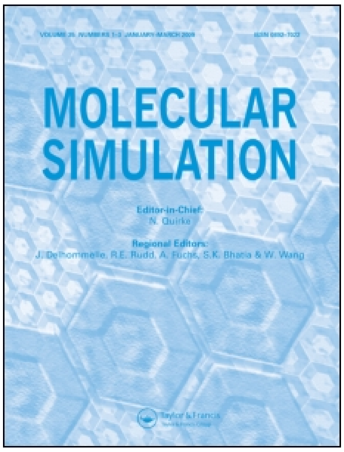

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A NEW POTENTIAL MODEL FOR CARBON DIOXIDE FROM *AB INITIO* CALCULATIONS

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Ab initio quantum chemical calculations have been carried out for carbon dioxide dimer and the results have been used to establish potential functions usable in molecular simulations. Since the intermolecular interaction in carbon dioxide is fairly weak, careful treatment is required: this study uses 6-31G* basis set and takes electron correlations by the 2nd order Møller-Plesset theory into account. The potential energy surface is elucidated using the four representative relative configurations of the dimer. A new potential function model has been proposed on the basis of these *ab initio* data. In the super-critical region, this model is used to calculate the PVT relation of carbon dioxide fluid by the Monte Carlo simulations and confirmed to reproduce reasonably well the experimental isotherms.

KEY WORDS: Carbon Dioxide, *ab initio* calculation, intermolecular potential model, Monte Carlo simulation, phase diagram

1 INTRODUCTION

Carbon dioxide fluid is a popular super-critical extraction solvent [1]. It is now widely used in industrial separation and purification processes. Their efficient operation requires exact information on the physical properties of the solvent and solutions. Carbon dioxide also plays an important role in world-wide environmental problems. In order to contribute to solving these problems, one of the starting points is to study the intermolecular interaction and the resulting fluid property and structure.

Carbon dioxide is a unique compound; the intermolecular interaction is fairly weak and the investigation requires careful treatment. This prevents the compound being the subject of conventional *ab initio* studies for the preparation of potential functions. Thus, only some empirical potential functions are available and they are based on experimental data such as lattice parameters and the second virial coefficient [2]. Although Böhm *et al.* [3] proposed the potential models partially constructed by *ab initio* calculations, the dispersion term of their models were determined by the experimental second virial coefficient. A few research groups have reported the results of extensive *ab initio* calculations [4, 5]. While their quality is extremely high, the main concern is the study of the most stable geometry. The

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calculations are limited to specific dimer orientations. They cannot be used for the molecular simulations of fluid states.

It is emphasized in these studies that the electrostatic interaction plays a significant role in this van der Waals complex system. Indeed, the stable geometries found are of slipped parallel (SP, C2h) and T-shape (T, C2v) configurations in which favorable electrostatic interaction arises between carbon and oxygen atoms.

In order to establish the potential function for this dimer, it is necessary to study other geometries of carbon dioxide dimer which might be less stable than the SP and T-shape. We have already published our preliminary results [6] which indicate that the parallel and perpendicular (PAP, D2d) configuration has a potential energy minimum. Among such electrostatic unfavorable configurations, the rectangular and parallel (RAP, D2h) configuration has been considered to have no minimum [5].

In the present study, we have carried out further *ab initio* quantum chemical calculations with 6-31G* basis set which is more flexible than that used before (3-21G). The potential energy surface of this dimer system is explained for the detailed feature using the above representative four configurations, SP, T-shape, PAP, and RAP. We have constructed two potential function models based on the two *ab initio* data. *One* empirical correction is introduced to these models which are to be used for Monte Carlo (MC) simulations.

MC calculations indicates that one of the present models can reproduce the PVT relation in super-critical region and the critical point of real carbon dioxide fluid reasonably well. From the comparison between two phase diagrams based on the each model, the role of the electron correlation, namely, the dispersion forces, is stressed for the description of the total potential energy surface of the system.

2 CALCULATIONAL DETAILS

2.1 Ab initio *calculations*

In our previous calculations for carbon dioxide dimer [6], a non-flexible basis set, 3-21G, was used and resultant potential curves had extremely deep minima for SP and T-shape configurations owing to the insufficiency of the basis set. In the present work, a more flexible basis set, 6-31G*, was adopted to reduce such artifacts. The wave function used was of the 2nd order Møller-Plesset(MP2) theory; the electron correlation effect was included to the Hartree-Fock (HF) wave function. The monomer structure was optimized at the total energy with the same wave function level; the resultant carbon-oxygen bond length was 1.180 Å. This structure was adopted for all the dimer configurations.

The dimer configurations considered were of 14 types and, for each configuration, the quantum chemical calculations were carried out at 14 different intermolecular (carbon-carbon) distances between 2.75 and 6.50 Å. All the calculations were carried out with the GAUSSIAN 90 package program [7].

2.2 *Potential models*

The next step is the preparation of potential energy function based on the *ab initio* data obtained above. As the data to be fitted, we used the following two sets:

1. DATA0: Those obtained by the combination of 6-31G* and HF
2. DATA1: Those obtained by the combination of 6-31G* and MP2

Moreover each one point of zero energy was included into them at 10 Å of C-C distance for each configuration.

There are many possibilities to select the analytical potential function for dimer. Here we adopted the 3-sites Lennard-Jones (LJ) model with Coulomb (C) term. It is written as

$$V_{ab\ initio}(\mathrm{r}) = \sum_{i=1}^{3} \sum_{j=1}^{3} \left\{ 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right\} + \frac{q_i q_j}{r_{ij}} \right\}, \tag{1}$$

where ε_{ij}, σ_{ij}, and q_i, are energy, size, and Coulomb parameters, respectively. The constraint, $q_c = -2q_o$, is imposed on the Coulomb parameters.

By using the above two kinds of *ab initio* data, we attempted to determine optimized parameter values for each data. Such resultant potential functions may suffer from some inadequate procedures and approximations involved: the insufficiency of the basis set, the error in the optimization of the potential parameters, and the neglect of the multi-body effect. The simplest way to take these problems properly into account is to introduce a scaling factor η and to write the potential function $V(\mathrm{r})$ as

$$V(\mathrm{r}) = \eta \times V_{ab\ initio}(\mathrm{r}). \tag{2}$$

The determination of the η value can be done most conveniently by using *one* experimental PVT data point in super-critical region; the detailed procedure will be explained in the later section.

2.3 *MC simulations*

The MC calculations have been carried out within an NVT ensemble by the use of conventional Metropolis scheme [8]. The system was described by 256 molecules with the usual periodic boundary condition. The cell length depended on the external conditions and the smallest value was 26 Å in this study. The long-range correction of the potential was neglected, since the energy value of our potential model was made converge to zero at 10 Å and the electroneutrality within a molecule was maintained by the constraint to the Coulomb parameters. To start each MC calculation, we used a well-equilibrated configuration at the neighboring external condition as the new initial state. Then the MC run proceeded 5,000 steps for the new equilibration and further 5,000 steps for the analysis. Here one step consisted of the configurations in which one molecule was selected at random for 256 times and tried to do the translation and rotation of the molecule.

3 RESULTS AND DISCUSSION

3.1 *Potential surface from* ab initio *data*

The present *ab initio* data gave the potential surface for the carbon dioxide dimer system. The qualitative feature of the potential surface of this dimer was almost same as the previous results [6]. In order to summarize the characteristic points of the potential surface, we first examine some of the potential curve with a fixed configuration in the dimer as a function of intermolecular distance. As pointed out in the previous section, there are roughly two kinds of potential curve. One is "attractive" type such as SP and T-shape, and the other is "repulsive" type such as PAP and RAP. Figure 1 shows potential curves for these four configurations. Comparison is made between two data groups, DATA0 and DATA1. Inspection to Figure 1 leads us to the following two important considerations.

1. Oxygen and carbon atoms in carbon dioxide molecule have different partial charge and, when they approach, the corresponding potential curves are "attractive". Since the interaction is due to the electrostatic force, inclusion of the electron correlation effect has a small influence on the potential curve as depicted in Figures 1 (a) and (b). For these SP and T-shape configurations, the potential minimum is in the range between 4.0 and 4.5 Å (carbon-carbon distance) and its depth between -3 and $-5\,\mathrm{kJ \cdot mol^{-1}}$.
2. When two carbon atoms approach each other, the corresponding potential curves are of "repulsive". The DATA0,→HF results, shows only repulsive curves; the inclusion of the electron correlations in DATA1 causes the minimum as seen in Figures 1 (c) and (d). The depth of this minimum is $\sim -3\,\mathrm{kJ \cdot mol^{-1}}$ for the PAP configuration. Of course, for such a peculiar minimum, there is a possibility of the artifact owing to the insufficiency of the basis set. We examined this point by the conventional counterpoise calculation [9]. Although this correction is widely known to overestimate the error for the correlated wave function, the resultant potential curve kept the minimum of $-0.4\,\mathrm{kJ \cdot mol^{-1}}$ for the PAP configuration. On the other hand, the RAP configuration lost the minimum after this treatment; this result is the same as the conclusion previously reported [5]. However, at least, it is clear that the dimer can approach nearer in DATA than in DATA0. This explains the significant role of the dispersion force in this type.

3.2 *Potential models*

The potential curves given above reveal the complex nature of the potential surface of the carbon dioxide dimer. In the present study, we used as an analytical potential function, equation (1). We have determined 2 sets of parameter in equation (1) which well reproduced each set of *ab initio* data.

Since the preliminary MC calculations based on these models could not reproduce the PVT relation of real carbon dioxide fluid with sufficient accuracy, *one* scaling factor was introduced as in equation (2). In order to determine appropriate η value, we selected an experimental phase point where $P = 408\,\mathrm{atm}$, $\rho = 0.466\,\mathrm{g.cm^{-3}}$, and $T = 500\,\mathrm{K}$ [10]. This point is in the homogeneous fluid region and temperature is high enough from the critical point. The η value is so determined as to reproduce the above phase point by the MC calculation.

The results are given in Table 1. Here we call our potential functions MODEL0 and MODEL1 depending on the use of *ab initio* data groups, DATA0 and DATA1. These results are compared in Figure 2 (a) ~ (d) for the representative four configurations with empirical model of 2-site LJ + point quadrupole interaction (2LJQ) [2]. It may be pointed out that the potential curves with MODEL1 for these configurations are in close agreement with those with 2LJQ.

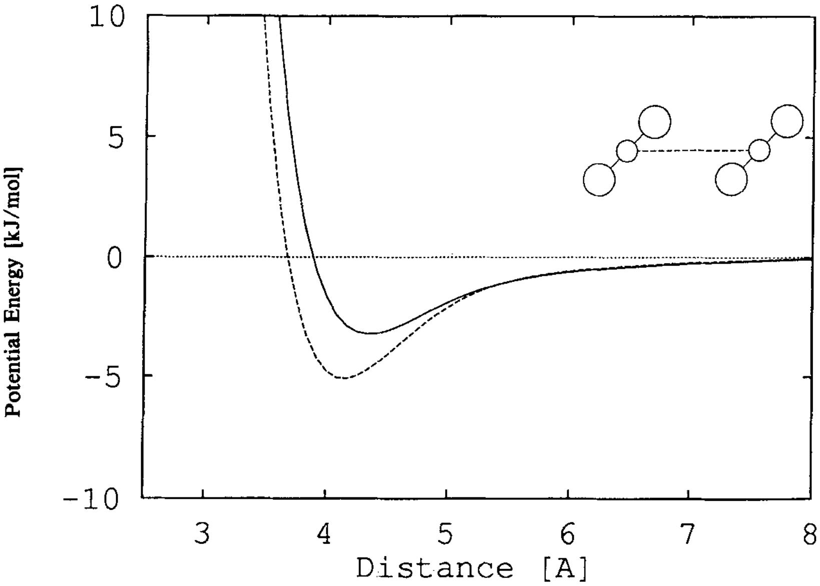


Figure 1a.

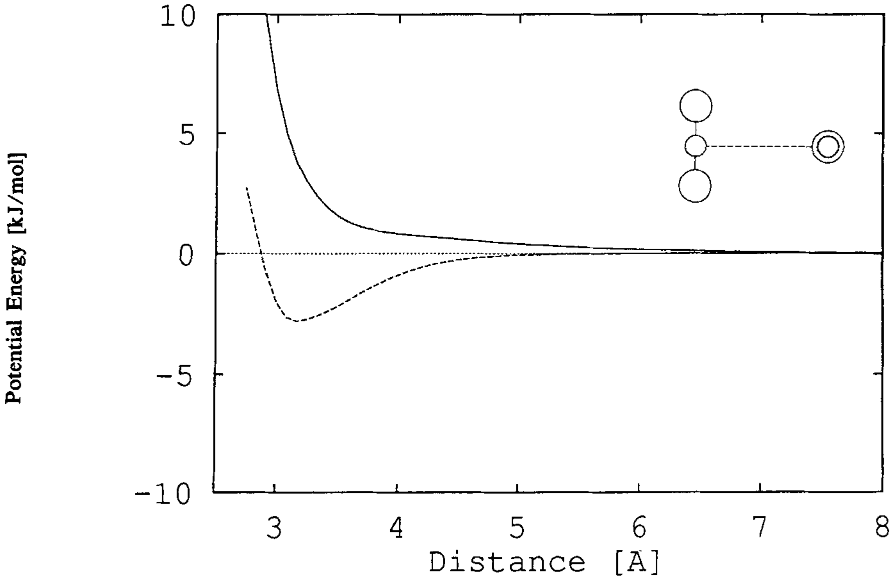


Figure 1b.

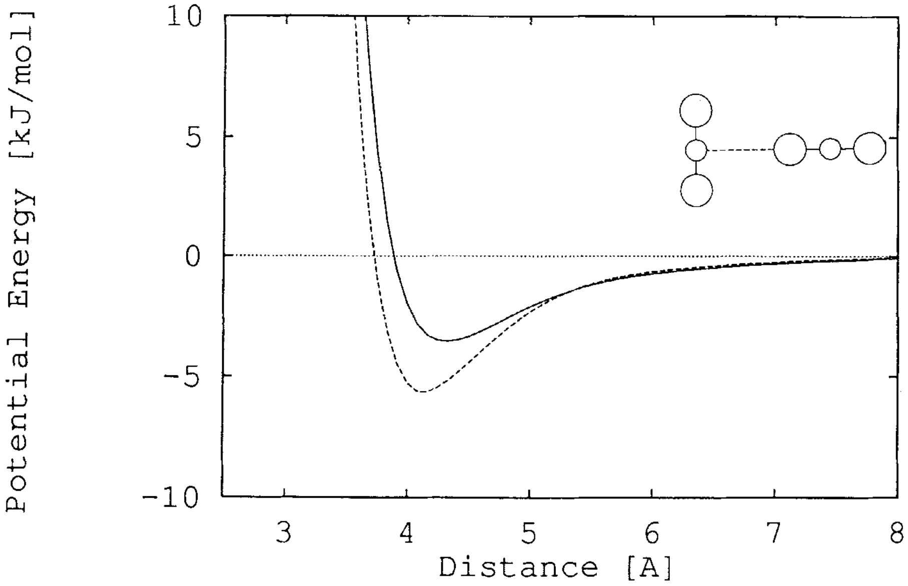


Figure 1c.

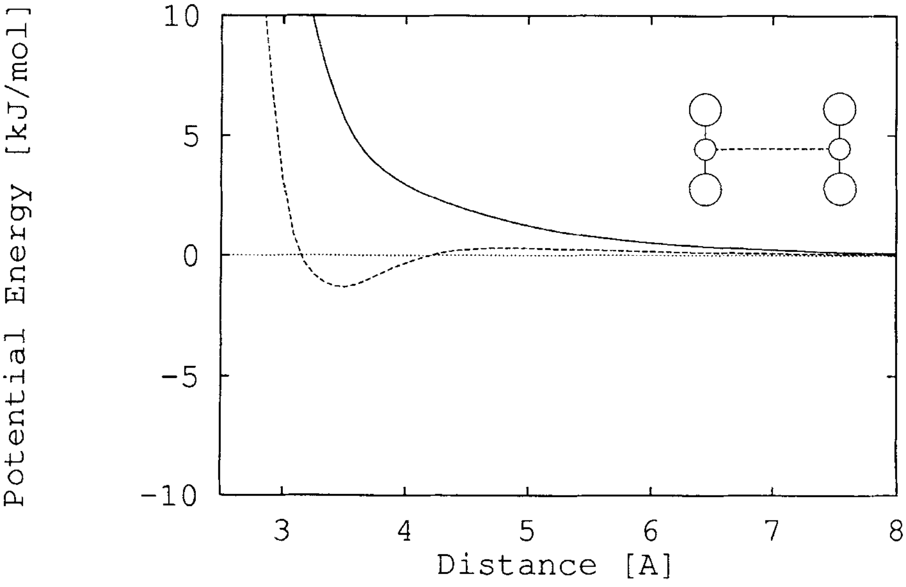


Figure 1d.

Figure 1 The comparison of *ab initio* data for the four representative configurations: (a) SP, (b) T-shape, (c) PAP, and (d) RAP. In these configurations, solid lines are HF, and broken lines are MP2.

Table 1 The parameters of two models.

	MODEL 0	*MODEL 1*
η	2.420	0.7309
$\varepsilon[\mathrm{kJ \cdot mol^{-1}}]$		
C-C	1.891×10^{-15}	3.581×10^{-13}
C-O	1.747×10^{-14}	1.181×10^{-1}
O-O	3.688×10^{-1}	1.871
$\sigma[\mathrm{Å}]$		
C-C	49.14	31.03
C-O	37.21	32.18
O-O	3.165	2.713
$q_C[(\mathrm{kJ \cdot Å \cdot mol^{-1}})^{1/2}]$	29.87	20.23

Table 2 The basis set dependency of potential minimum.

Basis set/Method	*Minimum energy* $[kJ \cdot mol^{-1}]$
6-31G*/MP2	−5.95
corrected for BSSE	−2.37
5s4p2d/MP2	−4.70
corrected for BSSE	−3.83

One may be surprised at the unphysical LJ parameters for C-C and C-O in Table 1. Our purpose is to make a model which reproduces the *ab initio* data; the inspection of the physical meaning of each parameter must be abandoned, though the model has LJ + C type as the working formula.

Finally, we want to state the meaning of $\eta = 0.7309$. For the quantitative description of the potential minimum, the basis set of extremely high quality must be required for the case of van der Waals complex such as carbon dioxide dimer. One example for T-shape is taken from the literatures [4, 5] and cited in Table 2. The results corrected for BSSE have not yet converged; the 6-31G* is considered as the insufficient basis set. The main reason of deep minimum may be attributed to this insufficiency; of course, one of reasons is the overestimate of dispersion energy calculated by MP2.

3.3 *PVT relation by MC calculation*

We now present and discuss the results of MC calculations. Figures 3 (a) and (b) show the P-V isotherms of carbon dioxide as calculated with MODEL0 and MODEL1, respectively, in comparison with the experimental data [10].

First, the MODEL0 cannot reproduce the experimental results. Except for the region near the present reference point mentioned above, the deviation from the experimental results is extremely large, especially at high density region. One can observe the van der Waals loop even at 320 K. Overestimation of the critical temperature and pressure may be ascribed to the deep minima for SP and T-shape configurations and the weak interactions for PAP and RAP configurations. The latter comes from the lack of the inclusion of the dispersion force. The former

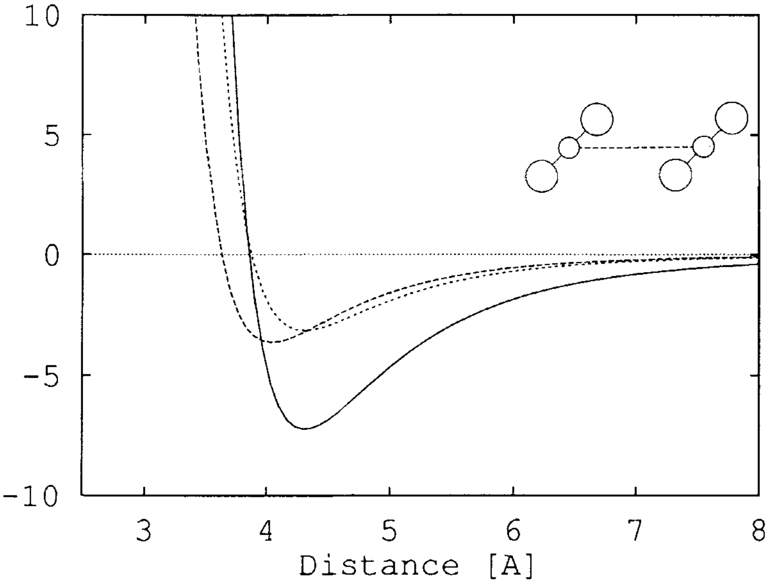


Figure 2a.

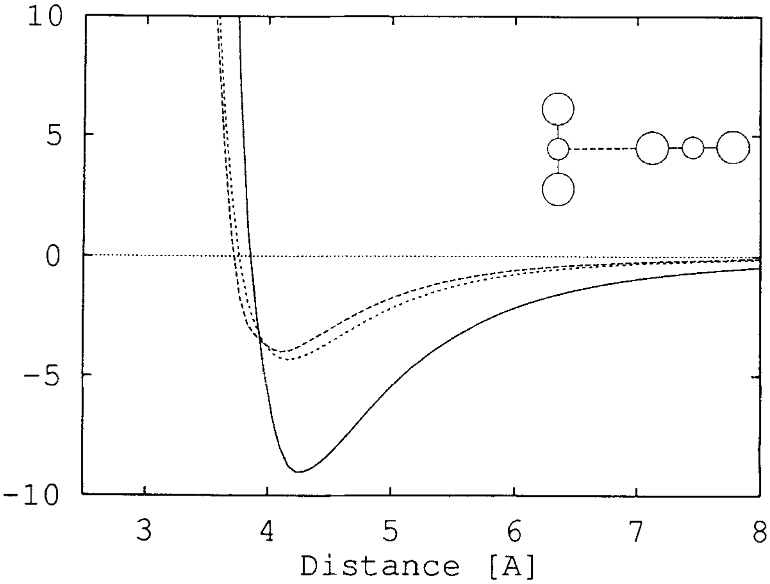


Figure 2b.

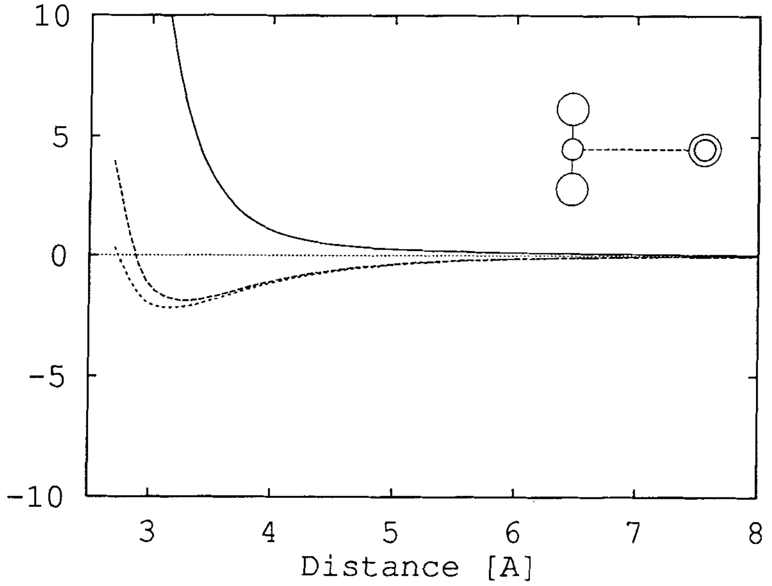


Figure 2c.

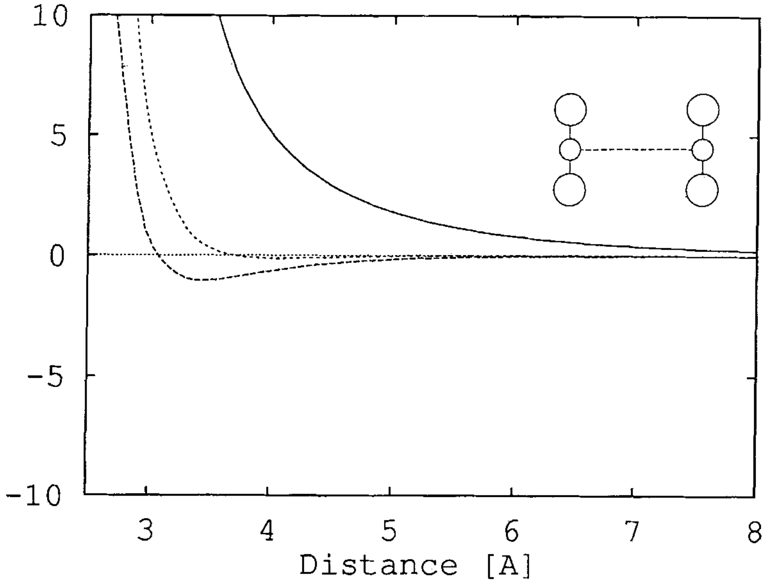
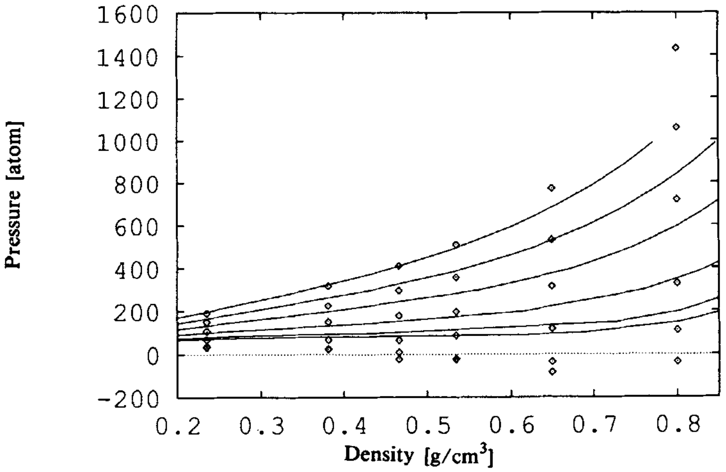
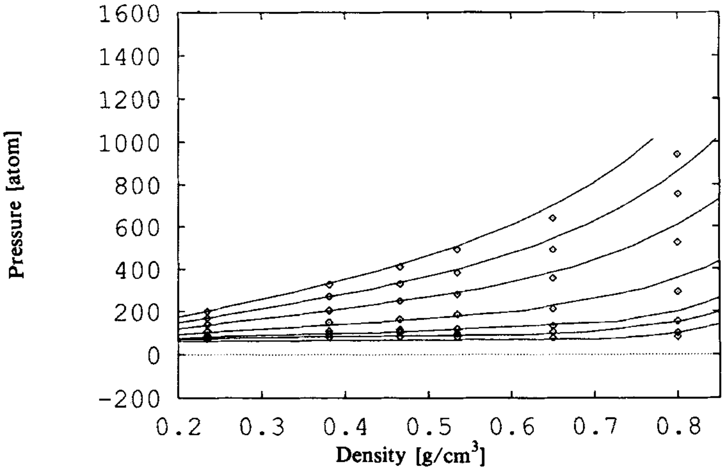


Figure 2d.

Figure 2 The comparison of models for the four representative configurations: (a) SP, (b) T-shape, (c) PAP, and (d) RAP. In these configurations, solid lines are MODEL0, broken lines are MODEL1, and dotted lines are 2LJQ.



(a)



(b)

Figure 3 The comparison of the experimental isotherms and the calculated ones by MODEL0 (a) and MODEL1 (b). The solid lines are plotted based on the experimental data [10]. The diamonds are calculated data. The data are at 500, 450, 400, 350, and 310 K, respectively (from top to bottom).

also indirectly comes from the same reason; it is because our procedure to determine the η value makes the minima of SP and T-shape deeper in order to compensate the repulsive curves of PAP and RAP.

On the other hand, the MODEL1 can reproduce experimental P-V isotherms fairly well for the almost all region calculated here. One can see that the P-V isotherms at 310 and 300 K have a flat region that is characteristic to the critical fluid. This is to be compared with the experimental critical constants of carbon dioxide, $T = 304\,\mathrm{K}$, $\rho = 0.466\,\mathrm{g\cdot cm^{-3}}$, and $\mathrm{P} = 70\,\mathrm{atm}$. From the practical point of view, the most important region for the super-critical extraction is just above the critical point, namely, the region $T = 304 \sim 400\,\mathrm{K}$ and $\rho = 0.3 \sim 0.6\,\mathrm{g\cdot cm^{-3}}$.

One can thus conclude that the MODEL1 gives phase diagram near the critical point reasonably well.

4 CONCLUSION

The purpose of this work is to establish an intermolecular potential function which can be used for molecular simulations. First, we have carried out *ab initio* quantum chemical calculations for dimer system with 14 configurations. Since the interaction energy in carbon dioxide dimer is fairly small, we have adopted 6-31G* basis set and performed MP2 calculations. In order to take the non-spherical nature of intermolecular interaction in the dimer into account, we considered not only "attractive" SP and T-shape configurations of dimer, but also rather "repulsive" PAP and RAP configurations.

Although we could determine two sets of optimized parameters in a 3-site LJ + imposed fractional charges (Coulomb) type potential function (see equation (1)), both the obtained models cannot reproduce accurately the PVT relation of real carbon dioxide fluid. To circumvent this difficulty, a scaling factor η was introduced as in equation (2). As the result, we find that the MODEL1 reproduces reasonably well the experimental P-V isotherms of carbon dioxide for almost all the fluid regions.

Further comparisons are in progress for other thermodynamic quantities and fluid structure.

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