# INTERACTION SECOND VIRIAL COEFFICIENTS OF DIMER CO-CO FROM NEW *AB INITIO* POTENTIAL ENERGY SURFACE

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## ABSTRACT

*The new 5-site ab initio intermolecular interaction potentials of dimer CO-CO were constructed from quantum mechanics using method CCSD(T) with Dunning's correlation-consistent basis sets aug-cc-pVmZ (m = 2, 3) [7]; ab initio energies were extrapolated to the complete basis set limit aug-cc-pV23Z. The ab initio intermolecular energies were corrected for the basis set superposition error (BSSE) with the counterpoise scheme [8]. The interaction second virial coefficients of dimer CO-CO resulting from the 5-site ab initio analytical potential functions obtained by integration; first-order corrections for quantum effects were included too. The results agree well with experimental data.*

**Keywords:** *Second virial coefficients, 5-site ab initio potentials.*

## I - INTRODUCTION

The knowledge of thermodynamic properties of the pure substance CO-CO is important for practical applications. It is also necessary for its safe use. Computer simulations have become indispensable tools for studying pure fluids and fluid mixtures and understand macroscopic phenomena. One of the first attempts Nasrabad and Deiters predicted phase high-pressure vapour - liquid phase equilibria of noble-gas mixtures [1, 2, 4] from the global simulations using the intermolecular potentials. Other mixed-dimer pair potentials for noble gases were published by López Cacheiro et al. [3], but not used for phase equilibria prediction, yet.

This work presents quantum mechanical calculations at a sufficiently high level of approximation to obtain pair potential data of carbon monoxide using the high level of theory CCSD(T) with Dunning's correlation-consistent basis sets aug-cc-pV$m$Z ($m$ = 2, 3) [7]; the complete basis set limit aug-cc-pV23Z is obtained

by *ab initio* intermolecular energies [8]. These *ab initio* energy results are corrected for the basis set superposition error (BSSE) with the counterpoise method. Two new 5-site *ab initio* potentials are developed for the dimer CO-CO; the interaction second virial coefficients of dimer carbon monoxide are compared with the experimental data and with those from the Deiters equation of state [15].

## II - COMPUTATIONAL DETAILS

### 1. Molecular orientation

Carbon monoxide asymmetric molecule is represented as 5-site model with two sites placed on the atoms C and O, one site in the center of gravity M, and two sites halfways between the atoms and the center N and A; the interatomic distance is set to 1.128206 Å for molecule CO [6]. The intermolecular potential is a function of distance $r$ (between the centers of gravity) from 2.8 to 15 Å with increment 0.2 Å and three angular coordinates, $\alpha$, $\beta$, and $\phi$ from

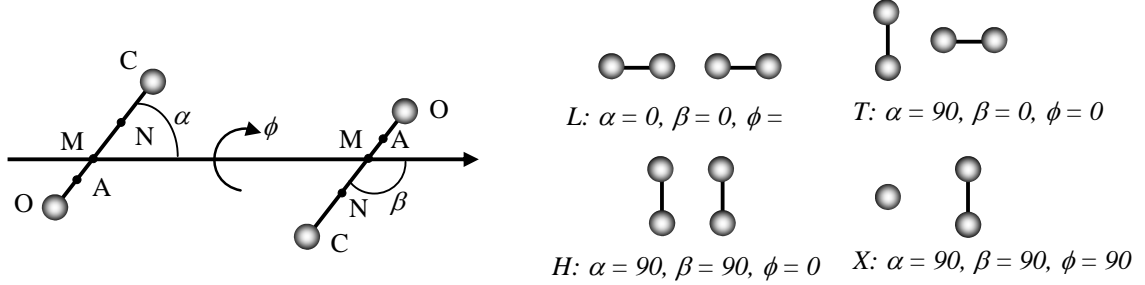0 to 180° with increment 45°, which are explained in Fig. 1.



*Figure 1*: 5-site model of dimer CO-CO and special molecular orientations

## 2. Quantum chemical calculation

The method CCSD(T) and the correlation-consistent basis sets of Dunning et al. [7]: aug-cc-pVDZ (for oxygen: 10s5p2d/4s3p2d, for carbon: 9s4p1d/3s2p1d), aug-cc-pVTZ (for oxygen: 12s6p3d2f/5s4p3d2f, for carbon: 15s6p3d1f/9s5p3d1f) were used. The *ab initio* energies were corrected for the basis set superposition error (BSSE) [8]:

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

$$\Delta E(m) = \Delta E(\infty) + cm^{-3} \quad (2)$$

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. With $m = 2$ (for the aug-cc-pVDZ basis set) or 3 (for the aug-cc-pVTZ basis set), the complete basis set limit aug-cc-pV23Z was calculated by *ab initio* intermolecular energies $\Delta E(m)$. *Ab initio* calculations were carried out with the Gaussian03 program package [9].

## 3. Potential functions

In this work two our new 5-site pair potentials were developed from [4] for dimer CO-CO:

$$u_1 = \sum_{i=1}^{5}\sum_{i=1}^{5}\left[ D_e^{ij}((1-e^{-\alpha_{ij}(r_{ij}-\beta_{ij})})^2 - 1) + f_1(r_{ij})\left( \sum_{n=6,8,10} \frac{C_n^{ij}}{r_{ij}^n} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right)\right] \quad (3)$$

$$u_2 = \sum_{i=1}^{5}\sum_{i=1}^{5}\left[ D_e^{ij}((1-e^{-\alpha_{ij}(r_{ij}-\beta_{ij})})^2 - 1) + f_2(r_{ij})\left( \sum_{n=6,8,10,12} \frac{C_n^{ij}}{r_{ij}^n} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right)\right] \quad (4)$$

With $f_1(r_{ij}) = (1 + e^{-2(\delta_{ij} r_{ij} - 2)})^{-15}$ and $f_2(r_{ij}) = 1 - e^{-\delta_{ij} r_{ij}} \sum_{k=0}^{10} \frac{(\delta_{ij} r_{ij})^k}{k!}$

Here the $r_{ij}$ site-site distances, the $q_i$, $q_j$ electric charges of sites, and the $C_{ij}^n$ dispersion coefficients; the leading dispersion term is always proportional to $r$. The two models differ mostly in the choice of the damping functions $f_1(r_{ij})$ from [5] and $f_2(r_{ij})$ from [10].

## III - RESULTS AND DISCUSSION

### 1. Fitting potential function

The optimal adjustable parameters of the potential functions Eq.3 and Eq.4 were estimated by nonlinear least-square fitting to the *ab initio* intermolecular energy values. The fit process has to be carried out by two steps. The global minima are coarsely located by means of the Genetic algorithm, and the parameters resulting from the Genetic algorithm are used as

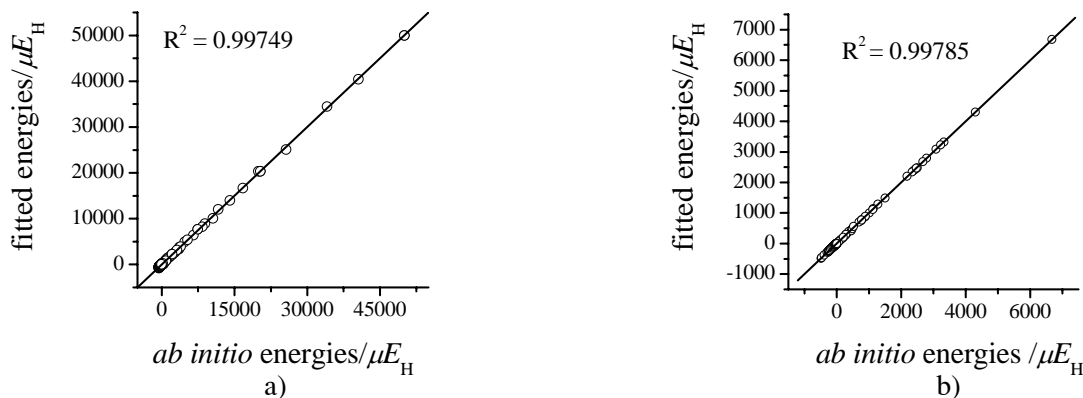initial values for the Marquardt-Levenberg algorithm.



*Figure 2*: Comparison of *ab initio* and calculated energies: a) Eq. 3; b) Eq. 4

The multiple correlation coefficients ($R^2$) of the fitted analytical potential functions Eq. 3 and Eq. 4 are given in Fig. 2a and Fig. 2b. The difference between them is insignificant for 780 *ab initio* interaction energy points.

## 2. Classical virial coefficient

The classical virial coefficients $B_{cl}^0$ of dimer CO-CO resulting from the formula Eq. 7 using the *ab initio* 5-site pair potentials Eq. 3 and Eq. 4 are depicted in Figs. 3a and 3b, respectively.
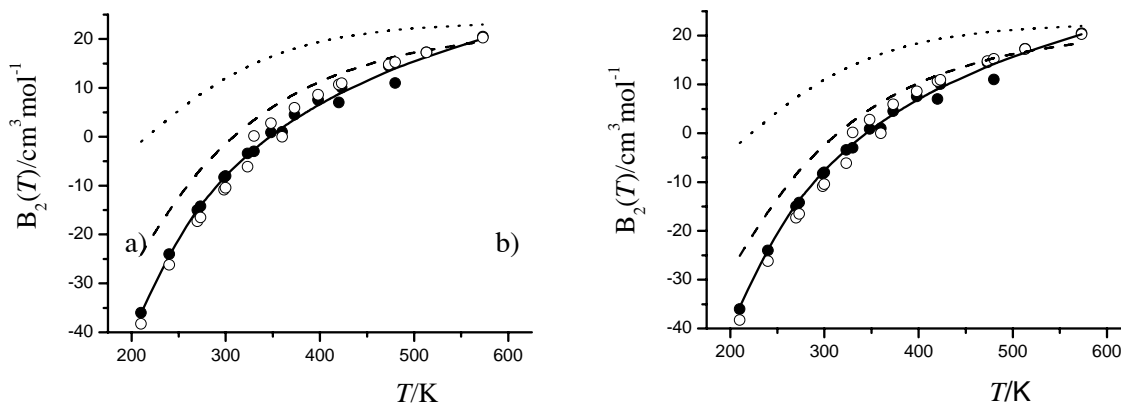


*Figure 3*: Second virial coefficients $B_{cl}^0$ of carbon monoxide resulting from the *ab initio* 5-site pair potentials: a): Eq. 3 and b): Eq. 4 at theoretical level CCSD(T); ⋯ : aug-cc-pVDZ; ----: aug-cc-pVTZ; —: aug-cc-pV23Z; •: experimental data [13,14]; ○: Deiters equation of state, EOS-D1 [15].

## 3. Quantum corrections

In this case the matter is more complicated because of quantum effects. The first-order quantum corrections to the second virial coefficients of linear molecules by Pack [11] and Wang [12] can be written as

$$B_2 = \frac{N_A}{2u \iint d\Omega_1 d\Omega_2} \iiiint \left\{ 1 - \exp(-\frac{u}{k_BT}) \left[ 1 + \frac{1}{12(k_BT)^2} H_0 u \right] \right\} dr_1 \, dr_2 \, d\Omega_1 \, d\Omega_2 \qquad (5)$$

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 $\mu^{-1}$ (reduced mass)):

$$B(T) = B_{cl}^0(T) + B_r^1(T) + B_{aI}^1(T) + B_{am}^1(T) \qquad (6)$$

The classical virial coefficient is given by:

$$B_{cl}^0 = -\frac{N_A}{4} \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\beta \, d\beta \int_0^{\pi} \sin\alpha \, d\alpha \int_0^{\infty} \left( \exp\left( -\frac{u}{k_BT} \right) - 1 \right) r^2 \, dr \qquad (7)$$

The first-order correction terms can write as:

$$B_r^1(T) = \frac{N_A \hbar^2}{96\mu(k_BT)^3} \int_0^{2\pi} \int_0^{\pi} \sin\beta \int_0^{\pi} \sin\alpha \int_0^{\infty} \exp\left( -\frac{u}{k_BT} \right) \left( \frac{\partial u}{\partial r} \right)^2 r^2 \, dr \, d\alpha \, d\beta \, d\phi \qquad (8)$$

$$B_{aI}^1(T) = -\frac{N_A \hbar^2}{48(k_BT)^2} \int_0^{2\pi} \int_0^{\pi} \sin\beta \int_0^{\pi} \sin\alpha \int_0^{\infty} \exp\left( -\frac{u}{k_BT} \right) \sum_{l_1 l_2 l} u_{l_1 l_2 l}(r) A_{l_1 l_2 l}(\alpha, \beta, \phi)$$
$$\times \left( \frac{l_1(l_1+1)}{2I_1} + \frac{l_2(l_2+1)}{2I_2} \right) r^2 \, dr \, d\alpha \, d\beta \, d\phi \qquad (9)$$

$$B_{a\mu}^1 = -\frac{N_A \hbar^2}{48(k_BT)^2} \int_0^{2\pi} \int_0^{\pi} \sin\beta \int_0^{\pi} \sin\alpha \int_0^{\infty} \exp\left( -\frac{u}{k_BT} \right) \sum_{l_1 l_2 l} u_{l_1 l_2 l}(r) A_{l_1 l_2 l}(\alpha, \beta, \phi)$$
$$\times \frac{l(l+1)}{2\mu r^2} r^2 \, dr \, d\alpha \, d\beta \, d\phi \qquad (10)$$

The terms $u_{l_1 l_2 l}(r) A_{l_1 l_2 l}(\alpha, \beta, \phi)$ represent a spherical harmonics expansion of the interaction potential. All these integrals were evaluated numerically with a 4D Gauss-Legendre quadrature method [16]. The resulting virial coefficients of dimer CO-CO included the first-order quantum corrections, as shown in Fig. 4, due to the effects of relative translational motions, and the molecular rotations.

The second virial coefficients of dimer CO-CO obtained from the two new *ab initio* pair potential functions Eq. 3 and Eq. 4 are very close to experimental data, as described in Fig. 4. The discrepancies between them are insignificant. The interaction second virial coefficients are generated almost within the uncertainties of the experimental measurements. The first-order quantum corrections contribute significantly to the second virial coefficients of dimer CO-CO even at high temperatures. Of these corrections, only the radial term is important; the angular terms are usually much smaller in size.
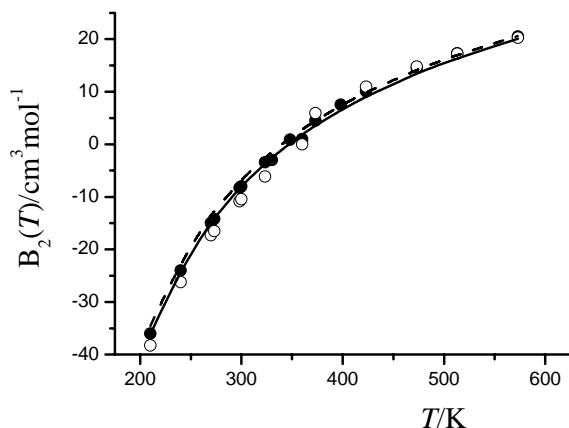
*Figure 4*: Second virial coefficients $B_2(T)$ of carbon monoxide included first-order quantum corrections resulting from the *ab initio* 5-site pair potentials: —: Eq. 3 and ----: Eq. 4 at theoretical level CCSD(T)/aug-cc-pV23Z(this work); others: see explanation in Fig. 3

## IV - CONCLUSION

We conclude that two our new *ab initio* 5-site pair potentials developed for the dimer CO-CO are reliable for predicting the thermodynamic properties. In coming work we will report the use of these *ab initio* 5-site pair petentials Eq. 3 and Eq. 4 for the Gibbs ensemble Monte Carlo (GEMC) simulation of vapor-liquid phase equilibria for pure liquid carbon monoxide. The thermodynamic behaviour of this system will be predicted by GEMC simulation.

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