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Theoretical study of intermolecular potential energy and second virial coefficient in the mixtures of CH_4 and H_2CO gases

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ABSTRACT

To get a mole of a gas, it is necessary to calculate the intermolecular interaction. These intermolecular interactions can be depicted by drawing the potential energy of a pair molecule in relation to the distance. The intermolecular potential energy surface in the mixtures of CH_4-H_2CO 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, MP_2, with the 6-311+G(2df,2pd) basis set, for six relative orientations of two CH_4- H_2CO molecules as a function of CH_4-H_2CO separation distance. Then, the adjustable parameters of Buckingham potential energy function are fitted to the ab initio MP_2/6-311+G(2df,2pd) interaction energies for six different orientations. Assuming a given set of parameters, we obtained theoretically second virial coefficients for CH_4- H_2CO system in different temperatures.

Keywords: IPS; Second virial coefficient; BSSE; CPC; MP_2

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

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the second virial coefficient of a moderately dense gas is straightforward if the intermolecular pair potential is accurately known [1]. 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 [2]. 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 [3]. Ab initio methods for calculating IPS have been reviewed by van der Avoird et al. [4] and van Lenthe et al.[5].

Theoretical studies of van der Waals complexes and intermolecular forces have been reviewed by Buckingham et al. [6]. In this work, the intermolecular potential energy surface, U(r), of the CH_4-H_2CO complex has been investigated. To determine the IPS components we used the Buckingham formula. We estimate theoretically second virial coefficients for CH_4-H_2CO system in different temperatures. All computations were done using the software Gaussian 98.

COMPUTATIONAL METHODS

In quantum chemistry, calculations of interaction energies are susceptible to basis set superposition error (BSSE) if they use finite basis sets. 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. The counterpoise approach (CP) calculates the BSSE by re-performing all the calculations using the mixed basis sets, through introducing ghost orbitals, 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:

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

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 [7]. This error can be eliminated to some extent by using the counterpoise correction method (CPC). 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

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

Table 1. The set of optimized parameters of Methane calculated at the MP_2/aug-cc-pvtz

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

The form for the second virial coefficient, derived using statistical mechanics for the nonspherical symmetric surfaces of interaction energy, can be expressed as[8]

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

where N_A is the Avogadro constant. The symbols α_1, β_1, γ_1, α_2, β_2, γ_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.

These values can be defined as described in Ref. [9]. 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.

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[10].

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

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

RESULTS 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. 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 dimmer relative to each other are shown in Fig 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 Fig 2.

It can be seen from Fig 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_{int} (R_e) = -E_{min}) of the potential well of the calculated IPS.

It is evident from Fig 2 and Table 2; the potential energy curves with the largest value of (De) are obtained with (1) orientation, at the MP_2 /6-311+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 CH_4-H_2CO system we used Buckingham potential model. Can be expressed as:

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

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 MP_2 /6-311+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 Fig 3. So, we have shown in our work that it is possible to obtain quite a potential function, U(r), for CH_4- H_2CO system by quantum mechanical calculations.

Therefore, to known $U(r)$ formula, we can estimate theoretically second virial coefficients, B_2, for optimum orientation, (1), CH_4- H_2CO system by quantum mechanical calculations. The second virial coefficients were calculated using Eq. (6); calculations were performed for a range of different temperatures and results of second virial coefficients are plotted in Fig. 4.

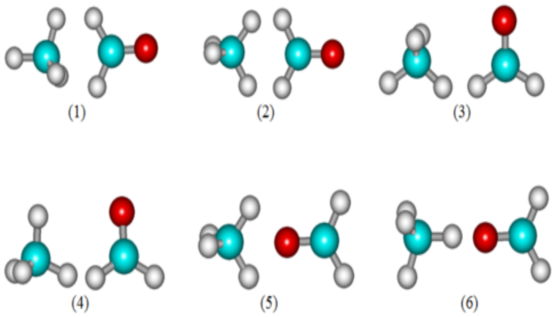


Fig. 1. Six different orientations of H_2CO and CH_4.

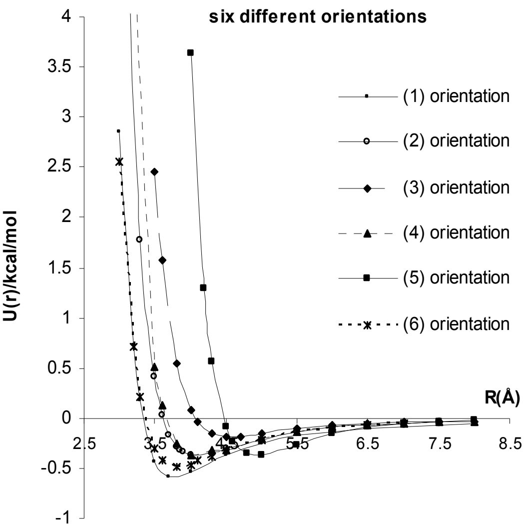
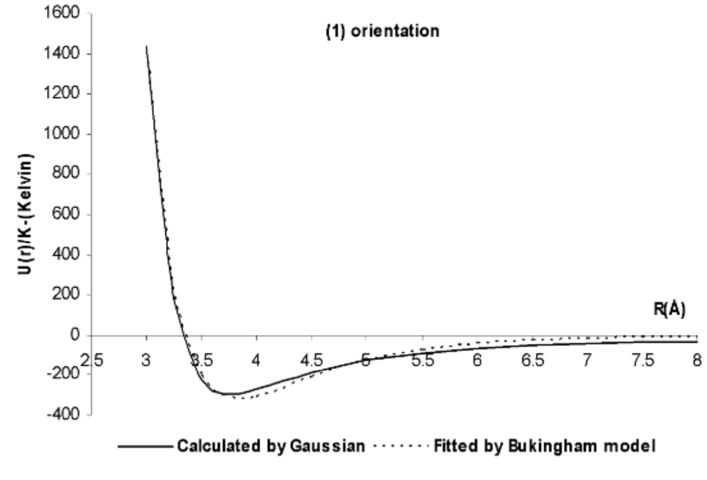
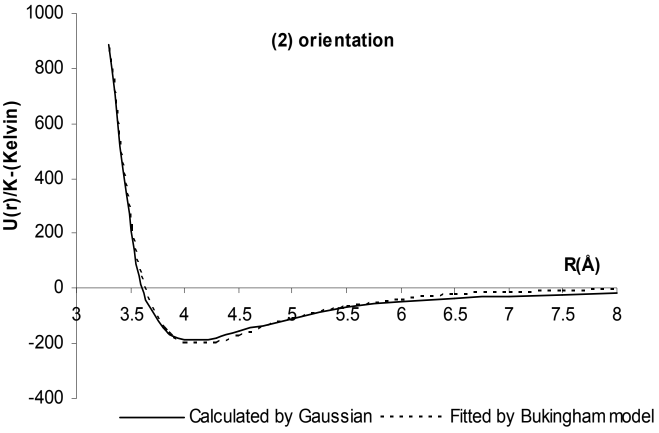


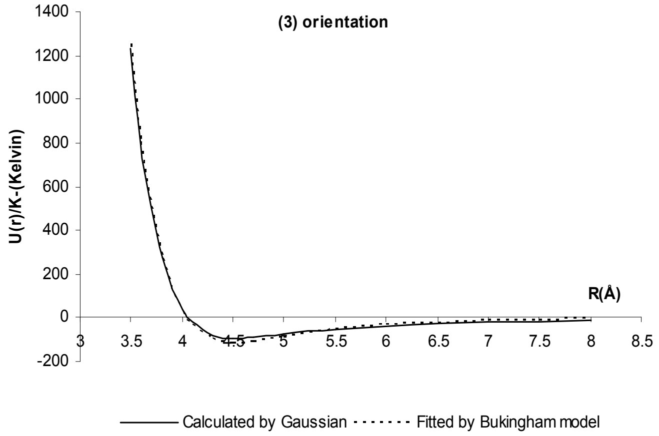
Fig. 2. The intermolecular potential energy obtained as a function of carbon- carbon (CH_4-H_2CO) separation distance at the MP_2 /6-311+G (2df,2pd).

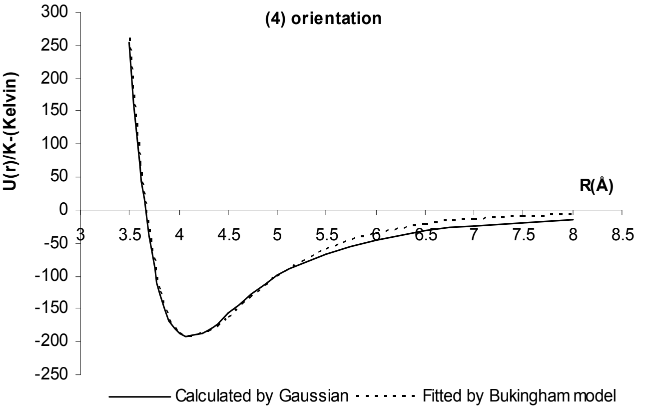
CONCLUSIONS

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 Fig. 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 Fig 4, the temperature dependence of second Virial coefficient is specified completely.




(2) orientation
U(r)/K-(Kelvin)
1000
800
600
400
200
0
-200
-400
R(Å)
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
Calculated by Gaussian
Fitted by Bukingham model


(3) orientation
U(r)/K-(Kelvin)
1400
1200
1000
800
600
400
200
0
-200
R(Å)
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
8.5
Calculated by Gaussian
Fitted by Bukingham model


(4) orientation
U(r)/K-(Kelvin)
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
R(Å)
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
8.5
Calculated by Gaussian
Fitted by Bukingham model

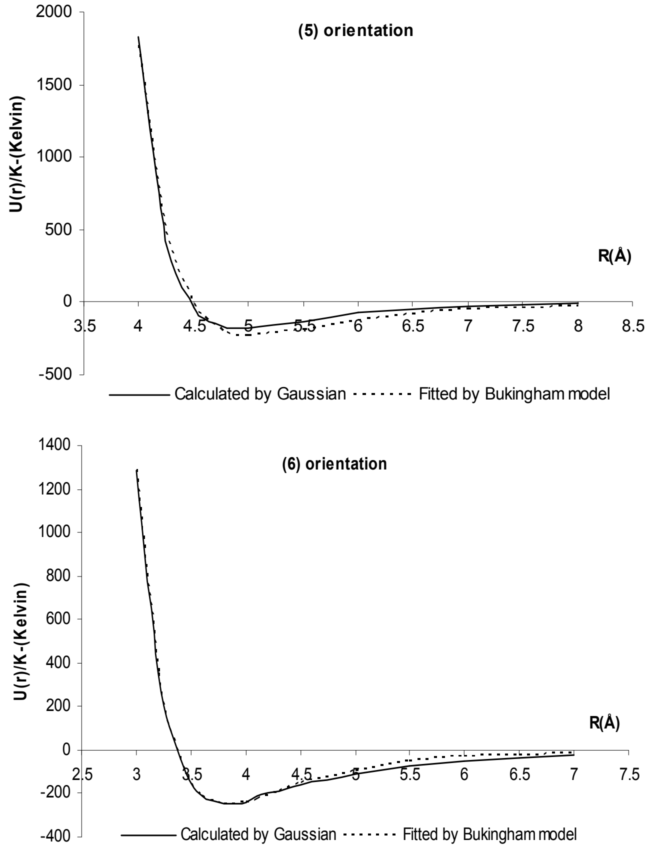


Fig. 3. The CH_4-H_2CO intermolecular potential energy interaction obtained at MP_2/-311+G(2df,2pd) are fitted to Buckingham potential model.

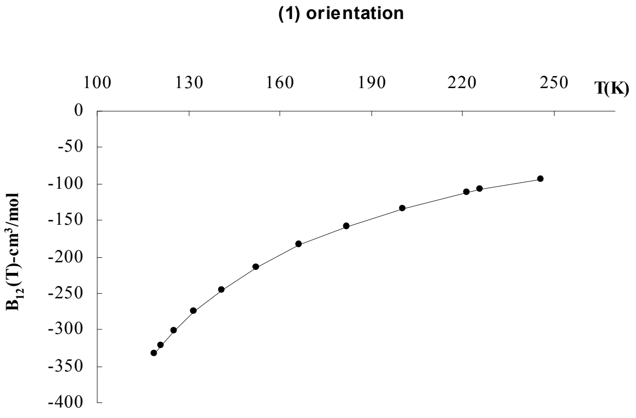


Fig. 4. Second virial coefficients curve for selected temperatures.

Table 2. Intermolecular potential energy surface values of the six different orientations at the MP_2/6-311+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 1415.8689	3.0, 3377.39975 3379.09093	3.0, 8407.87261 8402.815677	3.0, 3794.08964 3791.389177	3.0, 66099.718 66027.811	3.0, 1284.5814 1282.7981
3.2, 367.69197 390.16083	3.3, 889.888499 871.6032998	3.5, 1234.58332 1253.076409	3.5, 253.648350 262.2500141	3.5, 12837.881 13120.477	3.2, 354.65726 354.50533
3.3, 90.452310 106.37197	3.5, 210.743027 219.9787039	3.6, 789.211744 802.7887527	3.6, 66.9681972 73.0193157	4.0, 1826.7211 1904.1975	3.3, 104.75828 106.99874
3.5, -221.9725 -199.10662	3.6, 17.2813036 44.09869289	3.8, 271.652350 273.5928665	3.8, -127.136203 -123.462903	4.2, 648.83651 617.19508	3.5, -155.85785 -150.39229
3.7, -290.81287 -306.36967	3.7, -81.66571 -69.81856866	4.0, 38.3703522 29.22556296	4.0, -188.625797 -188.003057	4.3, 279.5084 247.22379	3.6, -212.74252 -206.81556
4.0, -272.27439 -309.56712	3.8, -140.608755 -140.4399267	4.1, -20.7498442 -34.20651116	4.3, -157.272042 -186.088207	4.5, -40.412624 -172.5808	3.8, -247.46819 -244.78958
4.5, -186.53219 -211.37438	3.9, -172.687219 -181.1282433	4.3, -77.7603306 -96.75116395	4.5, -157.235304 -162.992888	4.6, -115.58614 -279.29481	4.0, -237.61415 -232.88418
5.0, -127.25699 -127.23999	4.0, -187.010298 -201.407403	4.5, -92.9540681 -112.778106	5.0, -99.6928606 -102.116662	4.8, -178.55535 -376.19032	4.1, -213.6786 -223.69398
5.5, -88.092475 -75.497878	4.5, -155.601184 -173.9053088	4.7, -89.8438562 -108.3205246	5.5, -67.1161587 -60.9693902	5.0, -182.58655 -386.83105	4.3, -192.61371 -186.18572
6.0, -65.108109 -45.679366	5.0, -108.228328 -110.1395508	5.0, -74.3129274 -89.01502388	6.0, -44.6803582 -36.8739211	5.5, -134.36317 -294.24511	4.5, -163.35155 -153.55053
6.5, -50.65418 -28.469402	5.5, -69.6425768 -66.26358916	5.5, -50.9058148 -56.71414944	6.5, -31.7563708 -22.9569479	6.0, -75.998884 -193.6735	5.0, -108.17297 -90.277016
7.0, -41.011516 -18.299954	6.0, -47.6194581 -40.2406151	6.0, -37.6697996 -35.05928798	7.0, -23.7090749 -14.7465702	6.5, -44.066368 -124.54531	6.0, -48.802144 -31.762315
7.5, -34.574686 -12.108386	7.0, -26.4871283 -16.13663156	7.0, -20.0804944 -14.16283851	7.5, -18.4549305 -9.75404562	7.0, -26.643142 -80.999867	7.0, -35.027629 -19.734642
8.0, -30.32205 -8.2234808	8.0, -17.8812021 -7.251034332	8.0, -14.3130140 -6.368369316	8.0, -14.9421022 -6.62359958	8.0, -9.8691352 -36.611705	8.0, -25.878171 -12.668814

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

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