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INVESTIGATION OF BUCKINGHAM POTENTIAL IN MIXTURES OF METHANE - FORMALDEHYDE GASES

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ABSTRACT

The intermolecular potential energy surface in the mixtures of CH₄-H₂CO gases from ab initio calculations has been explored. In ab initio calculations the basis set superposition error (BSSE) is important. This error can be eliminated to some extent by using the counterpoise correction method (CPC). In this work ab initio calculation performed at the second-order Moller-Plesset theory, MP2, with the 6-311+G(2df,2pd) basis set, for six relative orientations of two CH₄- H₂CO molecules as a function of CH₄-H₂CO separation distance. Then, the adjustable parameters of Buckingham potential energy function are fitted to the ab initio MP2/6-311+G(2df,2pd) interaction energies for six different orientations. Assuming a given set of parameters, we obtained theoretically second virial coefficients for CH₄- H₂CO system in different temperatures.

Keywords: IPS, Second Virial Coefficient, BSSE, CPC, MP2, CHA

INTRODUCTION

To study intermolecular interaction in a chemical system can often lead to heavy numerical calculations in the form of ab initio quantum chemical methods or large scale molecular dynamics and Monte Carlo simulations. We will discuss these aspects to some extent, but intermolecular interactions can also be approached on a more descriptive level with a very modest amount of calculations done with paper and pen. The latter is the more fruitful approach for the ordinary chemist. Intermolecular interactions are of fundamental importance in understanding how atoms and molecules organize in liquids and solids. In the study of atomic and molecular forces one can discard forces whose effects do not coincide with molecular dimensions, i.e. gravitational forces are negligible. Only forces with an electrostatic origin, arising from the interaction between electrons and nuclei in different molecules, are of interest for the present applications. 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 (Alexander and Troya, 2006). The behavior of molecular clusters linked by hydrogen bonds is of special interest with a view to understanding a wide variety of chemical and biochemical problems (Bock *et al.*, 2000). Theoretical calculations provide detailed information about some aspects of the molecular interaction and the most likely structures for the clusters, which can rarely be accessed experimentally. Ab initio quantum mechanical calculations offer a way to obtain intermolecular potentials of molecules. This approach can be used to extract detailed information of the potential energy surface, which is sometimes difficult or practically impossible by other methods. Nevertheless, the quality of the potential is sensitive to the level of theory used for the calculation of the interaction energies. Also the BSSE has a significant effect on the calculated interaction potential and therefore it should be corrected for (Naroznik, 2003). Ab initio methods for calculating IPS have been reviewed by van der Avoird *et al.*, and van Lenthe *et al.*, Theoretical studies of van der Waals complexes and intermolecular forces have been reviewed by Buckingham *et al.*, In this work, the intermolecular potential energy surface, U(r), of the CH₄-H₂CO complex has been investigated. To determine the IPS components we used the Buckingham formula. We estimate theoretically second virial coefficients for CH₄-H₂CO system in different temperatures. All computations were done using the software Gaussian 98.

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Computational Methods

In quantum chemistry, calculations of interaction energies are susceptible to basis set superposition error (BSSE) if they use finite basis sets (Parra and Zeng, 2000). As the atoms of interacting molecules or two molecules approach one another, their basis functions overlap. Each monomer borrows functions from other nearby components, effectively increasing its basis set and improving the calculation of derived properties such as energy. If the total energy is minimised as a function of the system geometry, the short-range energies from the mixed basis sets must be compared with the long-range energies from the unmixed sets, and this mismatch introduces an error. Two methods exist to eliminate this problem. The chemical Hamiltonian approach (CHA) replaces the conventional Hamiltonian with one designed to prevent basis set mixing a priori, by removing all the projector-containing terms which would allow basis set extension (Rowley and Pakkanen, 1998). The counterpoise approach (CP) calculates the BSSE by re-performing all the calculations using the mixed basis sets, through introducing ghost orbital's, and then subtracts this error a posteriori from the uncorrected energy. Though conceptually very different, the two methods tend to give similar results.

In order to determination of potential energy surface, structures were fully optimized with the Moller-Plesset theory for the system. Our estimates are only approximate but interesting, nevertheless. The interaction energy, $U(r)$, for two A and B systems can simply be given as:

$$U(r) = E_{AB}(A...B) - E_{AB}(A + B) \quad (1)$$

where the arguments in parenthesis indicate the basis set being used. $E_{AB}(A...B)$ is the energy of the $A...B$ system at the (r) distance while $E_{AB}(A + B)$ is the energy of the two isolated components, at infinity ($r = \infty$). In ab initio calculations the BSSE is of paramount importance (Sabzyan and Noorbala, 2003). This error can be eliminated to some extent by using the counterpoise correction method (CPC) (Wang, 2003). 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

$$U = E_{AB}(A...B) - E_{AB}(A + B) + \Delta E_{CP} \quad (2)$$

where

$$\Delta E_{CP} = [E_A(A + B) - E_A(A...B)] + [E_B(A + B) - E_B(A...B)] \quad (3)$$

The form for the second virial coefficient, derived using statistical mechanics for the nonspherical symmetric surfaces of interaction energy, can be expressed as

$$B_2 = \frac{1}{(8\pi^2)^2} \frac{1}{2} N_A \int_0^\pi \sin(\vartheta) d\vartheta \int_0^{2\pi} d\varphi \int_0^\pi \sin(\beta_1) d\beta_1 \int_0^{2\pi} d\alpha_1 \int_0^{2\pi} d\gamma \int_0^\pi \sin(\beta_2) d\beta_2 \int_0^{2\pi} d\alpha_2 \int_0^{2\pi} d\gamma_2 \int_0^\infty \left\{ 1 - \exp\left[-\frac{V_{NB}}{RT}\right] \right\} r^2 dr_1 \quad (4)$$

where N_A is the Avogadro constant. The symbols $\alpha_1, \beta_1, \gamma_1, \alpha_2, \beta_2, \gamma_2$ are the Euler angles describing the orientation of the system of coordinates connected rigidly with the first and second reactant, respectively. The spherical coordinates r, ϑ, φ describe the mutual location of the reactant centers of mass.

Integration over angles requires the use of the normalization factor $(8\pi^2)^2$. To estimate the multiple integral (4) by the Monte-Carlo method we have to fix the number of necessary random points N and also the upper limit of the integral, r_{\max} . Both these values are strictly linked with the analyzed system and the temperature range. The simplest way to determine these values is as follows. For a given r_{\max} , we search for N starting from which the first three digits of integral (4) are fixed. Similarly, r_{\max} is selected so that its further increase does not result in any changes in integral (4).

The hard sphere approximation is very important in chemical kinetics. It is associated closely with average interaction energy between reactants that interact at different distances and at different orientations over some region of temperatures. Using this approximation we can obtain simple estimates of second virial coefficients, collisional frequencies, statistical sums and other parameters referring to the real reagents, even though these reagents are not spheres.

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Second Virial coefficient, B_2 , obtained either experimentally or estimated theoretically using the multidimensional interaction energy surface $U(r)$, Eq. (5), can be used to determine the magnitude of these parameters.

$$B_2 = 2\pi N_A \int_0^\infty \left\{ 1 - \exp\left[-\frac{U(r)}{KT}\right] \right\} r^2 dr \quad (5)$$

where $U(r)$ is the intermolecular potential energy, N_A is the Avogadro constant and r is the separation distance of two molecules.

RESULT AND DISCUSSION

In this work, the computational procedures started with geometry optimization of a methane molecule at MP₂ level of theory with aug-cc-pvtz basis set. The bond length, bond angle, dihedral angle parameters that explored at the ab initio method are listed in Table 1.

Table 1: The set of optimized parameters of Methane calculated at the MP2/aug-cc-pvtz

Optimized parameters	value
C-H bond length	1.089 Å
HCH bond angle	109.4712 °
HCHH dihedral angle	120 °

In order to determination of intermolecular potential energy surface, $U(r)$, of the CH₄-H₂CO system, H₂CO molecule has been approached to the CH₄ considered. A total of six different orientations of two CH₄-H₂CO molecules in the dimer relative to each other are shown in Figure 1. The intermolecular potential energy surface, $U(r)$, was calculated for different values of carbon-carbon separation, at the second-order Moller-Plesset theory, MP₂, with the 6-311+G (2df,2pd) basis set. IPS values of the (1) up to (6) orientations are listed in Table 2. The calculated $U(r)$ as a function of carbon- carbon separation distance of six different orientations are shown in Figure 2.

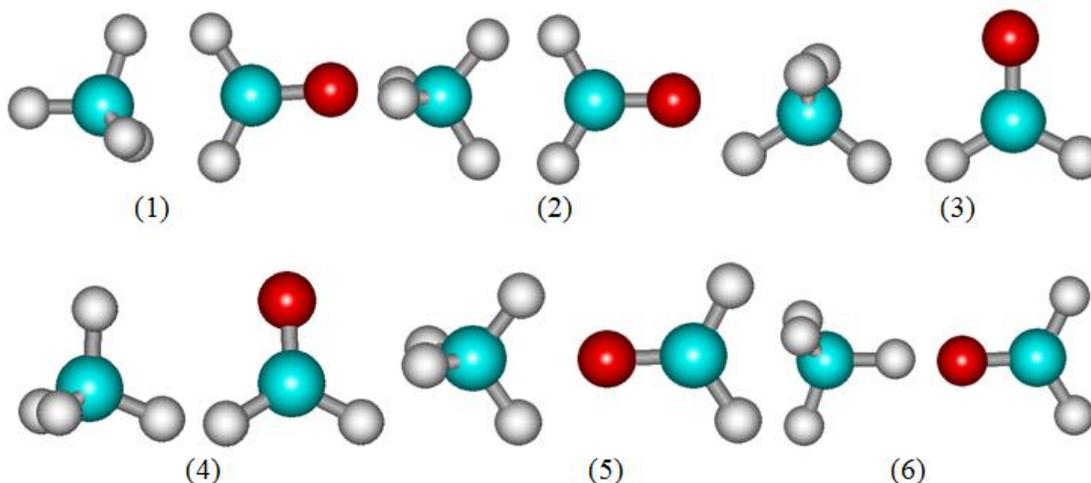


Figure 1: Six different orientations of H2CO and CH4

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Table 2: Intermolecular potential energy surface values of the six different orientations at the MP2 /6-311+G (2df, 2pd)

Energy					
Distance (Å), Calculated by Gaussian (Kelvin)					
Fitted by Buckingham model (Kelvin)					
Different orientations					
(1)	(2)	(3)	(4)	(5)	(6)
3.0, 1435.4060	3.0,	3.0,	3.0,	3.0, 66099.718	3.0, 1284.5814
1415.8689	3377.39975	8407.87261	3794.08964	66027.811	1282.7981
	3379.09093	8402.815677	3791.389177		
3.2, 367.69197	3.3,	3.5,	3.5,	3.5, 12837.881	3.2, 354.65726
390.16083	889.888499	1234.58332	253.648350	13120.477	354.50533
	871.6032998	1253.076409	262.2500141		
3.3, 90.452310	3.5,	3.6,	3.6,	4.0, 1826.7211	3.3, 104.75828
106.37197	210.743027	789.211744	66.9681972	1904.1975	106.99874
	219.9787039	802.7887527	73.0193157		
3.5, -221.9725	3.6,	3.8,	3.8,	4.2, 648.83651	3.5, -
-199.10662	17.2813036	271.652350	127.136203	617.19508	155.85785
	44.09869289	273.5928665	-123.462903		-150.39229
3.7, -	3.7, -81.66571	4.0,	4.0,	4.3, 279.5084	3.6, -
290.81287	-69.81856866	38.3703522	188.625797	247.22379	212.74252
-306.36967		29.22556296	-188.003057		-206.81556
4.0, -	3.8, -	4.1, -	4.3, -	4.5, -	3.8, -
272.27439	140.608755	20.7498442	157.272042	40.412624	247.46819
-309.56712	-140.4399267	-34.20651116	-186.088207	-172.5808	-244.78958
4.5, -	3.9, -	4.3, -	4.5, -	4.6, -	4.0, -
186.53219	172.687219	77.7603306	157.235304	115.58614	237.61415
-211.37438	-181.1282433	-96.75116395	-162.992888	-279.29481	-232.88418
5.0, -	4.0, -	4.5, -	5.0, -	4.8, -	4.1, -213.6786
127.25699	187.010298	92.9540681	99.6928606	178.55535	-223.69398
-127.23999	-201.407403	-112.778106	-102.116662	-376.19032	
5.5, -	4.5, -	4.7, -	5.5, -	5.0, -	4.3, -
88.092475	155.601184	89.8438562	67.1161587	182.58655	192.61371
-75.497878	-173.9053088	-108.3205246	-60.9693902	-386.83105	-186.18572
6.0, -	5.0, -	5.0, -	6.0, -	5.5, -	4.5, -
65.108109	108.228328	74.3129274	44.6803582	134.36317	163.35155
-45.679366	-110.1395508	-89.01502388	-36.8739211	-294.24511	-153.55053
6.5, -50.65418	5.5, -	5.5, -	6.5, -	6.0, -	5.0, -
-28.469402	69.6425768	50.9058148	31.7563708	75.998884	108.17297
	-66.26358916	-56.71414944	-22.9569479	-193.6735	-90.277016
7.0, -	6.0, -	6.0, -	7.0, -	6.5, -	6.0, -
41.011516	47.6194581	37.6697996	23.7090749	44.066368	48.802144
-18.299954	-40.2406151	-35.05928798	-14.7465702	-124.54531	-31.762315
7.5, -	7.0, -	7.0, -	7.5, -	7.0, -	7.0, -
34.574686	26.4871283	20.0804944	18.4549305	26.643142	35.027629
-12.108386	-16.13663156	-14.16283851	-9.75404562	-80.999867	-19.734642
8.0, -30.32205	8.0, -	8.0, -	8.0, -	8.0, -	8.0, -
-8.2234808	17.8812021	14.3130140	14.9421022	9.8691352	25.878171
	-7.251034332	-6.368369316	-6.62359958	-36.611705	-12.668814

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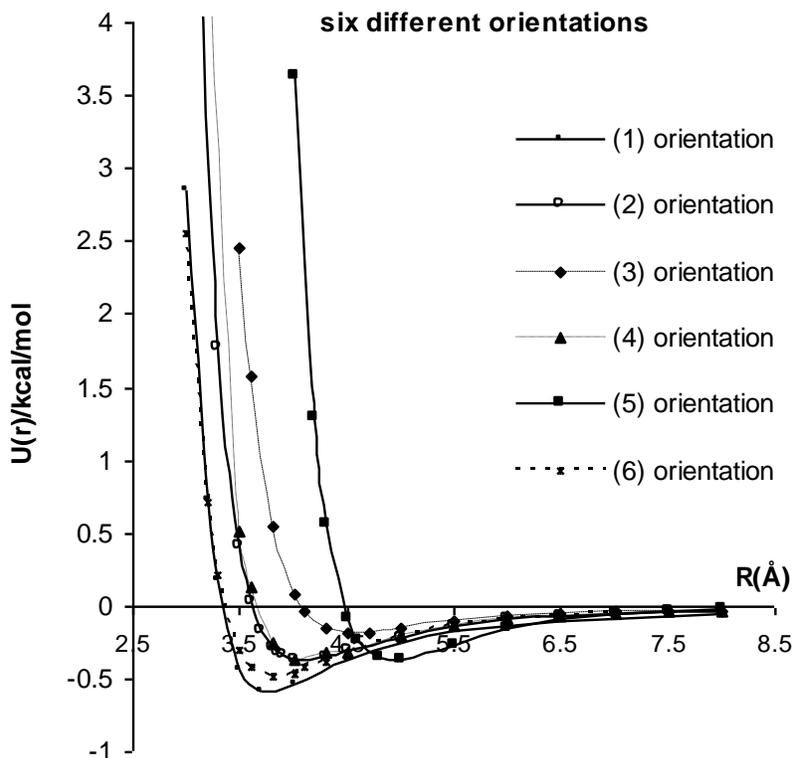


Figure 2: The intermolecular potential energy obtained as a function of carbon- carbon ($\text{CH}_4\text{-H}_2\text{CO}$) separation distance at the $\text{MP}_2/6\text{-311+G}$ (2df, 2pd)

It can be seen from Figure 2 that all of six orientations, separation distances of carbon-carbon have significant effects on the calculated potential energy curves (including position, depth and width of the potential well). Furthermore, the following trends with different distance can be deduced for the depth ($D_e = -E_{\text{int}}(R_e) = -E_{\text{min}}$) of the potential well of the calculated IPS.

It is evident from Figure 2 and Table 2; the potential energy curves with the largest value of (D_e) are obtained with (1) orientation, at the $\text{MP}_2/6\text{-311+G}$ (2df,2pd) level of theory. The calculated IPS can further be compared based on the values of the position of the minimum point (R_e) of the potential curves. These quantities are very sensitive to different orientations and values of separation distance of C-C at the Ab initio calculations. In ab initio calculations the BSSE is paramount importance. This error can be eliminated to some extent by using the counterpoise correction method (CPC). The Numerical values of D_e and R_e for (1) orientation are -0.577846 (Kcal/mol) or -290.81287 Kelvin and 3.7 (Å) respectively.

In this work, to estimate the IPS, $U(r)$, in the $\text{CH}_4\text{-H}_2\text{CO}$ system we used Buckingham potential model. Can be expressed as:

$$U(r) = A \exp(-Br_{ij}) + \frac{C}{r_{ij}^6} \quad (6)$$

where A, B and C are the adjustable parameters, and r is the separation distance between C-C. Then, the adjustable parameters of Buckingham potential model are fitted to the ab initio $\text{MP}_2/6\text{-311+G}$ (2df,2pd) interaction energies for six different orientations. The values of adjustable potential parameters for six different orientations are listed in Table 3. And curves of ab initio IPSs are fitted to Buckingham potential have been shown in Figure 3. So, we have shown in our work that it is possible to obtain quite a potential function, $U(r)$, for $\text{CH}_4\text{-H}_2\text{CO}$ system by quantum mechanical calculations.

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Table 3: Adjustable parameters for six different orientations are fitted to Buckingham potential model.

Different orientations	Adjustable parameters		
	A	B	C
(1)	71318.45	3.004243	-4284.14
(2)	140770.8	3.126231	-3777.43
(3)	311572.1	3.197714	-3317.8
(4)	219729	3.264426	-3450.37
(5)	1019001	2.989273	-12337.8
(6)	107931.8	3.228638	-3025.27

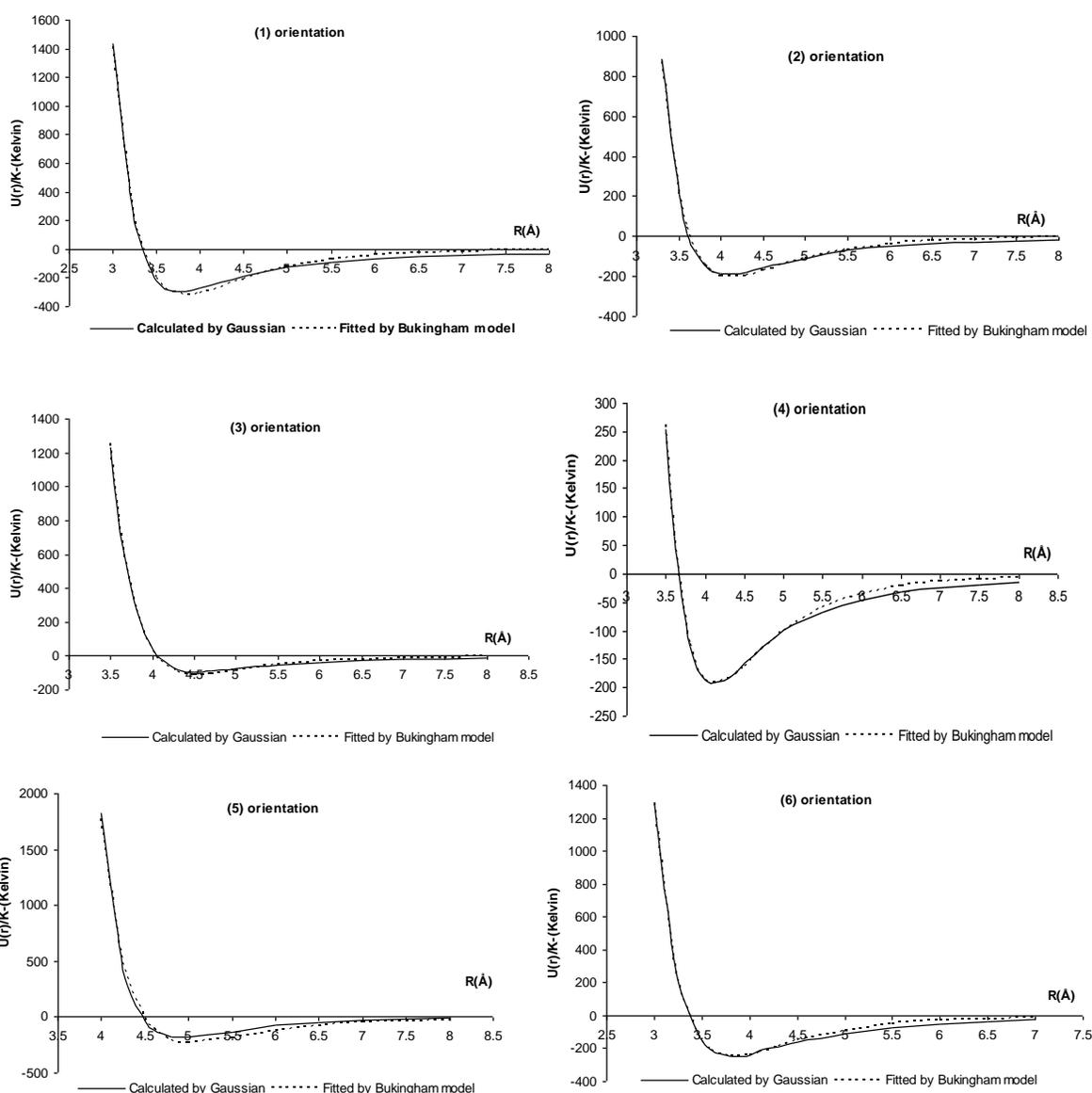


Figure 3: The CH₄-H₂CO intermolecular potential energy interaction obtained at MP₂ /- 311+G(2df,2pd) are fitted to Buckingham potential model

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Therefore, to know $U(r)$ formula, we can estimate theoretically second virial coefficients, B_2 , for optimum orientation, (1), $\text{CH}_4\text{-H}_2\text{CO}$ system by quantum mechanical calculations. The second virial coefficients were calculated using Eq. (5); calculations were performed for a range of different temperatures and results of second virial coefficients are plotted in Figure 4.

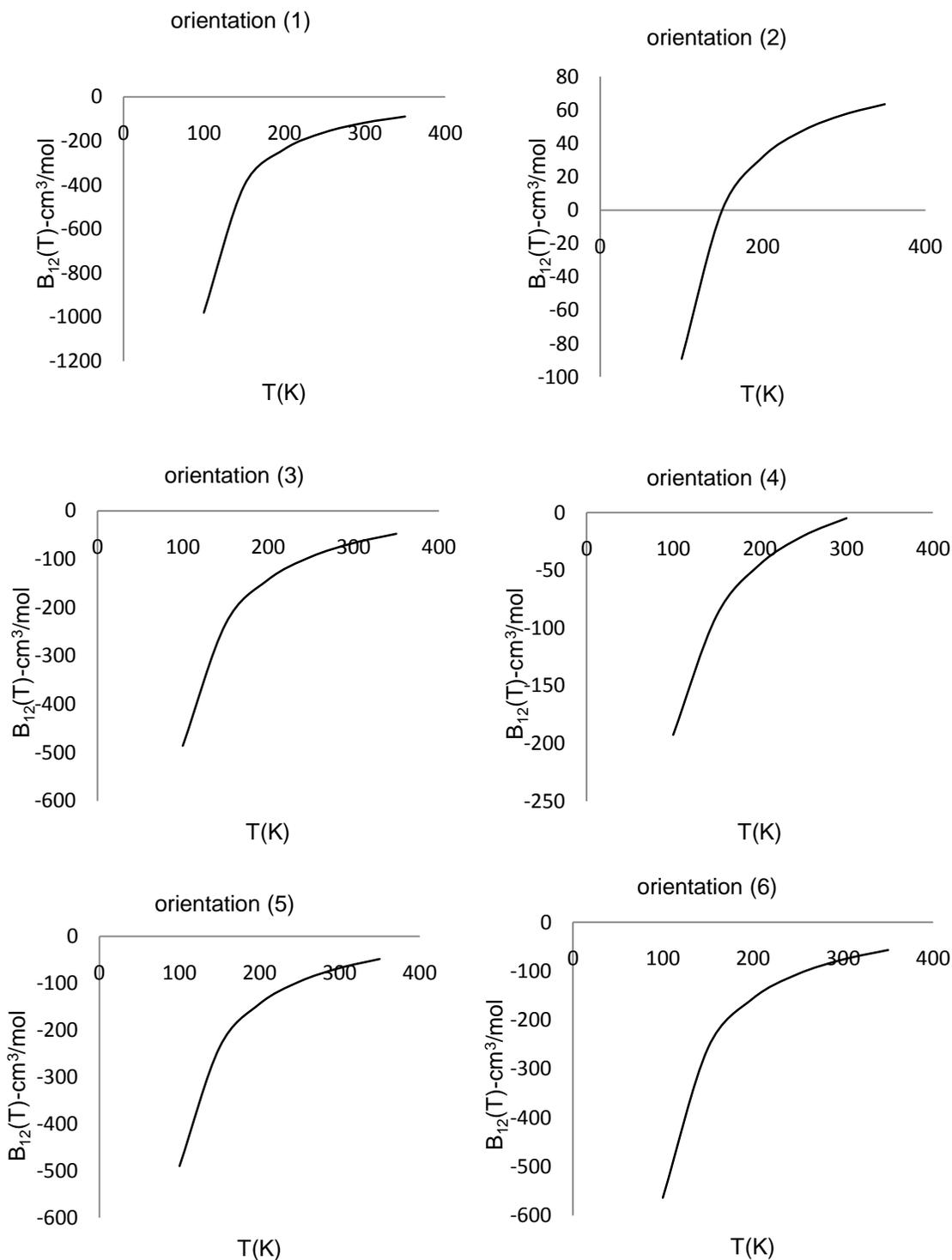


Figure 4: Second virial coefficients curve for selected temperatures.

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Conclusions

Addition and reduction of potential energy by distance changing from far to near, in 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. Thus, with respect to Figure 2, in (1) state which the spatial intruding of hydrogen atoms for approaching is lower rather than other states, so, electron clouds overlap weakly. Thus, two molecules can approach more and if they locate 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 London attraction between them. Therefore, it releases more energy toward other states and get increased the depth of potential well. In consideration with Figure 4, the temperature dependence of second Virial coefficient is specified completely.

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