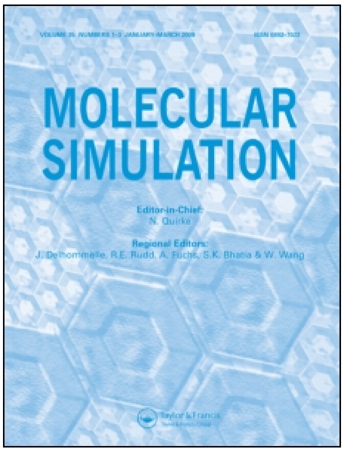

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INTERMOLECULAR INTERACTION OF FLUORO PROPANES

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Intermolecular interaction is investigated for an isomeric pair of fluoro propane, $CH_3CF_2CF_3$ (HFC-245cb, CB) and $CH_2FCF_2CHF_2$ (HFC-245ca, CA). CB has a larger dipole moment than CA. This may suggest that CB has a larger intermolecular attractive interaction than CA; the reverse is, however, found from the experimental data: normal boiling point, critical temperature, and heat of vaporization. Systematic *ab initio* calculations have been done for both CB dimer and CA dimer, and confirmed that the former has a smaller attractive interaction than the latter.

On the basis of these calculations, analytic functions have been constructed as the pair potential models for the two isomers. Each of these models has 11 Lennard-Jones and Coulomb interaction sites in the molecule. The present models can explain why CB dimer has a smaller attractive interaction than CA dimer, and they will easily be extended to a series of fluoro propanes, and make it possible to perform the systematic molecular simulation studies.

KEY WORDS: *Ab initio* calculation, CFC alternatives, fluoro alkane, pair potential model

1 INTRODUCTION

Since the Montreal protocol in 1987 limited the industrial production of certain chloro fluoro carbons (CFCs), the necessity has increased to search the environmentally safe refrigerants with a low contribution to the ozone depletion and the global warming. Hydro fluoro carbons (HFCs) are expected as a promising alternative refrigerant to CFCs; some fluoro ethanes have already been used for such a purpose, and some fluoro propanes have been synthesized and tested experimentally. Although a lot of experimental reports have appeared on the thermo-physical properties of HFCs [1, 2], there are few theoretical studies based on a microscopic consideration. Our main purpose is to study the thermodynamic (macroscopic) properties of fluoro propane fluid in connection with their intermolecular (microscopic) properties. Thermodynamic properties are governed by the intermolecular interaction. We start such a microscopic investigation from a construction of

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Table 1 The dipole moment and thermodynamic properties of CB and CA.

Formula	*dipole moment*† *(Debye)*	T_b *(K)*	T_c *(K)*	ΔH_{vap} *(kJ·mol^{-1})*
$CH_3CF_2CF_3$ (CB)	2.2363	254.85	381.65	23.65
$CH_2FCF_2CHF_2$ (CA)	1.7315	298.11	451.55	29.05

† Evaluated from our *ab initio* calculation (6–31G*/MP2).

reliable pair potential models for certain fluoro propanes, for there is no reliable model for them at present.

It is widely known for fluoro alkanes that the monomer properties do not seem to be consistent with the fluid thermodynamic properties: *when an isomer has a fully fluorinated terminal carbon (CF_3), its boiling point is lower than that of the other isomers without CF_3*. One can see a typical example in the case of a pair of isomer, $CH_3CF_2CF_3$ (HFC-245cb, CB) and $CH_2FCF_2CHF_2$ (HFC-245ca, CA)[2]. In Table 1, some of their physical properties are summarized with the dipole moments evaluated from our *ab initio* calculation. Since CB molecule has CF_3 group, its dipole moment is larger than that of CA; thus CB may be expected to have a larger intermolecular attractive interaction than CA. The experimental thermodynamic properties, however, suggest that CA has a larger attractive interaction than CB; for example, CA has a nearly 40 K higher normal boiling point (T_b) than CB. In this article, we mainly discuss such an reversal. Furthermore, we try to extract the intrinsic factor of the intermolecular interaction which is dominant for a series of fluoro propanes.

2 QUANTUM-CHEMICAL CALCULATIONS

Systematic quantum-chemical calculations have been carried out to estimate the magnitude of the intermolecular interaction for both CB and CA using GAUSSIAN 90 package program [4]. Throughout the calculations, the 3–21G basis set was used, and the electron correlation effects were introduced by the second order of Møller-Plesset (MP2) perturbation theory.

There are some rotational isomers for CA. The structure of each rotational isomer was optimized by the energy gradient method. The ratio of Boltzmann factor was found to be about 9 : 1 at 300 K between the most stable rotational isomer and the second one; thus we treated only the most stable rotational isomer for CA in this work. On the other hand, there is no rotational isomer for CB. In our calculations, such optimized molecular structure was used as a rigid body.

The calculations have been done at several intermolecular distances for 29 (CB) and 30 (CA) kinds of dimer configuration; eight representative configurations are depicted in Fig. 1 (a) to (d) for CB, and (e) to (h) for CA, respectively. We call these configurations as CA1 to CA4 and CB1 to CB4.

The potential curves for CB1 to CB4 are shown in Fig. 2 (a) to (d) with dashed lines and open circles; those for CA1 to CA4 are shown in Fig. 3 (a) to (d). From these figures, one can see an attractive interaction in cases CB2 to CB4 and CA2 to CA4. We call attention to the following observations:

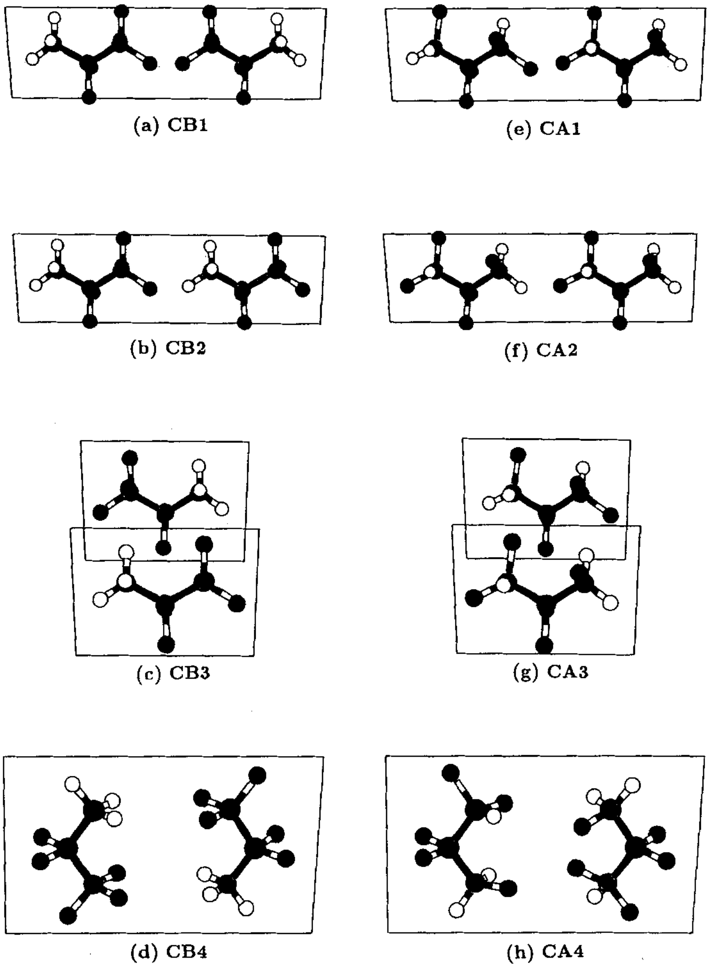

Figure 1 Definitions of the dimer configurations for (a) CBI, (b) CB2, (c) CB3, (d) CB4, (e) CA1, (f) CA2, (g) CA3, and (h) CA4. In these figures, white, black, and gray spheres refer to H, F, and C, respectively.

1. The attractive interaction is characterized by the intermolecular electrostatic interaction between H and F. If there exists the hydrogen bond like interaction such as C–H· · ·F–C, the potential curve shows large attractive interaction. We call such a interaction as H· · ·F bond hereafter. If the H· · ·F bond cannot be formed, the potential curve is repulsive type as seen in the cases of CA1 and CB1.
2. There is a noticeable difference in the potential minimum between CA2 and CB2 configurations, for which one H· · ·F bond is formed. *Note that the order is reverse of the magnitude of the dipole moment given in Table 1.*
3. The magnitude of the attractive interaction is almost proportional to the number of the H· · ·F bond as seen from the comparisons among CA2 to CA4 and CB2 to CB4 in which one, two, and four H· · ·F bonds are formed.

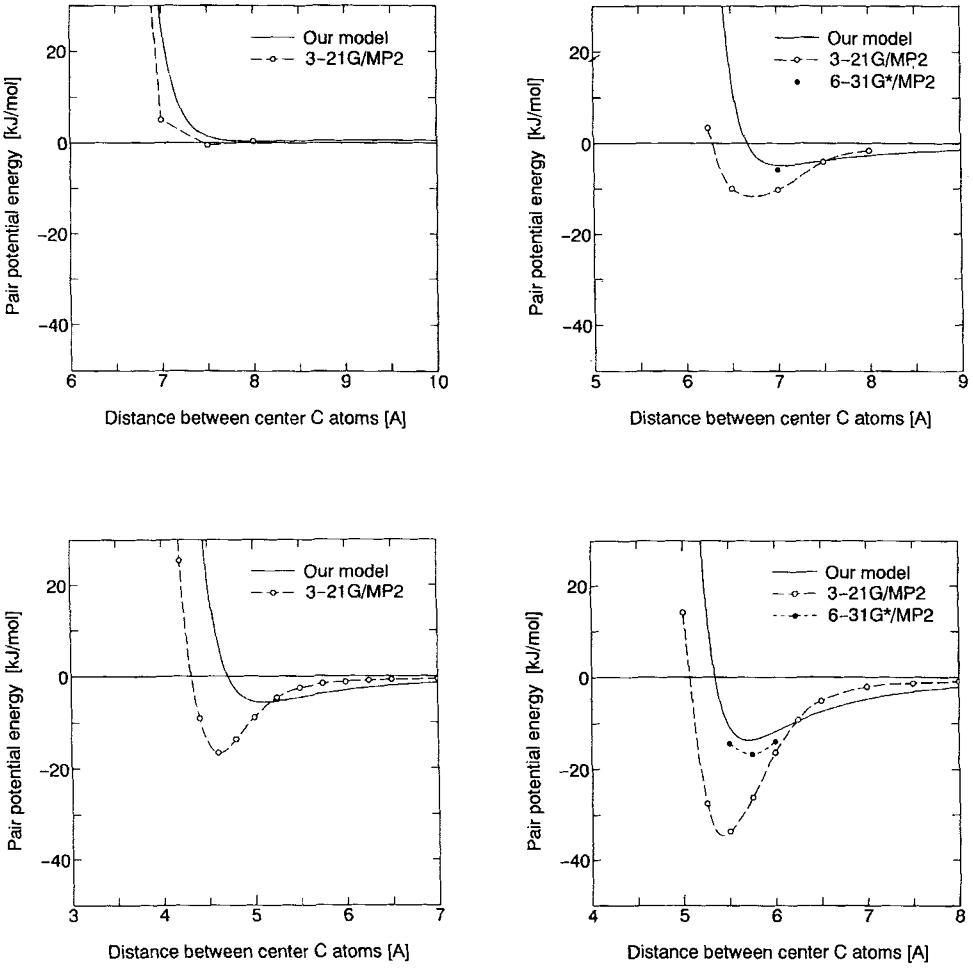

Figure 2 Comparison of the intermolecular potential curves of CB dimer: (a) CB1, (b) CB2, (c) CB3, and (d) CB4. In these figures, solid lines are our model; dashed lines with open circles are 3-21G/MP2 data; dotted lines with filled circles are 6-31G*/MP2 data.

The above differences in the potential minima are considered as one of the origins that makes the peculiar difference in the thermodynamic properties between CB and CA.

3 POTENTIAL MODELS

In the previous section, we have shown that CA dimer has a larger attractive interaction than CB dimer in certain configurations in which the H···F bonds are formed; this is consistent with the magnitude of the fluid thermodynamic properties,

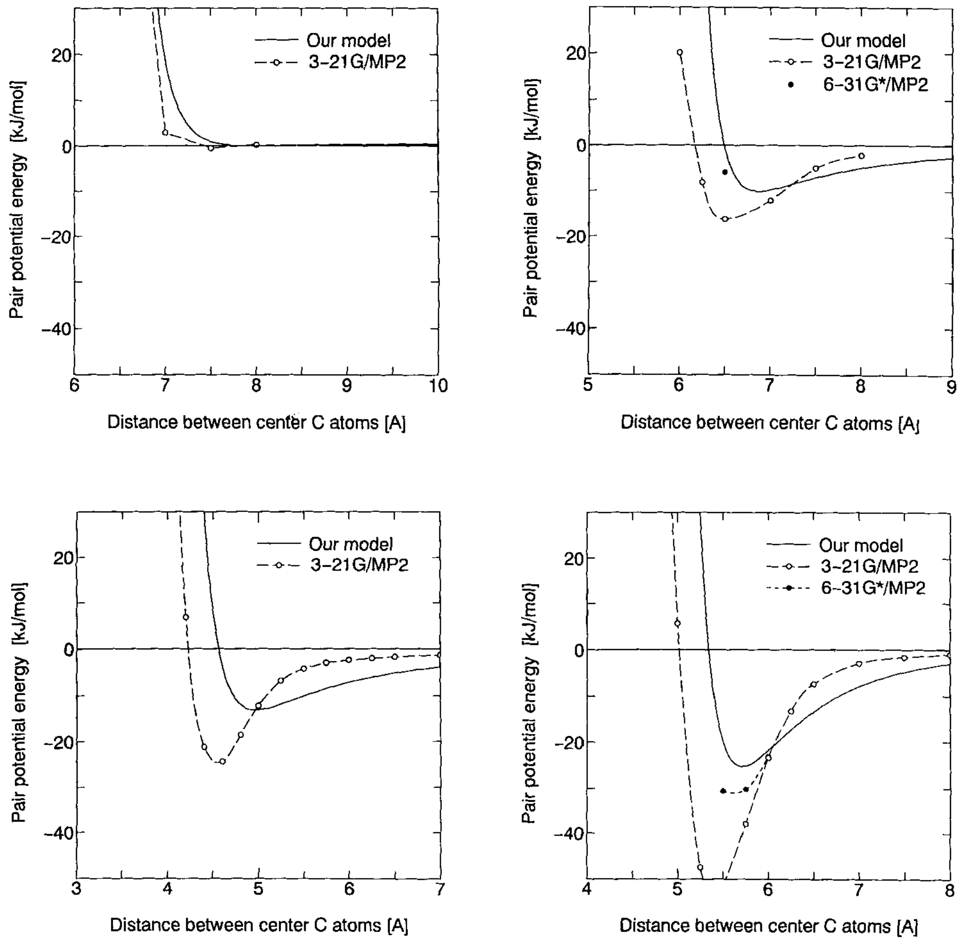

Figure 3 Comparison of the intermolecular potential curves of CA dimer: (a) CA1, (b) CA2, (c) CA3, and (d) CA4. In these figures, solid lines are our model; dashed lines with open circles are 3-21G/MP2 data; dotted lines with filled circles are 6-31G*/MP2 data.

but does not agree with that of the dipole moment of each monomer. To investigate this discrepancy, we tried to perform the molecular simulations on the fluid structures. For such the purpose, the pair potential models have been constructed for CB and CA. We have adopted the 11 sites "Lennard-Jones (LJ) + Coulomb" type function as

$$E_{pair} = \sum_{a}^{11}\sum_{b}^{11}\left[4\varepsilon_{ab}\left(\left(\frac{\sigma_{ab}}{r_{ab}}\right)^{12} - \left(\frac{\sigma_{ab}}{r_{ab}}\right)^{6}\right) + \frac{e^2 z_a z_b}{4\pi\varepsilon_0 r_{ab}}\right], \tag{1}$$

where subscripts a and b refer to the a-th and b-th sites in the paired molecules, r_{ab}, ε_0, and e are the distance between sites, the dielectric constant of vacuum, and the charge of the electron. The L-J parameters (ε_{ab}, σ_{ab}) for each atom (C, H, F)

Table 2 Potential parameters common to CB and CA.

Atom	σ_{aa} *(Å)*	ε_{aa}/k_B *(K)*	z_a *(e)*
H	2.370	21.14	+0.21
F	2.940	39.25	−0.30
C	3.207	45.44	†

† To be determined to give neutral charge for each carbon unit (CH_3, CF_2, CF_3, CH_2F, and CHF_2).

were taken form CHARM package program [3] without any modifications, and the cross terms were determined by the Lorentz-Berthelot combining rule. The partial charges (z_a, z_b) for H and F atoms were evaluated from our Mulliken population analysis on CB and CA monomers with the 6–31G*/MP2 level. The Mulliken population analysis showed that the partial charges for H atoms are almost identical in both CB and CA monomers; the same is true for F atoms. Thus, the common values are used for CB and CA. These parameters are summarized in Table 2. The population analysis also shows that a partial charge for each carbon unit (CH_3, CF_2, CF_3, CH_2F, and CHF_2) is almost neutral; thus we put a partial charge on each C atom to give a neutral charge for above-mentioned each carbon unit. For example, we put a partial charge of $-0.63e$ on C atom in CH_3.

In Figs. 2 and 3, our pair potential models are compared with data. Although our models show qualitative agreement with the *ab initio* data, systematic differences are observed quantitatively. It seems that these quantitative differences between our models and *ab initio* data are attributed to the insufficient basis set; this was confirmed by the comparison with the results using a more flexible basis set (6–31G*/MP2) at several points, which were also plotted in Figs. 2 and 3.

4 ANALYSIS OF H· · ·F BOND

In this section, our potential models are used to discuss the difference between the attractive interaction of CB dimer and that of CA dimer. CB2 and CA2 are adopted as a specific pair of configurations, in which one H· · ·F bond is formed by the sum of each site-site interaction. The molecular interaction energy can be divided into the several contributions of each site-site interaction. These divisions are summarized in Table 3. The energy values used in those divisions are at the points where the both potential curves show minimum values. This table shows that the difference in the attractive interaction is explained by the difference in the coulomb term. In particular, the Coulomb term between the pair of opposite terminal carbon units is the predominant factor; this term consists of 16 site-site components as shown in Fig. 4(a) and (b). The difference in the Coulomb term between the pair of opposite terminal carbon units is explained as below.

1. CB2 has nine pairs of H–F interaction; on the other hand, CA2 has five pairs of H–F, two pairs of H–H, and two pairs of F–F interaction. These site-site interactions make CB2 have over 5 times larger attractive interaction ($-210.6\,\mathrm{kJ\cdot mol^{-1}}$) than CA2 ($-37.6\,\mathrm{kJ\cdot mol^{-1}}$).

Table 3 Factors contributing to the total interaction in CB2 and CA2 configurations (in kJ·mol^{-1})

	Coulomb							L–J	Total
	Opposite terminal carbon unit					Other	Total		
	H–F	H–H F–F	C–C	C–H C–F	Total				
CB	−210.6		−183.9	392.2	−2.3	−1.2	−3.5	−0.0	−3.5
	−210.6		208.3						
CA	−123.8	86.2	−15.1	42.3	−10.4	1.4	−9.0	−0.9	−9.9
	−37.6		27.2						

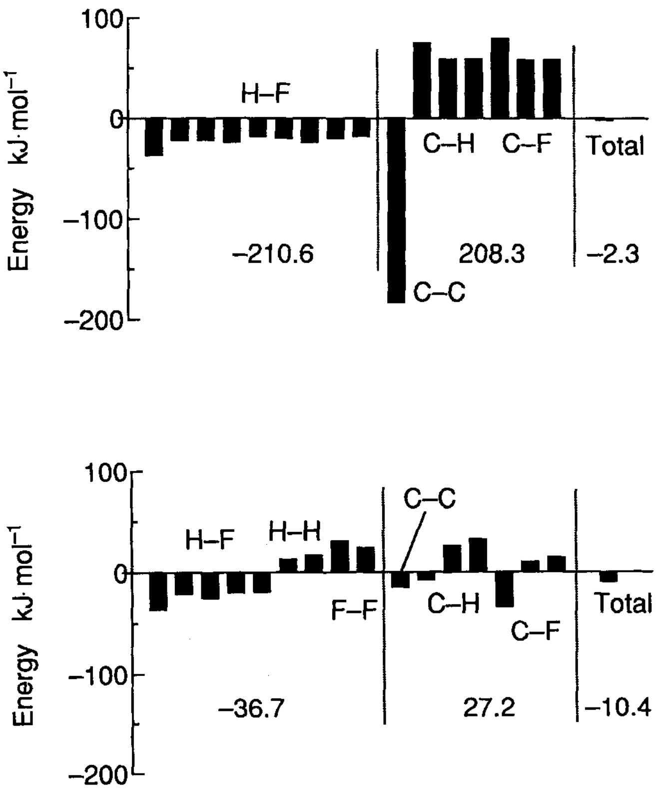

Figure 4 The site-site contributions of the interaction between opposite terminal carbon units for (a) CB2 and (b) CA2.

2. As explained in our model, all carbon units are set to be electrostatically neutral. This leads the each terminal carbon to have notable different partial charge. These values are $0.9\,e$ and $-0.63\,e$ in CB2; on the other hand, those are $0.39\,e$ and $-0.12\,e$ in CA2. The former pair causes a large C–C attractive interaction and, at the same time, extra large C–H and C–F repulsive interactions. The latter pair causes a small C–C attractive interaction and small C–H and C–F repulsive interactions. These site-site interactions make CB2 have over 7 times larger repulsive interaction ($208.3\,\mathrm{kJ \cdot mol^{-1}}$) than CA2 ($27.2\,\mathrm{kJ \cdot mol^{-1}}$).

As demonstrated here, the difference in the partial charge of the terminal C causes large differences in the magnitude of the repulsive C–H and C–F interactions. On the delicate balance between the attractive H–F interaction and the disturbance to them, CA2 has a larger attractive interaction than CB2.

5 CONCLUDING REMARKS

Ab initio quantum-chemical calculations and subsequent preparation of intermolecular potential function have been carried out for a pair of isomers, CB and CA, as representative fluoro propanes. It is because the experimental data indicate that CB has a smaller intermolecular attractive interaction than CA, in spite of the fact that CB has a larger dipole moment than CA.

The *ab initio* calculations showed that the attractive interaction is characterized by the electrostatic intermolecular interaction between H and F. It was also confirmed that the order in the magnitude of the attractive interaction for CB dimer and CA dimer is reverse to that of the dipole moment values. This difference in the attractive interaction can be the reason for the peculiar differences in thermodynamic properties between CB and CA.

To understand the above contents in more detail, we planed to do the molecular simulation for the study on fluid structures. For such a purpose, the pair potential functions have been constructed for CB and CA using atom-atom interaction models. On the basis of our model, this difference is explained as follows. The partial charges located on the C atoms disturb the attractive interaction between H and F. This effect is more significant in CB dimer than in CA dimer because the absolute values of the partial charges on each C atoms are larger in CB than in CA. This make CB dimer have a smaller intermolecular interaction than CA dimer.

The procedure which we adopted to construct the pair potential models for CB and CA is simple and transferrable to other fluoro propanes in general. We can construct the pair potential models and perform the systematic molecular simulation studies in the following manner.

1. The structure of any fluoro propane molecule is optimized by the energy gradient method with *ab initio* quantum-chemical calculations.
2. The L–J parameters can be taken from Table 2.
3. The partial charges for H and F are taken from Table 2, and those for C are determined to give a neutral charge for each carbon unit.
4. The pair potential models are constructed by putting these L–J and Coulomb interaction sites on the optimized atomic positions.
5. One can perform molecular simulations to evaluate thermodynamic properties.

Table 4 Comparison of the critical temperature between experimental and MC results.

	CB *K*	*CA* *K*	*Ratio (CA/CB)*
Experiment	381.65	451.55	1.18
Monte Carlo	446.0	556.2	1.25

Preliminary Monte Carlo (MC) simulations have already been performed using our potential models for CB and CA. The result of our MC simulations for their critical temperatures are shown in Table 4 with the experimental values. Although the MC values are higher than the experimental one for both CB and CA, a good agreement is observed for the ratio (T_c for CA/T_c for CB) between MC results and experimental data. Our potential models appear to represent the qualitative difference of the thermodynamic properties between CB and CA. The result of extensive MC studies will be reported in near future.

Acknowledgements

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