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Theoretical study of basis set effects on the nano intermolecular potential energy surface of alanine - methionine: Calculation of second-virial coefficients

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The potential energy of Alanine-Methionine was studied on the basis of ab initio calculations performed by using the HF, DFT-B3LYP and MP2 methods with 6-31G and 6-31G* basis sets. The following trends with basis set can be deduced for the depth ($D_e = -E_{\text{int}}(R_e) = -E_{\text{min}}$) of the potential well of the calculated intermolecular potential energy surfaces (IPSS). 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, to estimate the interaction energy $U(r)$ in the system we use the Morse potential model, and we estimate adjustable parameters used in the Morse model and theoretically second virial coefficient for the system. To determine the second virial coefficients B_2 , $U(r)$ is used to obtain the model's parameters over the range of temperatures of interest.

Key words: IPS, second virial coefficient, basis set superposition error, counterpoise correction method, MP2, HF and DFT-B3LYP method.

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, that is, gravitational forces are negligible. Only forces with an electric 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 (Hobza and Zahradnik, 1988). 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 (Boys and Bernardi, 1970). 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

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Abbreviations: IPS, intermolecular potential energy surfaces; BSSE, basis set superposition error; CPC, Counterpoise Correction, DFT, Density Function Theory; HF, Hartree-Fock; MP2, second order Moller-Plesset perturbation theory.

impossible by other methods (Ghiasi and Monajjemi, 2008; Monajjemi et al., 2004). 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 (Bock, 2000). *Ab initio* methods for calculating IPS have been reviewed by van der Avoird et al. (1980) and van Lenthe et al. (1988). Theoretical studies of van der Waals complexes and intermolecular forces have been reviewed by Buckingham et al. (1988). Also, much more studies have been reported on the CH₄ complexes, CH₄-He (Specchio et al., 2000), CH₄-Ar (Wanglera et al., 2003), CH₄-H₂O (Azczesniak et al., 1993), CH₄-HF (Legon et al., 1990), CH₄-NO (Akiike et al., 1995) and CH₄-NO⁺ (Lee et al., 1997). The second virial coefficient B₂ depends only on the pair interaction between the particles, the third (B₃) depends on 2- and non-additive 3-body interactions, and so on (Leonhard and Deiters, 2002). Also, Fifth virial coefficients for a system of hard disk have been done by Kratky (1976). A basis set in chemistry is a set of functions used to create the molecular orbitals, which are expanded as a linear combination of such functions with the weights or coefficients to be determined. Usually these functions are atomic orbitals, in that they are centered on atoms. Otherwise, the functions are centered on bonds or lone pairs. Pairs of functions centered in the two lobes of a p orbital have also been used. Additionally, basis sets composed of sets of plane waves down to a cutoff wavelength are often used, especially in calculations involving systems with periodic boundary conditions and the basis set effects for CF₄-CF₄, F₂-F₂, CH₄-CO complex have been done (Tanaka et al., 2004; Parra and Zeng, 2000; Sabzyan and Noorbala, 2003). The aim of this investigation has been studied of intermolecular interactions for larger systems such as the Alanine and Methionine in protein-protein system. The additional question arises as to where to position the ghost orbitals. This becomes problematic once the structures of the monomers change substantially on dimer formation. In this work, basis set effects on the calculated IPS of the Ala-Meth system have been investigated. In this study, HF, DFT-B3LYP and MP2 methods have been used with various basis sets to find the most appropriate basis set(s), which is (are) suitable for the derivation of the Ala-Meth IPS.

COMPUTATIONAL DETAILS

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 (Ghiasi et al., 2004; Ghiasi and Monajjemi, 2007). 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 practice, structures were fully optimized with the HF method in order to locate the stationary points on the potential surface 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. 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

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

where

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

Our calculations were performed by using the program package GAUSSIAN 98 exclusively.

The form for the second virial coefficient, derived using statistical mechanics for the nonspherical symmetric surfaces of interaction energy, can be expressed as shown by Smirnova (1980).

$$B_2 = \frac{1}{(8\pi)^2} N_A \int_0^\pi \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} \left\{ 1 - \exp\left[-\frac{V_{NB}}{RT}\right] \right\} r^2 dr \quad (4)$$

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.

These values can be defined as described by Naroznik (2003). 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

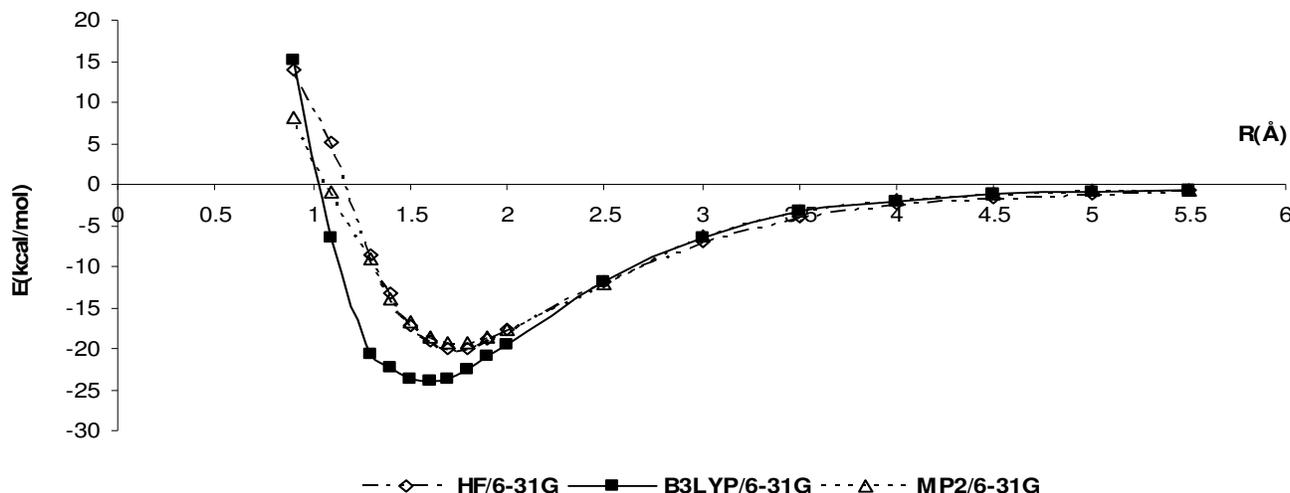


Figure 1. The Ala-Meth intermolecular potential energy interactions obtained at RHF, B3LYP and MP2 levels.

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 (Equation 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.

The second virial coefficient is an important parameter for determining the thermodynamic properties. The virial expansion truncated after three terms (Hirschfelder et al., 1967).

$$Z = \frac{P}{\rho kT} = 1 + B_2 \rho + B_3 \rho^2 \quad (5)$$

where Z is the compressibility factor, k is the Boltzmann's constant and T is the absolute temperature, P is the pressure, ρ is the density, B_2 is the second virial coefficient, and B_3 is the third virial coefficient.

Second virial coefficient, B_2 , obtained either experimentally or estimated theoretically using the multidimensional interaction energy surface U_{AB} , Equation (6), can be used to determine the magnitude of these parameters. In this work, known form for $U(r)$ to estimation of second virial coefficients (Narožnik, 2003):

$$B_2 = 2\pi N_A \int_0^{\infty} \left\{ 1 - \exp \left[-\frac{U(r)}{KT} \right] \right\} r^2 dr \quad (6)$$

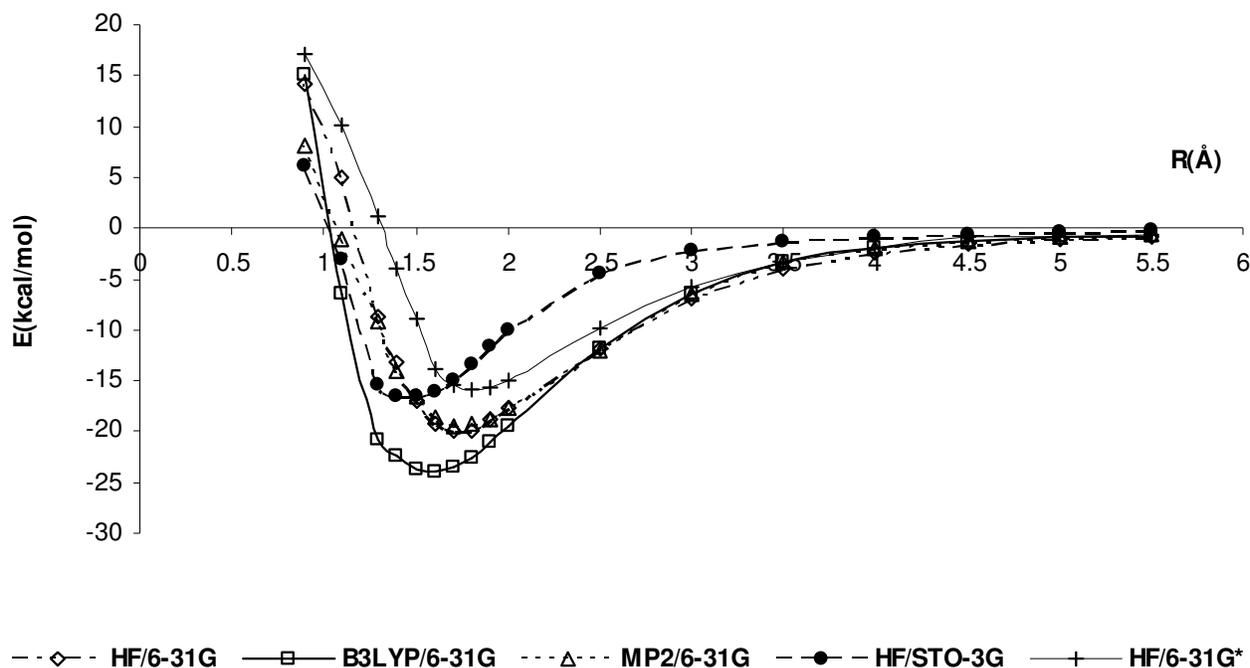
where $U(r)$ is the intermolecular potential energy, N_A is the Avogadro constant. The second virial coefficients calculated this way are fitted to the initial coefficients B_2 varying ϵ and r_0 , eventually some other parameters.

RESULTS AND DISCUSSION

To evaluate the methods effects, we calculated the intermolecular interaction energies of the Ala- Meth system at HF, DFT-B3LYP and MP2 levels of theory with 6-31G basis set, that are plotted in Figure 1 as functions of R ; the distance between Ala and Meth (Monajjemi et al., 2007; Monajjemi et al., 2003). So, to determine the effects of basis sets, we calculated the intermolecular interaction energies of the Ala- Meth system at HF, DFT-B3LYP and MP2 levels of theory with 6-31G, 6-31G* and STO-G basis sets, that are given in Table 1 and Figure 2. It can be seen from these figures, that at all three levels of theory, basis sets has significant effects on the calculated potential energy curves (including position, depth and width of the potential well). Furthermore, the following trends with basis set can be deduced for the depth ($D_e = -E_{\text{int}}(R_e) = -E_{\text{min}}$) of the potential well of the calculated IPSs. Numerical values of D_e are given in Table 2; as can be seen from Figure 2 and Table 2, the potential energy curves with the largest value of D_e are obtained with 6-31G basis set, at B3LYP level of theory. The calculated IPSs can further be compared based on the values of the position of the minimum point (R_e) of the potential curves. As is evident from this table, these quantities are very sensitive to the basis set used in the computations. The values of D_e and R_e for MP2, B3LYP and HF methods with the 6-31G basis set are -19.3608 (1.7), -23.9198 (1.6) and -19.99640 (1.7) respectively. These quantities are very sensitive to the basis set. For

Table 1. The Ala-Meth intermolecular potential energy surface values in different methods and distance.

| Distance (Å) | E (kcal/mol) | | | | |
|--------------|--------------|------------|------------|------------|------------|
| | B3LYP | MP2 | HF | | |
| | 6-31G | 6-31G | 6-31G | STO-3G | 6-31G* |
| 5.5 | -0.790235 | -0.603915 | -0.758282 | -0.245544 | -0.606927 |
| 5 | -0.852346 | -0.803411 | -1.062938 | -0.301984 | -0.853977 |
| 4.5 | -1.212724 | -1.218746 | -1.542732 | -0.561997 | -0.857554 |
| 4 | -1.987426 | -1.911895 | -2.366777 | -0.841107 | -1.921559 |
| 3.5 | -3.367466 | -3.350524 | -3.945528 | -1.320544 | -3.274595 |
| 3 | -6.507022 | -6.366334 | -6.921116 | -2.277231 | -5.837030 |
| 2.5 | -11.882770 | -12.107642 | -11.790338 | -4.533465 | -9.929961 |
| 2 | -19.457061 | -17.628875 | -17.761217 | -10.071590 | -15.023267 |
| 1.9 | -21.023198 | -18.710825 | -18.887602 | -11.692823 | -15.652984 |
| 1.8 | -22.502389 | -19.339403 | -19.937545 | -13.368525 | -15.932654 |
| 1.7 | -23.606907 | -19.360801 | -19.996405 | -14.922489 | -15.372288 |
| 1.6 | -23.919832 | -18.514572 | -19.155919 | -16.088025 | -13.763918 |
| 1.5 | -23.699402 | -16.635465 | -17.103398 | -16.527282 | -8.826485 |
| 1.4 | -22.411498 | -14.02357 | -13.273645 | -16.529227 | -3.917102 |
| 1.3 | -20.716724 | -9.134212 | -8.613320 | -15.429290 | 1.098345 |
| 1.1 | -6.501324 | -1.034215 | 5.045314 | -3.031542 | 10.106787 |
| 0.9 | 15.109123 | 8.102317 | 14.058378 | 6.096753 | 17.049727 |

**Figure 2.** The Ala-Meth intermolecular potential energy interactions obtained at HF, B3LYP and MP2 levels of theory with 6-31G, 6-31G*, STO-3G basis sets.

example, the values of D_e and R_e for HF method with 6-31G, 6-31G* and STO-3G basis sets -19.99640 (1.7), -15.93265 (1.8) and -16.52922 (1.4) respectively.

Energies below the asymptote in kilocalories per mole. Values between parentheses correspond to the Ala-Meth distance in angstroms. In this work, to estimate the

Table 2. Numerical values of D_e and R_e for Ala-Meth intermolecular potential energy obtained at different methods and basis sets.

| Method | Basis set | D_e (kcal/mol) | R_e (Å) |
|--------|-----------|------------------|-----------|
| MP2 | 6-31G | -19.3608 | 1.7 |
| B3LYP | 6-31G | -23.9198 | 1.6 |
| HF | 6-31G | -19.99640 | 1.7 |
| | 6-31G* | -15.93265 | 1.8 |
| | STO-3G | -16.52922 | 1.4 |

Table 3. The Ala-Meth intermolecular potential energy surface values obtained at B3LYP/6-31G by Gaussian and Fitted by modified Morse potential model.

| Distance (Å) | E (kcal/mol) | |
|--------------|------------------------|---------------------------|
| | Calculated by Gaussian | Fitted by potential model |
| 5.5 | -0.790235 | -0.353401 |
| 5 | -0.8523461 | -0.656140 |
| 4.5 | -1.2127248 | -1.214766 |
| 4 | -1.9874261 | -2.236982 |
| 3.5 | -3.3674669 | -4.077433 |
| 3 | -6.5070225 | -7.284870 |
| 2.5 | -11.882770 | -12.493356 |
| 2 | -19.457061 | -19.537427 |
| 1.9 | -21.023198 | -20.916123 |
| 1.8 | -22.502389 | -22.135772 |
| 1.7 | -23.606907 | -23.078777 |
| 1.6 | -23.919832 | -23.584692 |
| 1.5 | -23.699402 | -23.436848 |
| 1.4 | -22.411498 | -22.345015 |
| 1.3 | -20.716724 | -19.922996 |
| 1.1 | -6.501324 | -8.881545 |
| 0.9 | 15.109123 | 16.027810 |

Table 4. Adjustable potential parameters used in the modified Morse potential model.

| Adjustable parameters | Values |
|-----------------------|----------------------------|
| ϵ_{mn} | 23.62074 (K) |
| A_{mn} | 1.24405 (Å ⁻¹) |
| r_{mn} | 1.56796 (Å) |

interaction energy, $U(r)$, in the system we use the modified Morse potential model. This has three adjustable parameters,

$$U(r) = -\epsilon_{mn} \left(1 - \left\{ 1 - \exp[-A_{mn}(r - r_{mn}^*)] \right\}^2 \right) \quad (7)$$

where ϵ_{mn} , A_{mn} and r_{mn}^* are adjustable parameters.

Some of the parameters are treated as constants, taken from the literature, and some parameters are varied. The intermolecular potential energy interactions obtained at B3LYP that fitted to modify Morse potential model are given in Table 3 and the set of adjustable parameters are listed in Table 4, and calculated results are plotted in Figure.3. Assuming a given set of parameters, we estimate theoretically second virial coefficients for the system, Equation (6). To determine the virial coefficient

B_2 in Equation (6), using U_{AB} , the model's parameters were obtained earlier over the range of temperatures of interest. The B_2 coefficient can, of course, be taken from the experiment, if the data are available. Calculated results and temperature dependence of the second

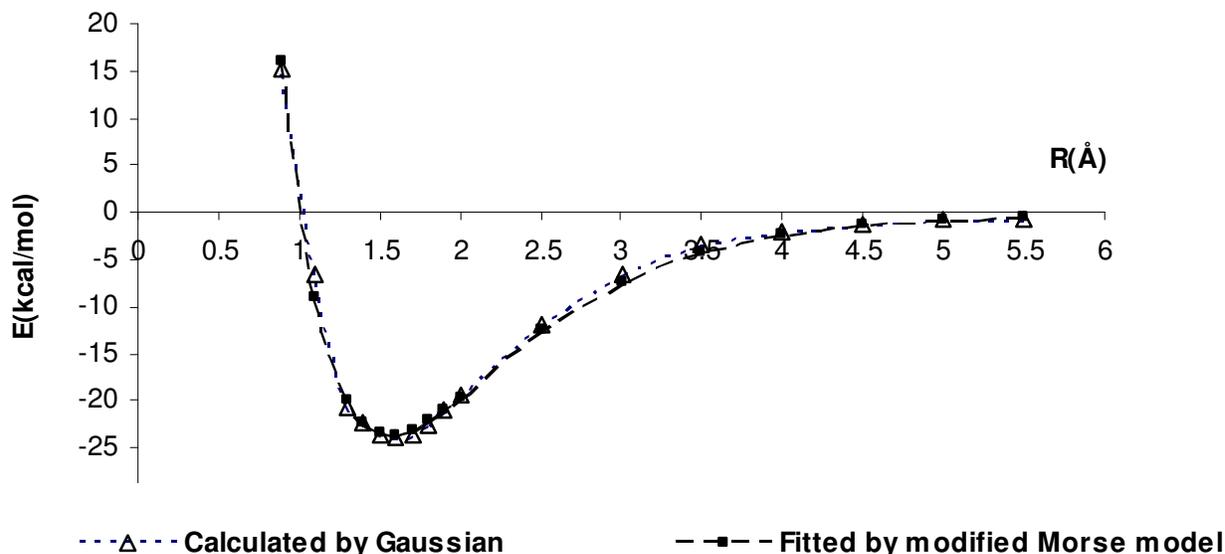


Figure 3. The Ala-Meth intermolecular potential energy interactions obtained at B3LYP/6-31G are fitted by modified Morse model.

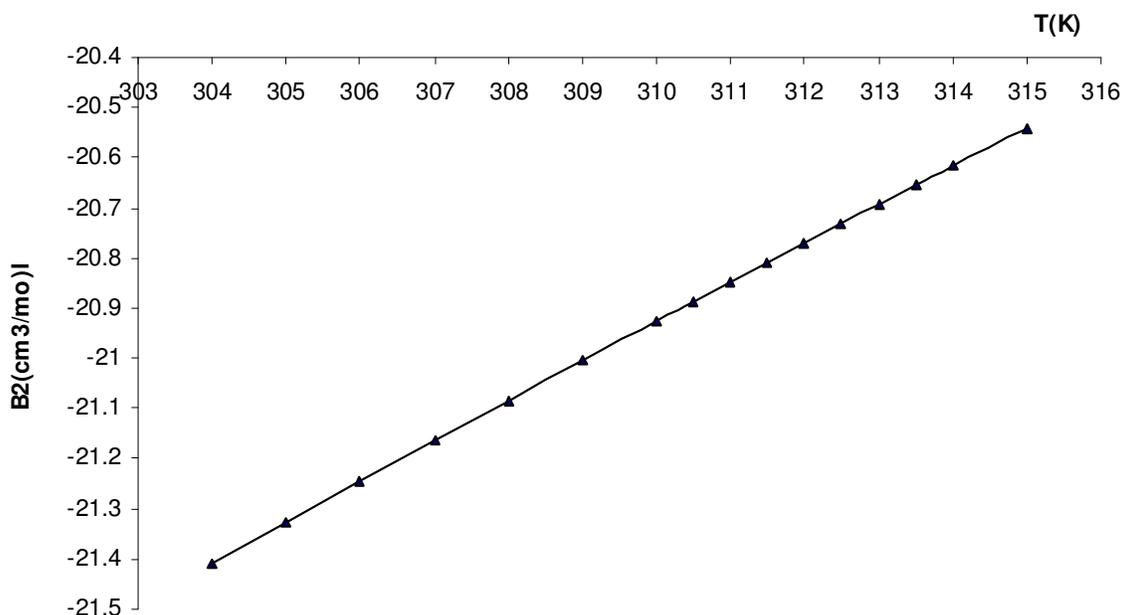


Figure 4. Temperature dependence of second virial coefficients for Ala-Meth system.

virial coefficients are plotted in Figure 4.

Conclusion

We have studied the interaction potentials between the Alanine and the Methionine molecules. In our calculations we used the HF, DFT-B3LYP and MP2 methods with 6-31G and 6-31G* basis sets. 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.

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. Thus, with respect to Figure 2, B3LYP/6-31G releases more energy toward other methods and increased the depth of potential well. In this work, we have been estimate the IPSs in the Ala-Meth system by using the modified Morse potential model, to obtain the adjustable parameters of potential equations and theoretically second virial coefficients. The depth of wells and location along the Ala-Meth calculated by Gaussian at B3LYP/6-31G are fitted to modified Morse potential model are -23.919832, -23.584692 (1.6) respectively. Potential energies are in kilocalories per mole. Values between parentheses correspond to the Ala-Meth distance in angstroms. Trivial differences can be seen between intermolecular potential energy fitted to modified Morse potential model and computational results. In consideration with Figure 4, the temperature dependence of second Virial coefficient is specified completely.

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