DEVELOPMENT OF NEW CROSS INTERMOLECULAR PAIR POTENTIAL *AB INITIO* AND PREDICTION OF CROSS SECOND VIRIAL COEFFICIENTS FOR DIMER H_2O-CH_4

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ABSTRACT

The site-site intermolecular pair potential of dimer H_2O-CH_4 was constructed from the ab initio calculations at high level of theory CCSD(T) with basis set cc-pVTZ. The cross second virial coefficients of this system were calculated accurately using this ab initio pair potential. These results were compared with experimental data and those from literatures. The discrepancies between them are insignificant.

Keywords: *cross intermolecular pair potential, cross second virial, ab initio potential.*

I - INTRODUCTION

The thermodynamic data needed for designing processes of gaseous fuels in several industrial applications. The methods for predicting the physical properties of the natural gas mixtures are need that can be used with the great significance for a wide range of temperatures, pressures and compositions. The empirical methods are also useful for correlation of quantities of data on specific components. But these were not generated the properties of new components accurately. In recent years computer simulations have become indispensable tools for studying fluids and fluid mixtures. One of the first attempts Nasrabad and Deiters predicted phase high-pressure vapor-liquid phase equilibria of noble-gas mixtures [1,2] from the global Monte Carlo simulations using the intermolecular potential *ab initio*. These simulations are to predict the thermodynamic properties of microscopic systems using the intermolecular potentials, and we can be understood macroscopic behaviours

[3]. The reliability of these depends only on the accuracy of intermolecular potentials.

In this work we report the development of an accurate cross potential *ab initio* between molecules water and methane using the high level of theory CCSD(T) with the Dunning's contracted basis set cc-pVTZ. The cross second virial coefficients of dimer H_2O-CH_4 are predicted using this cross intermolecular potential. The cross second virial results are compared with the experimental data and those from literatures.

II - COMPUTATIONAL DETAILS

1. Potential energy surface

Six orientations for dimer H_2O-CH_4 were chosen with the fixed molecule methane at the origin. One atom H of methane is on the X axis and another H is in the plane XY.

The intermolecular pair potential is a function of distance *r* (between the center of gravity of two molecules) and the angular coordinates α, β and ϕ, as are explained in Fig. 1. Intermolecular

energies were calculated for all values of r from 6 to 15 Å with increment 0.5 Å; the angles α and β for molecular plane H_2O was varied from 0 to 180º with increment 30º along Y and Z axis.
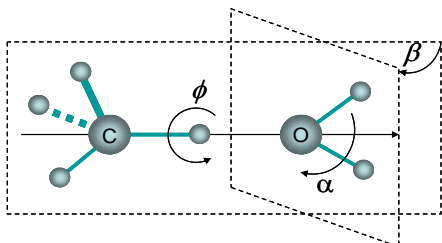

Figure 1: Dimer orientation for *ab initio* calculation

2. *Ab initio* calculations

The CCSD(T) method appears to account for the most significant electron correlation effects.

The Dunning's contracted correlation-consistent basis set cc-pVTZ (for hydrogen: 5s,2p,1d/3s,2p,1d; for oxygen: 10s,5p,2d,1f/4s,3p,2d,1f; carbon: 10s,5p,2d,1f/4s,3p,2d,1f) were used in this work [4, 5]. The *ab initio* energies were corrected for BSSE with the counterpoise correction method proposed by Boys and Bernardi [6]:

$$\Delta E_{int} = E_{AB} - (E_{Ab} + E_{aB}) \qquad (1)$$

where E_{AB} denotes the total electronic energy of a dimer AB, E_{Ab} the energy of a dimer consisting of an A atom and a B ghost atom (an atom without nucleus and electrons, but having its orbitals), and E_{aB} vice versa. *Ab initio* calculations were carried out with the Gaussian03 program package [7]. The potential energy surfaces for six orientations resulting from *ab initio* interaction energies are depicted in Fig. 2.
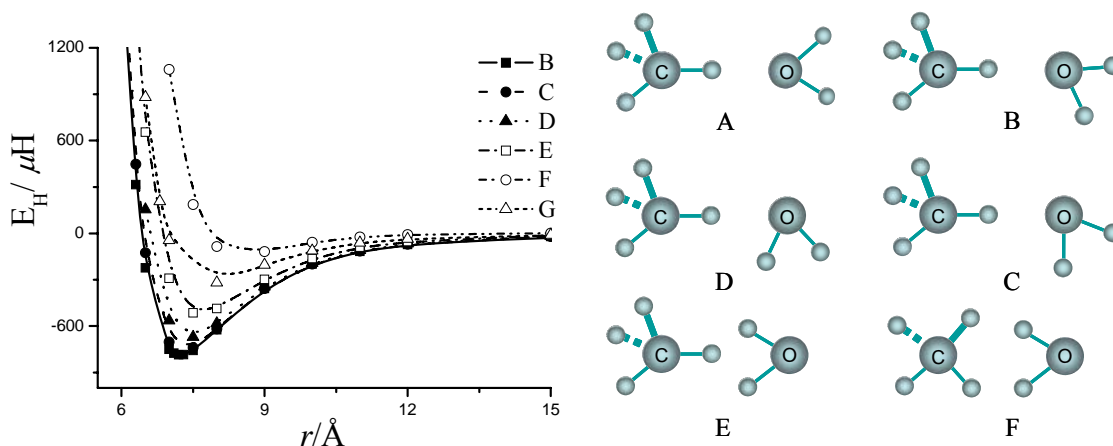

Figure 2: Potential energy surface of six special orientations for *ab initio* calculations

The geometry parameters of monomers methane and water obtained by quantum calculations *ab initio* at the level of theory CCSD(T)/ cc-pVTZ, as given in table 1.

Table 1: Optimization geometry of monomers methane and water

No	methane			water		
	parameter	*ab initio*	Exp.[15]	parameter	*ab initio*	Exp.[15]
1	angle H-C-H	109.49	109.5	angle H-O-H	104.62	104.0
2	bond length H-C	1.091 Å	1.10 Å	bond length H-O	0.946 Å	0.95 Å
3	charge on C	-0.144		charge on O	-0.292	
4	charge on H	0.036		charge on H	0.146	

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3. Potential function

The new cross intermolecular potential function for dimer H_2O-CH_4 was developed in this work by incorporating the interaction contribution from the terms of the site-site potentials in publications [3, 8], as shown in Eq. 2. The adjustable parameters of this potential function can be estimated by nonlinear least-square fitting to the 800 *ab initio* interaction energy values.

$$u(r_{ij}) = \sum_\alpha D_\alpha \sum_{ij} e^{-A_\alpha r_{ij}} + f_1(r_{ij}) \frac{C_n^{ij}}{r_{ij}^n} + f_2(r_{ij}) B_{ij} \sum_{ij} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{2}$$

With $f_1(r_{ij}) = (1 + e^{-2(\delta_{ij} r_{ij} - 2)})^{-15}$ and $f_2(r_{ij}) = 1 - e^{-\beta_{ij} r_{ij}}$.

The fit has to be carried out by means of the Genetic algorithm (GA) and the Levenberg-Marquardt algorithm [9]. The values of root mean-square deviations (rms) of 0.1325 and multiple correlation (R^2) of 0.9987 are appeared here to be important for assessing the fitting quality. This fit turns out to be very satisfactory.

4. Cross second virial coefficients

The fitted cross potential Eq. 2 was used to calculate the cross second virial coefficients $B_2(T)$ for dimer H_2O-CH_4. These virial coefficients $B_2(T)$ were also corrected quantum effects using the formula proposed by Pack [10] and Wang [11] for this cross potential:

$$B_2(T) = \frac{N_A}{2u(r) \iint d\Omega_1 d\Omega_2} \iiiint \left\{ 1 - \exp(-u(r)/k_B T)\left[1 + \frac{1}{12(k_B T)^2} H_0 u(r) \right] \right\} dr_1 dr_2 d\Omega_1 d\Omega_2 \tag{3}$$

Here N_A is Avogradro's constant, k_B Boltzmann's constant, T the temperature, and $u(r, \alpha, \beta, \phi)$ the pair potential; H_0 is the translation-rotation Hamiltonian for a pair of molecules. This expression can be broken down into a classical term and first-order quantum corrections (radial part, angular part proportional to I^{-1} (moment of inertia), angular part proportional to μ^{-1} (reduced mass)):

$$B_2(T) = B_{cl}^0(T) + B_r^1(T) + B_{aI}^1(T) + B_{am}^1(T) \tag{4}$$

Where $B_{cl}^0(T)$ the classical second virial coefficient is given by

$$B_{cl}^0(T) = -\frac{N_A}{4} \int_0^{2\pi} d\phi \int_0^\pi \sin\beta \, d\beta \int_0^\pi \sin\alpha \, d\alpha \int_0^\infty \left(\exp\left(-\frac{u}{k_B T} \right) - 1 \right) r^2 \, dr \tag{5}$$

All these integrals were estimated numerically with a Gaussian quadrature method [12] over the molecular orientation vectors r, α, β and ϕ. The cross second virial coefficients, $B_2(T)$ including quantum corrections are given in table 2.

The cross 2nd virial coefficients $B_2(T)$ including quantum corrections at the level of theory CCSD(T) with basis set cc-pVTZ are illustrated in Fig. 3.

Table 2: Cross second virial coefficient, $B_2(T)$ (cm^3/mol); Beck: calculated by Beck potential [13]; exp.: experimental data [14]; D1-EOS: Deiters equation of state [16]

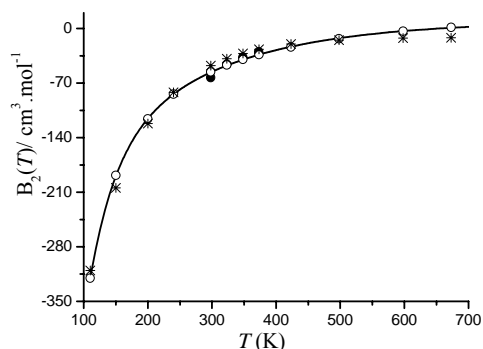| T(K)	Eq.2 (this work)	Beck [13]	D1-EOS[16]	Exp.[14]
200.0	-115.292	-116.07	-122.154	
240.0	-84.152	-84.232	-81.925	
298.2	-56.086	-55.594	-47.757	-63
323.2	-47.378	-46.939	-38.709	-46
348.2	-39.979	-39.708	-31.896	-37
373.2	-33.625	-33.579	-26.771	-30
423.2	-23.373	-23.777	-20.027	
498.2	-12.443	-13.168	-14.987	
598.2	-3.332	-3.584	-12.465	

Figure 3: Cross second virial coefficients $B_2(T)$ of dimer H_2O-CH_4; —: potential Eq. 2 at CCSD(T)/cc-pVTZ (this work);
●: experimental data [14];
○: *ab initio* potential proposed by Beck [13];
∗: D1-EOS Deiters equation of state [16]

III - CONCLUSION

The cross second virial coefficients of dimer H_2O-CH_4 obtained from the cross pair potential Eq.2 are very close to experimental data, as described in Fig 3. The discrepancies between them are insignificant. The results are generated almost within the uncertainties of the experimental measurements. The quantum corrections contributed significantly to the virial coefficients at temperatures. The new *ab initio* cross pair potential of the dimer H_2O-CH_4 is reliable for predicting the thermodynamic properties.

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