ/6-31G* calculation indicated that the elongated form is energetically more favored than the compressed form. However, the contact spin density for the elongated form disagrees with that measured by electron spin resonance spectroscopy in the condensed phase. By contrast, the spin density for the compressed form is in reasonable agreement with the experiment. The formation mechanism of the compressed form in the condensed phase is discussed on the basis of direct ab initio dynamics calculation. The present results strongly indicated that the CCl_4^- has the compressed form in condensed form. (Int J Mass Spectrom 177 (1998) 17–21) © 1998 Elsevier Science B.V.

Keywords: Direct ab-initio dynamics; Trajectory; CCl_4^-; Spin density

1. Introduction

Tetrachlorolomethane CCl_4 is one of the most popular molecules in radiation chemistry because of its ability to capture electrons and holes [1]. In addition, its ionic species formed in the condensed phase, anion and cation radicals, have been extensively studied as a model of halocarbons [2]. A large number of the studies on electron spin resonance (ESR), pulse and γ radiolysis of CCl_4 have been presented [1,2].

For the anion radical of CCl_4^-, Bonazzola et al. [3] measured hyperfine coupling constant (hfc) and spin density by electron spin resonance spectroscopy. The ESR spectrum of CCl_4^- trapped in CCl_4 matrices at 77 K indicated that CCl_4^- has a C_{3v} structure and the excess electron is occupied in σ^* antibonding orbital. In addition, they carried out an ab-initio MO calculation of CCl_4^- with a minimal basis set (STO-3G) and suggested that the CCl_4^- has the compressed form in which one of the C–Cl bonds is shortened.

For CCl_4^-, the elongated and compressed forms are competitive after the electron attachment of the neutral CCl_4 molecule. However, the previous study considered only the compressed from of CCl_4^- [3]. In our recent article [4], by using direct ab initio molecular orbital (MO) dynamics calculation, we suggested that the vertical electron attachment of CCl_4 leads to

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the elongated form in the gas phase. The discrepancy between experiment and theoretical calculation is still not resolved [4].

From a theoretical point of view, Gutsev [5] investigated the electronic and geometric structures of the anion radicals CCl_n^- (n = 1–4) by means of the local density functional (LDF) method. The calculations implied that the anion CCl_4^- is nonrigid because of the presence of a number of local minima on the potential energy surface. Lunell and co-workers [6] calculated the structure of $CFCl_3^+$, which is very similar to CCl_4^+, by means of the HF/3-21G* method. They suggested that $CFCl_3^+$ is unstable and spontaneously dissociates to $CFCl_2^+$ and a Cl atom. Although the structures of ionic species of CCl_4 seem to be understood theoretically, the formation mechanism is scarcely known.

In the present study, in order to elucidate the formation mechanism of CCl_4^- in the condensed phase, direct ab initio dynamics calculations are carried out for the electron capturing process in CCl_4. In addition, the spin density of CCl_4^- is calculated by the ab initio MO method, including electron correlation with large basis sets. The structure of CCl_4^- and formation mechanism in the condensed phase is discussed on the basis of theoretical results.

2. Method of calculations

The structures of the elongated and compressed forms of CCl_4^- were chosen as those obtained by the Møller-Plesset fourth-order perturbation (MP4SDQ) method with /6-31G* basis set [7], previously obtained by us [4]. The electronic states of the complexes were further calculated at the MP2/6-31+G* level.

In order to elucidate the formation mechanism of the CCl_4^- anion, direct ab initio dynamics calculations were carried out for the electron capturing process. Details of the direct ab initio dynamics method are described in our recent article [4,8]. The full dimensional potential energy surface used in the direct MO dynamics was calculated at the HF/STO-3G level.
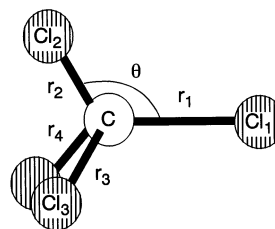

Fig. 1. Structure and geometric parameters of the CCl_4 system.

Geometric parameters used are given in Fig. 1. The symmetry of the complex was assumed to be C_{3_v} in the ab initio MO calculations, whereas no symmetry restriction was used in the direct MO dynamics calculations.

3. Results and discussion

3.1. Structures of CCl_4^-

The structures of CCl_4 for neutral and anion molecules calculated at the MP4SDQ/6-31G* level, previously obtained by us [4], are employed in the present study throughout. The characteristics of the structures are summarized as follows. The geometry optimizations of CCl_4^- gave two stationary points corresponding to the elongated and compressed forms of CCl_4^-. In the elongated form, one of the C–Cl bonds is longer than the other C–Cl bonds, whereas that one is shorter than the others in the compressed form. The optimized parameters are given in Table 1. For neutral CCl_4, bond distance of C–Cl is calculated to be 1.776 Å at the MP4SDQ/6-31G* level.

Table 1
Geometric parameters used in the present study

| | CCl$_4$ | CCl$_4^-$ | |
		Compressed	Elongated
r_1	1.776	1.816	2.482
r_2	1.776	1.985	1.777
θ	109.5	106.6	108.6

The parameters for CCl_4 and CCl_4^- were calculated at the MP4SDQ/6-31G* level. Bond lengths and angles are in angstroms and in degrees. The values cited are from our previous study [4].

Table 2
Contact spin densities on atoms of CCl_4^- for the elongated and compressed forms

Atom[a]	MP4SDQ/6-31G*		MP2/6-31+G*	
	Compressed	Elongated	Compressed[b]	Elongated
C	1.496	0.694	1.470 (1.365)	0.680
Cl(1)	0.032	0.250	0.042 (−0.017)	0.235
Cl(3)	0.203	0.028	0.192 (0.235)	0.031

The value is in a.u.
[a] Cl(3) indicates three equivalent chlorine.
[b] HF/6-31+G* values are given in parentheses.

In the case of the elongated form of CCl_4^-, a longer C–Cl bond is calculated to be 2.482 Å, which is 40% longer than the others ($r_2 = 1.777$ Å). By contrast, the compressed form has three equivalent C–Cl bonds (1.985 Å) which are slightly longer than the other one (1.816 Å).

Total energies for the compressed and elongated forms are calculated to be −1876.4483 and −1876.4672 a.u., respectively [3], suggesting that the elongated form is energetically favored, although the energy difference amounts to only 4.2 kcal/mol.

3.2. Spin densities

The spin density on each Cl atom for the elongated and compressed forms is calculated by both the MP4SDQ/6-31G* and MP2/6-31+G* levels. The values are given in Table 2. Cl(3) means three equivalent chlorine atoms in CCl_4^-, and Cl(1) is a chlorine atom located on the C_3 axis. In the compressed form, contact spin density on the Cl(3) atom is much larger than that of Cl(1). On the other hand, in the elongated form, the Cl(1) atom is significantly larger than that of Cl(3).

Bonazzola et al. [3] measured the spin densities of CCl_4^- formed in the CCl_4 matrix at 77 K. By analyzing the ESR spectrum of CCl_4^-, it was suggested that the CCl_4^- has C_{3_v} symmetry and the contact spin density of Cl(3) is four times larger than that of Cl(1). The present study indicated that contact spin density on Cl(3) is larger than that of Cl(1) in the compressed form, whereas in the elongated form spin density on Cl(1) is larger than that on Cl(3). This result strongly
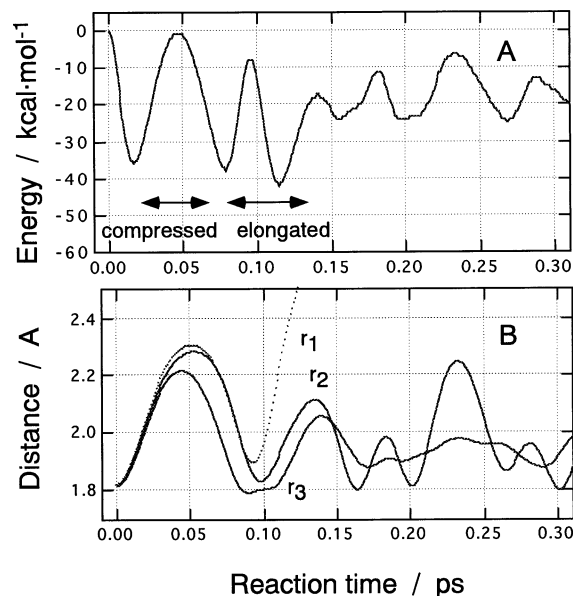

Fig. 2. A sample trajectory for the CCl_4^- anion formed by the vertical electron attachment of CCl_4 plotted as a function of reaction time. (A) The potential energy of the reaction system, and (B) interatomic distances, r_1, r_2, and r_3 vs. time.

indicates that CCl_4^- has a compressed structure in the condensed phase.

3.3. Trajectory of CCl_4^- formation

As mentioned above, the ab initio MO calculation shows that the CCl_4^- observed in the condensed phase would be the compressed form, although the compressed form is energetically less favored than the elongated form. In this section, in order to elucidate the formation mechanism of the compressed form in the condensed phase, we have made direct ab initio dynamics calculations of the electron attachment process in CCl_4. The optimized structure and several points around the optimized structure of CCl_4 were chosen as the initial structure of the CCl_4^- in the dynamics calculation.

The potential energy for the trajectory is plotted in Fig. 2 as a function of reaction time. The energy is lowered at the short time region of 0.0–0.02 ps. This is because CCl_4^- is deformed spontaneously by the Jahn-Teller effect. The C–Cl bond distances are plot-

ted in Fig. 2(B) (three bond distances r_1, r_2, and r_3 only are given). All C–Cl bond distances in CCl_4^- are equivalent at time zero. At short time region (0.03– 0.08 ps), all C–Cl bonds are elongated. Three equivalent C–Cl bonds (denoted by r_1, r_2, and r_4) especially, are much elongated, whereas the expansion of C–Cl distance r_3 is shorter than those of the others: one of the C–Cl bonds is shorter than that of the others. Hence, the structure of CCl_4^- has the elongated form in the first stage. In the second stage (0.08 < t < 0.13 ps), by contrast, one of the C–Cl bonds is much elongated, suggesting that CCl_4^- has the elongated form in the second stage. In the case of this trajectory, Cl^- ion dissociated from the CCl_3 moiety at long time region. All trajectories show similar results, i.e. all trajectories proceed via the compressed form at the first stage.

3.4. Formation mechanism

On the basis of the present calculation, we would propose a reaction model on the formation of the compressed form CCl_4^- in the condensed phase. Schematic representation of the model is illustrated in Fig. 3, where a trapping cavity and medium are expressed by a circle and hatched region around the cavity, respectively. At neutral state, CCl_4 molecule is surrounded by medium. Fig. 3(A) shows the neutral CCl_4 molecule trapped in the cavity. All C–Cl bonds of CCl_4 are equivalent. By electron capturing [Fig. 3(B)], the electronic state of CCl_4 is suddenly changed, so that the structural deformation of CCl_4^- occurs. At the first stage, CCl_4^- has the compressed form: three equivalent C–Cl bonds are largely elongated [Fig. 3(C)]. This deformation may cause the energy transfer to surrounding medium and the excess energy on CCl_4^- would disperse to medium molecule in condensed phase. If the energy transfer is large enough to keep the structure, CCl_4^- exists as the compressed form because of activation barrier between the compressed and elongated forms. Thus, this model reasonably explains the experimental feature in condensed phase.
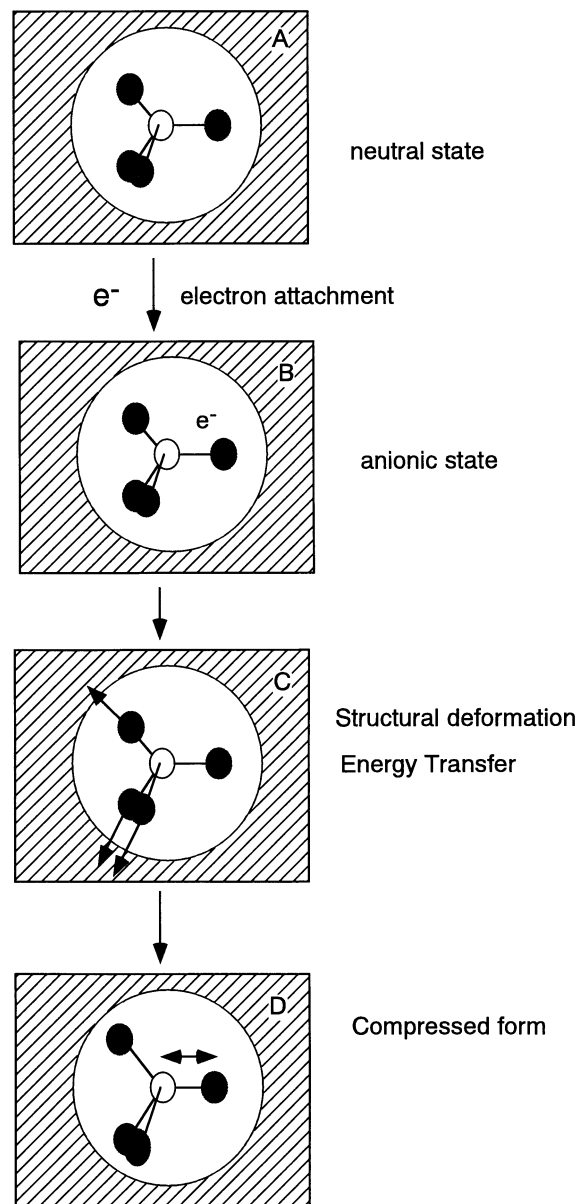

Fig. 3. Reaction model for the electron capturing process of CCl_4 in the condensed phase. (A) The neutral CCl_4 molecule trapped in cavity. (B) The anionic state of CCl_4^- after the electron attachment. (C) Energy transfer from CCl_4^- to medium molecule. Arrows indicate the direction of the energy transfer. (D) The anionic state CCl_4^- stabilized in the cavity. The compressed form is preferentially formed in the cavity. The arrow indicates the compressed C–Cl bond of CCl_4^-.

Acknowledgements

References

[1] A. Lund, M. Shiotani, in A. Lund (Ed.), Radical Ionic Systems, Kluwer, Dordrecht, 1991.

[2] (a) A.S. Domazou, A.M. Quadir, R.E. Bühler, J. Phys. Chem. 98 (1994) 2877. (b) R.E. Bühler, B. Hurni, Helv. Chim. Acta 61 (1978) 90. (c) J.L. Gebicki, A.S. Domazou, T.-K. Ha, G. Cirelli, R.E. Bühler, J. Phys. Chem. 98 (1994) 9570. (d) J.P. Suwalski, Radiat. Phys. Chem. 46 (1995) 53. (e) A.E. Reed, F. Weinhold, R. Weiss, J. Macheleid, J. Phys. Chem. 89 (1985) 2688.

[3] L. Bonazzola, J.P. Michaut, J. Roncin, Chem. Phys. Lett. 153 (1998) 52.

[4] H. Tachikawa, J. Phys. Chem. 101 A (1997) 7454.

[5] G.L. Gutsev, J. Phys. Chem., 95 (1991) 5773.

[6] M.-B. Huang, S. Lunell, K. Karlsson, Chem. Phys. Lett. 171 (1990) 265.

[7] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Ab-initio MO calculation program: Gaussian 94, Gaussian 94, Revision D.3, Gaussian, Inc., Pittsburgh, PA, 1995.

[8] (a) H. Tachikawa, K. Komaguchi, Int. J. Mass Spectrom. Ion Processes 164 (1997) 39. (b) H. Tachikawa, J. Phys. Chem. 100 (1996) 17090. (c) H. Tachikawa, J. Organometal. Chem. 555 (1998) 161.