SEEDMOL
Simpósio de Estrutura Eletrônica e Dinâmica Molecular
Brasília, 07 a 11 de Novembro

Second Virial Coefficient for the $Cl_2 \cdots Cl_2$ System

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Keywords: second virial coefficient, $Cl_2 \cdots Cl_2$, potential energy surface.

Abstract

The analytical representation of intermolecular interactions combines dynamical and structural viewpoints, utilizing a spherical harmonics expansion based on high-level ab initio generated stereodirected configurations. The potential energy surface of the $Cl_2 \cdots Cl_2$ system is built by a number of selected cuts (leading configurations); the best fits of their dependence on the intermolecular distance are phenomenologically represented by the Pirani et al. potential functions. The quality of the representation is validated by accurate calculations of a property of the gaseous mixture, the second virial coefficient, in a range of temperatures, with good agreement with reference data.

Introduction

In the past few years we have been working in developing potential energy surface (PES) using the spherical harmonic expansion. A good application for this PES is calculating the second virial coefficient that is related with the state equation of a real system, given by:

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots$$

where p is pressure, T temperature, V molar volume, R gas constant, B, C, D, $\cdots$ are the series of virial coefficients, second, third, fourth, respectively.

The main point for these coefficients are that they are directly related to the interaction between molecules, the second virial coefficient comes from diatom interaction, third virial for triatomic interaction and so on.

The second virial coefficient is given by:

$$B_{cl}(T) = -2\pi N_A \int \left(e^{-U(\Omega)/RT} 1\right) \Omega^2 d\Omega$$

where $U(\Omega)$ is the PES and Ω is the Jacobi coordinate for the molecules, in our case $\Omega = (R, \theta_1, \theta_2, \phi)$, N_A is the Avogadro number. The interval of temperatures of interest are such that we only need to calculate the classical correction of the second virial coefficient given by the expression above.

Methodology

In previous papers for $H_2 \cdots H_2$ [1], $F_2 \cdots F_2$ [2], we use the five LC, leading configuration, minimum expansion and six LC extended expansion system, with the three angles (θ_1,θ_2,ϕ): H (π/2,π/2,0), L (0,0,0), T (0,π/2,0), S (π/3,π/4,π/2), Z (π/4,π/4,0), and X (π/2,π/2,π/2), as we are going to use here. We use *Molpro* [3] to calculate a set of 100 *ab initio* points at varying intermolecular distances $3.0 \leqslant R \leqslant 20.0$ ˚A, for each LC, at the CCSD(T)/aug-cc-pVXZ level, with X = D and T, and use the CBS expansion [4]:

$$E_{CBS} = a + \frac{b}{E_X^n}$$

where a and b are fitting parameters, E_X represents the energy at X level and n the number of basis set.

The equilibrium distances were obtained at the same basis set level getting

2.008 ˚A at CBS level. These results are in good agreement with the experimental data, 1.988 ˚A [5]. To fit the ab initio point we use the Pirani potential [6-7]:

$$V(R,\gamma) = \varepsilon[\frac{m}{n(R,\gamma)-m}(\frac{R}{R_m})^{n(R,\gamma)} - \frac{n(R,\gamma)}{n(R,\gamma)-m}(\frac{R}{R_m})^{m}]$$

$$n(R,\gamma) = \beta + \alpha(\frac{R}{R_m})^2$$

where R is the distance between the centers of the monomers and $\gamma \equiv (\theta_1, \theta_2, \phi)$, according to the well-known Jacobi coordinates. The free parameter are *m*, β and α, while R_{eq} and ε are minimum position of the well, and the depth of the well respectively.

The PES is given by:

$$V(R,\theta_1,\theta_2,\phi) = 4\pi \sum_{L_1,L_2,L} v^{L_1,L_2,L}(R) Y^{L,0}_{L_1,L_2}(\theta_1,\theta_2,\phi)$$

where *R* is the distance between the center of mass of Cl_2, $v^{L_1,L_2,L}(R)$ represents the isotropic and anisotropic terms of the potential, $Y^{L,0}_{L_1,L_2}(\theta_1,\theta_2,\phi)$ is the bipolar spherical harmonics, and $L_1, L_2 = 0,1,2,\cdots$ with $L_1 - L_2 \leq L \leq L_1 + L_2$.

Result

The most stable LC is the X, with energy of 69.5 meV and distance of 3.479 Å while the less stable is the L one with energy of 18.1 meV and distance of 5.399 Å. The isotropic one is given by v^{000} that can be measured experimentally and be compared with different system. For the system analyzed, here the isotropic distance are 4.893 Å with 23.2 meV energy.

Figure 1(a) shows the ab initio point and the fitting data, using the Pirani potential, while the figure 1(b) compares the ab initio/fitting points for the X – LC calculate considering the BSSE correction, there is a increasing in the distance of 1.5% and 29.5% in the energy. For the T – LC the increase in the distance is 0.41% and for the L – CL is 53.4% in the energy. It shows the importance of considering the BSSE correction for the system.

Figure 1(c) and 1(d) shows the PES cut in the isotropic distance and dihedral angle of 0 and π/2, respectively. In figure, 1(c) shows the T as the most stable one while in figure 1(d) shows the X as the most stable one. Comparing figure 1(a) one can see the X as the most stable one and the T as de second most stable with a difference of 0.88Å in distance and -9.7meV in the energy. The L – LC is the less stable one. Figure 1(e) shows the isotropic and anisotropic terms of the potential. One can see the terms v^{220} and v^{222} have a repulsive character.

Figure 1(f) compares the virial coefficient for the system using the minimum, with five LC, PES and the extended, with six LC one, with the experiment data [8]. For low temperature, the extended one is closer with the experimental data, while at high temperature the minimum one fits better.

Conclusion

The second virial coefficient for the $Cl_2 \cdots Cl_2$ system are presented with good agreement with reference data. Using two different model, one with five LC and other with six LC.

Acknowledgements

FAPESP

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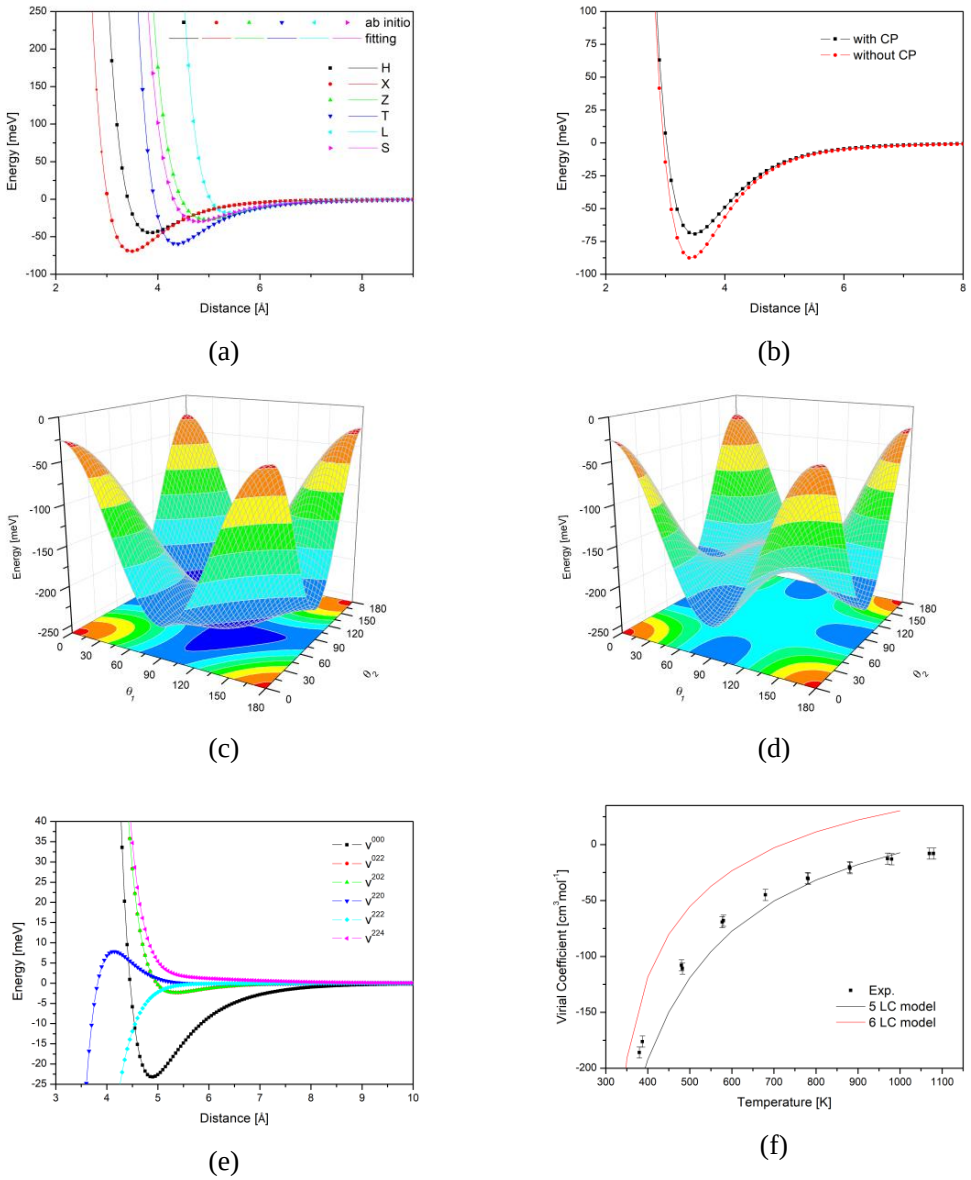

Fig. 1: (a) ab initio points compared with Pirani Potential fitting, (b) X LC with and withou BSSE correction, (c) PES cutting with R=4.893Å and ϕ=0, (d) PES cutting with R=4.893Å and ϕ=π/2, (e) isoprotic term of the potential, (f) virial coefficient compared with reference [8]