Computation of the CO_2-C_2H_2 and CO_2-C_2H_4 Complexes potential energy surface via ab initio method

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Introduction

The concept of intermolecular forces has been central to the molecular theory of matter since the work of van der Waals. As the theoretical investigations between molecules, ab initio quantum mechanical calculations offer a way to obtain intermolecular potentials of molecules [1]. Up to now, several intermolecular interaction of acetylene (C_2H_2) and ethylene (C_2H_4) have been proposed [2]. In the 1990 a minimum potential energy surface (PES) for CO_2-C_2H_2 at the ab initio SCF/4- 31G,SCF/D95 , SCF/6-31G** level of theory has been investigated.[3]. Rovira et al. computed minimum energy structures, vibrational frequencies and hydrogen bond energies for H_2O….C_2H_2, H_2O….C_2H_4 on the basis of ab initio MP2/6-31** G(2d,2p) calculations [4]. In this work, the interaction energies for CO_2-C_2H_2 have been calculated for various basis set and finally the extrapolation to complete basis set (CBS) limit was taken. Than the CBS energies have fitted to a theoretical based analytical function.

Keywords: Intermolecular potential surface, Van der Waals complex, Ab initio

Computational details

For an accurate description of the PES of CO_2-C_2H_2 and CO_2-C_2H_4 systems by ab initio calculations the GAUAUSSIAN 98 program [5] has been used. All calculations have been done using cc-pVXZ and aug-cc-pVXZ correlation consistent basis sets X=D, T, Q at second order Møller–Plesset perturbation theory (MP2) Level of theory where supermolecular frame work. the interaction energy of a complex AB can be defined as the difference $\Delta E(R) = E^{AB}(R) – E^{A}– E^{B}$, where R is the A-B distance and E^{A} and E^{B} are assumed to be the energy of isolated monomers limitations. This approach suffers from two, the so-called basis set superposition error (BSSE) and basis set

incompleteness error (BSIE). These two problems can be handle by the counterpoise method (CP) and extrapolation to complete basis set (CBS) respectively [6].

Results and Discussion

Coordinate system

In this study have considered as linear moieties. The Z-axis has taken along the two molecular center of masses. The direction of each molecular axis is defined by polar angles θ_A .and θ_B. Potential energy depends on four independent parameters, namely the distance R between central mass of two molecules, the angles θ_A and θ_B between each molecular axis and Z-axis, and the different between azimuthal angles $\phi = \phi_A - \phi_B$. By this choice of coordinate system, each point on the PES will be referred as (b_A, b_B, ϕ, R) and especially, the (0,0,0,R), (0,90,0,R), (90,90,0,R), (90, 90, 90, R) and (90,0,0,R) conformations will be referred here in after by L (linear, D1h), T_1 (Tshaped, C2v), H (parallel, D2h), X (X-shaped, D2d) and T_2 (Tshaped, C2v) form, respectively.

ab initio results

The calculated intermolecular potential energy of CO_2-C_2H_2 and CO_2-C_2H_4 at different level of theory for H configuration is shown in Figs. 1 and 2, respectively. Also the CBS limit of interaction energy at the local minimum of selected configuration of $CO_2 – C_2H_2$ and CO_2-C_2H_4 have shown in table 1 and 2, respectively.

Table 1. The calculated interaction energies (μH) at the local minimum (Bohr) of selected configurations for CO_2-C_2H_2

	T_1	T_2	H	L	X
R_e	-	9.5	6	9.8	6.5
E_{min}^{CBS}	-	-150	-3900	-2000	-1900

Table 2. The calculated interaction energies at the local minimum of selected configuration for CO_2-C_2H_4 (all values are in μH)

	T_1	T_2	H	L	X
R_e	8.5	6.5	7	10	7
E_{min}^{CBS}	-1400	-900	-1780	-1050	-890

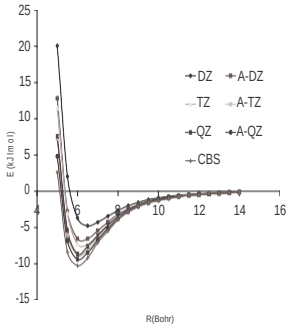

Figure 1. Radial dependence of interaction for H configuration different levels of theory and the CBS limit of MP2 method for CO_2-C_2H_2.

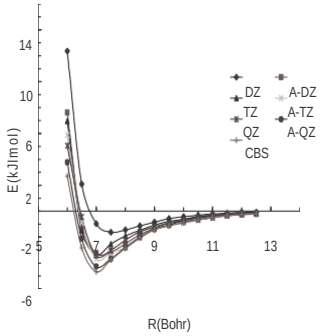

Figure 2. Radial dependence of interaction for H configuration different levels of theory and the CBS limit of MP2 method for CO_2-C_2H_4.

Conclusion

Two complexes show the strongest adsorption for the parallel configuration. Moreover the CO_2 adsorbs more by C_2H_2 than C_2H_4

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