

**Ab initio interaction potential of methane and carbon dioxide:
Calculation of second-virial coefficient**

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ABSTRACT

An interaction potential at different orientation for the CH₄ and CO₂ complex was derived at the B3LYP level of theory and 6-31+G* basis sets. The potential energy surface was computed on some molecular geometries. The complete basis set limit of the interaction energies were fitted to well-known analytical functions. To determine the second virial coefficients B, $U(r)$ is used to obtain the model's parameters over the range of temperatures of interest.

Keywords: B3LYP method; DFT; Second virial coefficient; Carbon dioxide; Methane interaction

INTRODUCTION

Knowledge of the intermolecular interaction potential is basic for understanding the properties of gases, liquids and solids. In principle, the evaluation of a macroscopic property like the second virial coefficient of a moderately dense gas is straightforward if the intermolecular pair potential is accurately known [1]. As well as knowledge of the inter/intramolecular Potential Energy Surface (PES) for nuclear motion is essential for the understanding of many physical, chemical, and biological processes as well as the intrinsic properties of molecules or their clusters [2,3]. In the last two decades, the ab initio potentials of CH₄-H₂O and CO₂-H₂O system have been studied by several research Groups [4, 5]. The Langmuir constants are

computed from the ab initio potential for the application in van der Waals Platteeuw model to predict the cage occupancy and equilibrium pressures of CH₄ and CO₂ hydrate. Similar work was published by Anderson et al. [6]. Ab initio calculations have pointed out as a powerful tool for studying intermolecular interactions [7].

Ab initio calculations are an alternative way to generate potentials and have the advantage of being able to model systems where no experimental data are available. Ab initio potential energy surfaces for all of the fluorinated methane dimers have been calculated at the HF/6-31+G* level, with some additional calculations using the MP2 method [8]. These potentials have been used to calculate the free energy of solvation of all of these compounds in

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CO₂ [9].

Potentials derived entirely from ab initio calculations reproduce the phase-coexistence properties of CO₂ and CH₄ well [10, 11].

The CO₂-CH₄ interaction energy is crucial in the understanding the thermodynamic and transport properties of methane and carbon dioxide mixture in bulk [12, 13] and in porous media [14, 15]. In view of a few previous works and the importance of the methane-carbon dioxide interaction energy, we have conducted here the ab initio calculations of interaction potentials for the ground state of these molecules.

Different geometry orientations of CO₂-CH₄ molecules and the computational details are given in the next section. We present our results about PES and the fitting procedure respectively. Calculation of second virial coefficients for CO₂-CH₄ has presented and conclusion presented in last part of this paper.

COMPUTATIONAL METHOD

Initially, structure of CH₄ and CO₂ was fully optimized with the B3LYP, DFT method and 6-31+G* basis set in order to locate the stationary points on the potential surface. Our calculations were performed by using the program package Gaussian 98 [16]. In ab initio calculations the basis set superposition error (BSSE) is of paramount importance. This error can be eliminated to some extent by using the counterpoise method (CP). In this method both the physicochemical compound A---B and the A and B components at $r=\infty$ are calculated by using the full basis set for the A---B, hence

$$V = E_{AB}(A---B) - E_{AB}(A+B) + \Delta E_{CP} \quad (1)$$

Where

$$\Delta E_{CP} = [E_A(A+B) - E_A(A---B)] + [E_B(A+B) - E_B(A---B)] \quad (2)$$

The significant of the BSSE on the intermolecular interaction has been highlighted in a number of papers. The various points on the ab initio potential energy surface were used to obtain a fit to the Leonard - Jones potential energy function.

The second virial coefficient is an important parameter for determining the thermodynamic properties. Second virial coefficient, B , obtained either experimentally or estimated theoretically using the multidimensional interaction energy surface U_{AB} , Equation (3), can be used to determine the magnitude of these parameters. In this work, known form for $U(r)$ is used to estimate the second virial coefficients [17]:

$$B = \frac{1}{2} \pi N_A \int_0^{\infty} (1 - e^{-U(r)/kT}) r^2 dr \quad (3)$$

where $U(r)$ is the intermolecular potential energy, N_A is the Avogadro constant. The second virial coefficients calculated this way are fitted to the initial coefficients B varying e and r_0 , eventually some other parameters.

RESULTS AND DISCUSSION

The results of geometry optimization for the carbon dioxide's bond length is $R_e = 1.169$ a.u. and bond angle $\theta = 180^\circ$ and methane's bond lengths and bond angles are $R_e = 1.092$ a.u., and $\theta = 109.47^\circ$ respectively. Both monomers were regarded as rigid during the PES calculations. The calculation of interaction energies for all possible orientations is impractical so in our model we have considered 4 fixed orientations. The studied configurations have shown in Fig. 1. The angles between the carbon dioxide molecular axis and positive direction of Z- and X-axis have been indicated by α and β ,

respectively. The angle between the positive X-axis and one of the C–H bonds of methane is denoted as Θ . The calculation of potential energy surface performed over more than 50 intermolecular separation from $R \approx 0.5 \text{ \AA}$ to $R \approx 4 \text{ \AA}$ three angles $\Theta : (0.0, 35.3, 70.8)$ and two set of angles α and $\beta: (90.0, 0.0)$ and $(0.0, 90.0)$ which characterized in Fig. 1.

The energy and the distance at the

minimum of potential energy for the configurations in Fig. 1 are as: **a**: $\{-4.873, 0.8\}$, **b**: $\{-2.045, 0.8\}$, **c**: $\{-11.685, 0.55\}$, **d**: $\{-3.839, 0.8\}$ where the first entry was the energy in kcal/mol and the second entry was the minimum distance in Angstrom, respectively. The calculated intermolecular potentials of $\text{CH}_4\text{-CO}_2$ are presented in Fig. 2.

The relative stability for different orientations did not change after the BSSE correction .

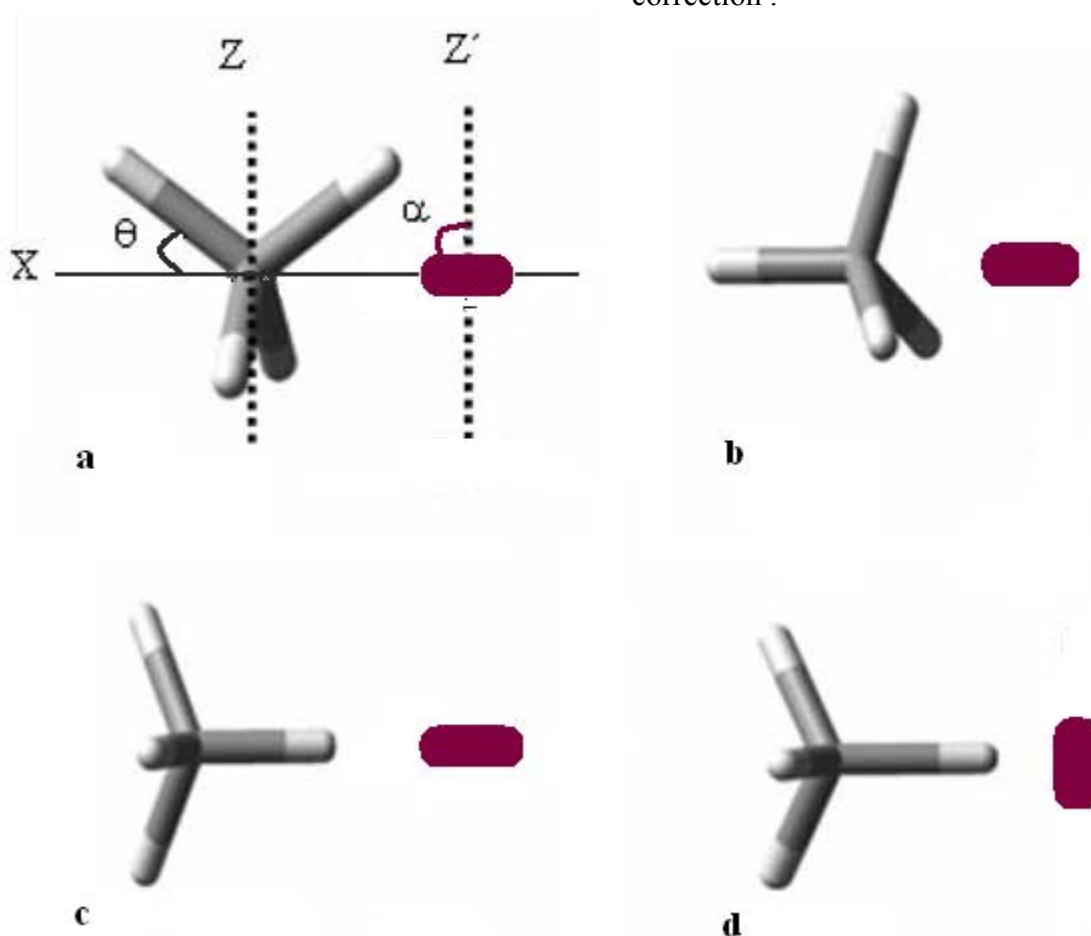


Fig. 1. All of the orientation interactions between CH_4 and CO_2 considered in this work.

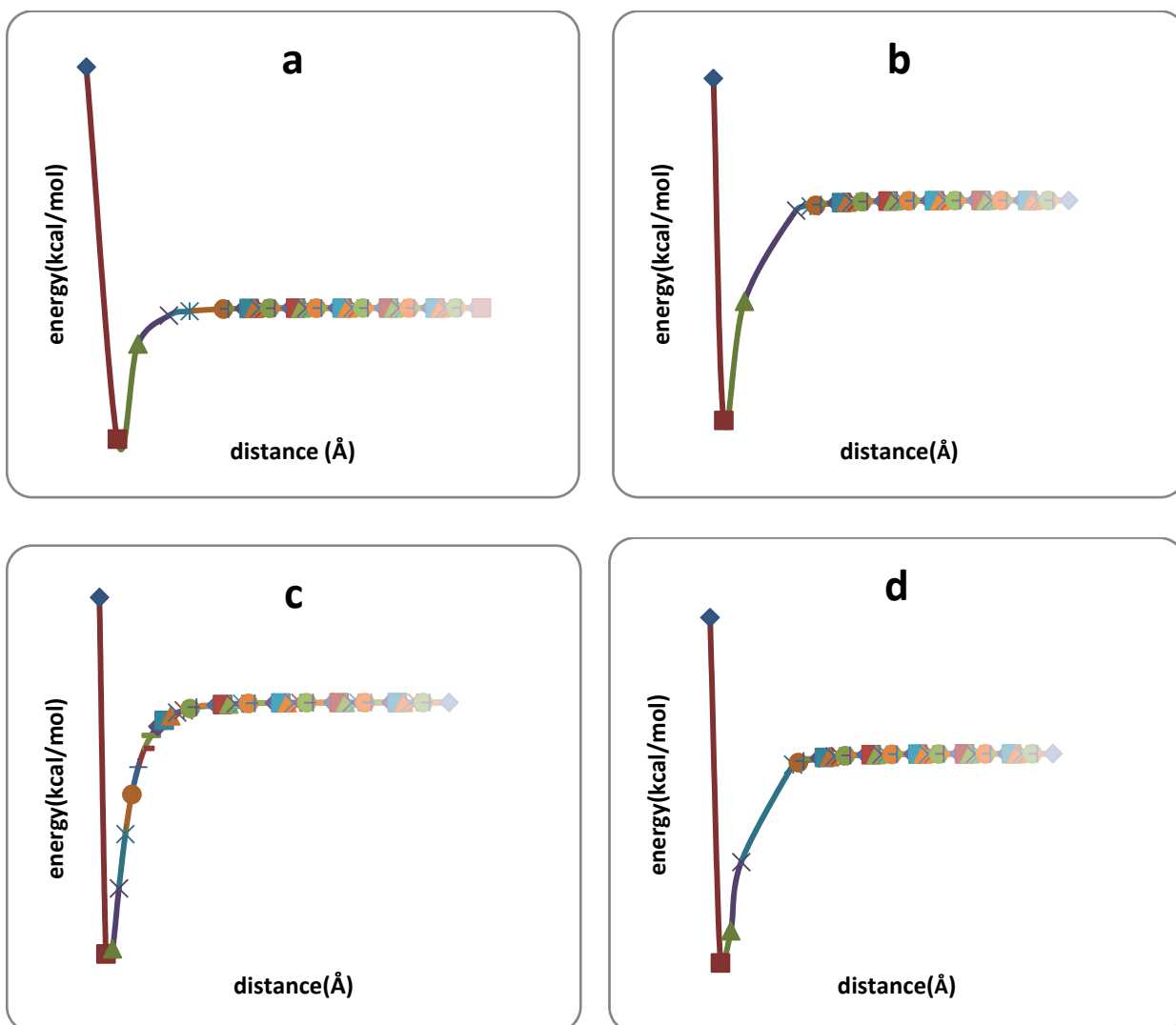


Fig. 2. Potential energy curves of configurations (*a*, *b*, *c* and *d*) via distances.

The orientation *c* has the deepest energy well depth (-11.685 kcal/mol) and the minimum distance (0.55Å). The *a* orientation has the most shallow energy well depth (-4.873 kcal/mol) and the minimum distance (0.8Å).

Assuming a given set of parameters, we estimate theoretically second virial coefficients for the system, Equation (3). To determine the virial coefficient *B* in Equation (3), using U_{AB} , the model's parameters were obtained earlier over the range of temperatures of interest. The *B* coefficient can, of course, be taken from the experiment, if the data are available.

Calculated results and temperature dependence of the second virial coefficients are plotted in Figure 3.

For given a numerical ab initio interaction potential of carbon dioxide – methane, it is useful to have an analytical potential function that can represent the methane carbon dioxide interaction accurately. To keep the fitted potential as simple as possible, methane and carbon dioxide have considered as one-center interaction or spherical interaction sites. The fitting of calculated ab initio energies U_{ab} was carried out with an initial guess for the potential parameters chosen in the

neighborhood of the values for some well-known site-site potentials. The functional form of the model potentials Lennard-Jonnes (12-6), is expressed as below:

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (4)$$

where r is the distance between the center of mass of molecules, ε and r are the

depth of the attractive well and effective diameter interaction, respectively. The second virial coefficient as a pure two body interaction property has been calculated to give a first simple test of the quality of intermolecular interaction potential. The values of them are listed in tables 1, 2, 3, 4 and calculated results plotted in figure (3).

Table 1. Calculated second virial coefficients for *a*

T(K)	B(cm ³ /mol)	T(K)	B(cm ³ /mol)	T(K)	B(cm ³ /mol)
75	-450.20	475	19.08	875	25.62
100	-178.60	500	19.95	900	25.77
125	-91.94	525	20.70	925	25.91
150	-52.55	550	21.36	950	26.04
175	-30.84	575	21.94	975	26.16
200	-17.35	600	22.46	1000	26.26
225	-8.27	625	22.92	1025	26.36
250	-1.79	650	23.33	1050	26.45
275	3.02	675	23.70	1075	26.53
300	6.73	700	24.03	1100	26.61
325	9.66	725	24.33	1125	26.67
350	12.02	750	24.60	1150	26.74
375	13.95	775	24.84	1175	26.79
400	15.57	800	25.07	1200	26.84
425	16.93	825	25.27		
450	18.09	850	25.45		

Table 2. Calculated second virial coefficients for *b*

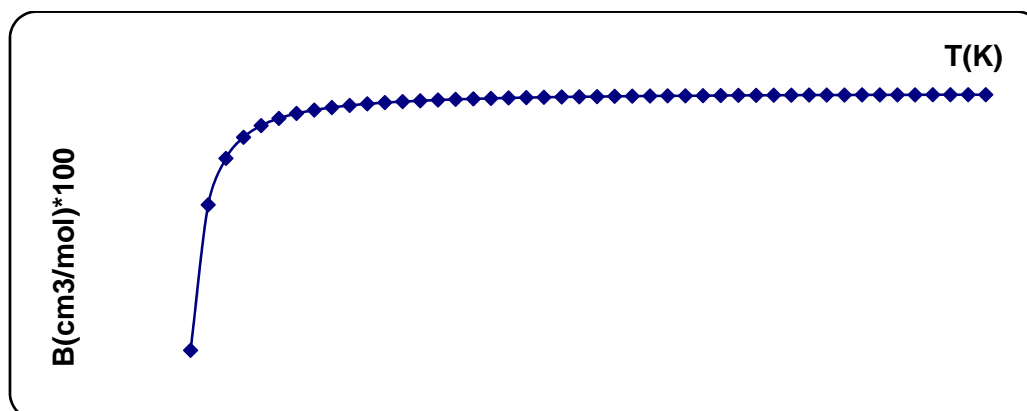
T(K)	B(cm ³ /mol)	T(K)	B(cm ³ /mol)	T(K)	B(cm ³ /mol)
75	-629013	475	-77.45	875	-5.41
100	-48378.8	500	-66.89	900	-3.82
125	-10600.2	525	-58.00	925	-2.36
150	-3880.26	550	-50.42	950	-1.01
175	-1890.2	575	-43.91	975	0.24
200	-1095.21	600	-38.26	1000	1.40
225	-710.03	625	-33.32	1025	2.48
250	-496.91	650	-28.98	1050	3.48
275	-367.14	675	-25.12	1075	4.42
300	-282.23	700	-21.69	1100	5.30
325	-223.53	725	-18.62	1125	6.12
350	-181.12	750	-15.85	1150	6.89
375	-149.4	775	-13.35	1175	7.61
400	-124.96	800	-11.09	1200	8.29
425	-105.68	825	-9.02		
450	-90.16	850	-7.14		

Table 3. Calculated second virial coefficients for *c*

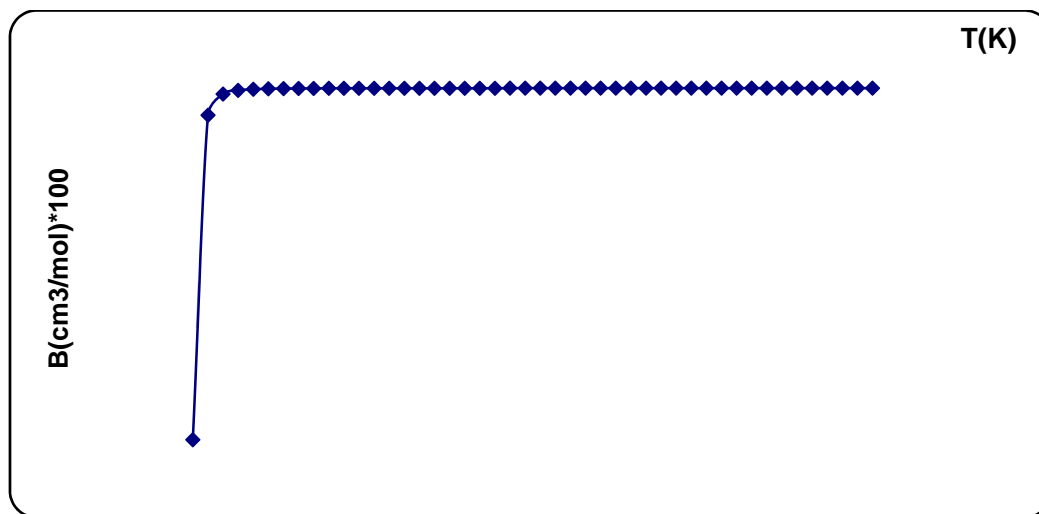
T(K)	B(cm ³ /mol)	T(K)	B(cm ³ /mol)	T(K)	B(cm ³ /mol)
75	-85487.4	475	-29.57	875	-2.67
100	-9178.8	500	-25.78	900	-2.04
125	-2447.62	525	-22.55	925	-1.46
150	-1016.81	550	-19.78	950	-0.91
175	-540.08	575	-17.38	975	-0.40
200	-332.94	600	-15.28	1000	0.006
225	-226.05	625	-13.43	1025	0.50
250	-163.93	650	-11.79	1050	0.915
275	-124.59	675	-10.33	1075	1.30
300	-98.01	700	-9.02	1100	1.66
325	-79.13	725	-7.84	1125	2.00
350	-65.18	750	-6.77	1150	2.32
375	-54.54	775	-5.80	1175	2.63
400	-46.20	800	-4.92	1200	2.91
425	-39.53	825	-4.10		
450	-34.08	850	-3.36		

Table 4. Calculated second virial coefficients for *d*

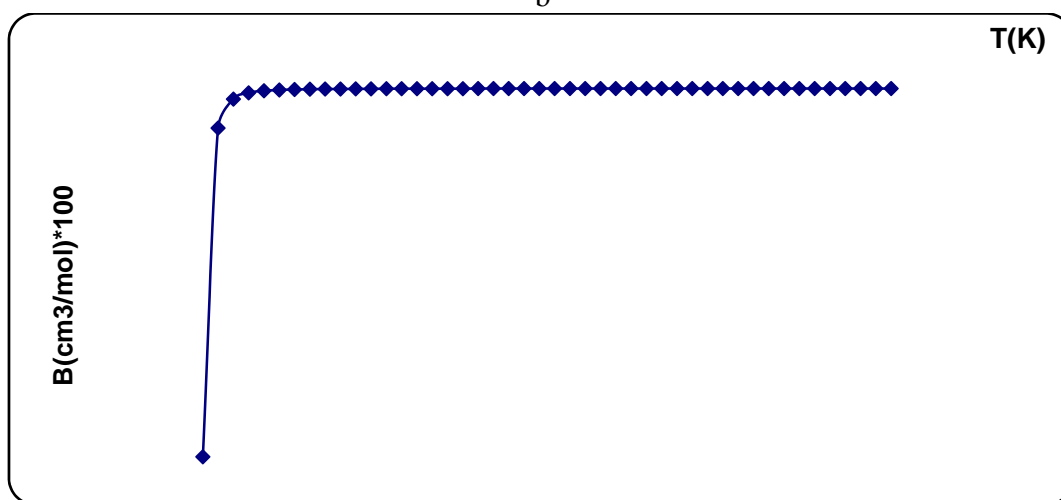
T(K)	B(cm ³ /mol)	T(K)	B(cm ³ /mol)	T(K)	B(cm ³ /mol)
75	-409.86	475	18.62	875	20.65
100	-134.12	500	18.98	900	20.66
125	-58.51	525	19.28	925	20.66
150	-27.46	550	19.53	950	20.66
175	-11.62	575	19.73	975	20.66
200	-2.38	600	19.91	1000	20.65
225	3.50	625	20.06	1025	20.64
250	7.50	650	20.18	1050	20.62
275	10.35	675	20.28	1075	20.60
300	12.45	700	20.37	1100	20.58
325	14.05	725	20.44	1125	20.56
350	15.28	750	20.50	1150	20.54
375	16.26	775	20.55	1175	20.51
400	17.04	800	20.58	1200	20.49
425	17.67	825	20.61		
450	18.19	850	20.63		



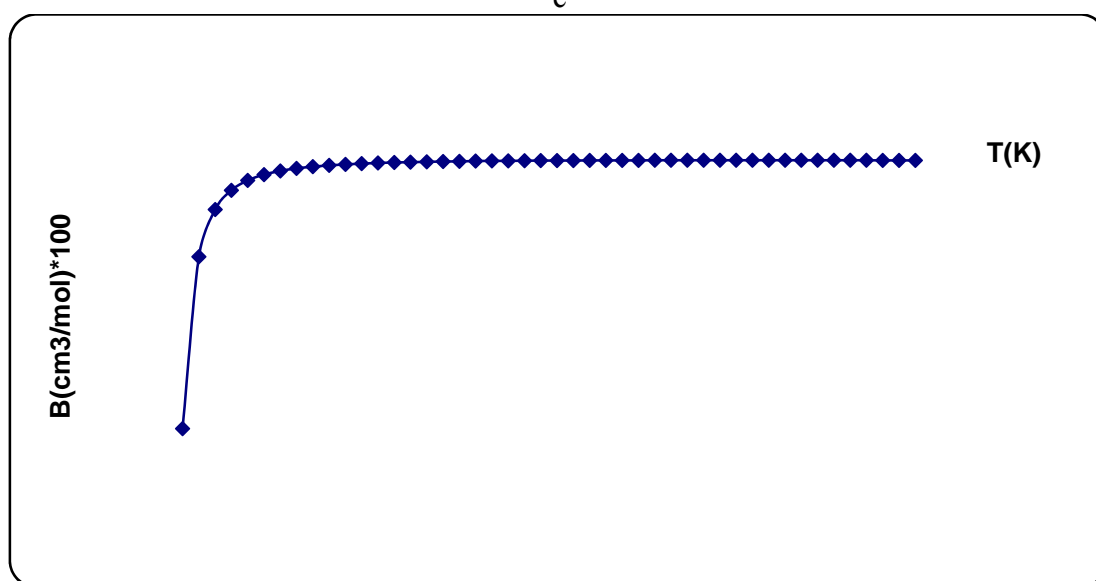
a



b



c



d

Fig. 3. Second virial coefficient (B) for LJ (12-6) potentials calculated in this work.

CONCLUSION

A new intermolecular potential for carbon dioxide–methane at the B3LYP level of theory and 6-31+G* basis set in order to locate the stationary points on the potential surface. Addition and reduction of potential energy by distance changing from far to near, on the other hand, depth of potential well in the case of approaching two molecules is lower than the state of approaching two atom or one atom and a molecule in order to form a bond. Generally, by increasing in approach of two molecules and the attraction force between them, the depth of the potential well increases. If electron clouds overlap was weak, two molecules can approach more and if they are located in proper distance from each other, one of molecules includes dipole moment and induces inductive dipole moment in neighboring molecule and this leads to generate longer attraction between them. Therefore, it releases more energy toward other states and increased the depth of potential well. In this work, we have been estimate the IPSs in the CO₂-CH₄ system by using the Lennard–Jones (12-6) potential model, to obtain the adjustable parameters of potential equations and theoretically second virial coefficients. The energy and the distance at the minimum of potential energy for the configurations in Fig. 1 are as: **a**: { -4.873 , 0.8}, **b**: { -2.045 , 0.8}, **c**: { -11.685 , 0.55 }, **d**: { -3.839 , 0.8 } where the first entry was the energy in kcal/mol and the second entry was the minimum distance in Angstrom, respectively. In consideration with Figure 3, the temperature dependence of second Virial coefficient is specified completely.

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