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Ab Initio Intermolecular Potential Energy Surface of CO_2–C_2H_2 Complex

Saeid Yeganegi and Naser Darzi

Department of Physical and inorganic chemistry, Faculty of Chemistry, University of Mazandaran,
Babolsar, Iran P.O. Box: 47416-95447

** Corresponding author: E-mail: yganegi@umz.ac.ir*
Tel: +98-112-2542002, Fax: +98-112-2542002

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Abstract

A new four-dimensional potential energy surface for CO_2–C_2H_2 complex has been calculated by the ab initio methods at MP2/cc-pVXZ and MP2/aug-cc-pVXZ theory. For calculating the PES of the CO_2–C_2H_2 complex, we have chosen to follow the supermolecule approach. The complete basis set limit of potential energy surface has been taken by extrapolation. Our MP2 results showed the most stable form of CO_2–C_2H_2 complex is a parallel configuration. The complete basis set limit of ab initio potential energy surfaces have fitted to an analytic function and performance of fitting assessed. The electrostatic contribution to the PES has calculated and shows that it is anisotropic.

Keywords: Intermolecular potential, carbon dioxide, acetylene, supermolecule, potential energy surface.

1. Introduction

Intermolecular forces have been central to the molecular theory of matter since the work of van der Waals. As a theoretical method, ab initio quantum mechanical calculations offer a way to obtain intermolecular potentials of molecules.[1] In recent years, high-level quantum mechanical computational methods have been used widely to construct numerous accurate potential energy surfaces (PES) for most of the small- and medium-sized molecular species.[2–4]

Acetylene and carbon dioxide are important molecules from the industrial and academic point of views. For an asymmetric dimer containing two centro symmetric molecules having quadrupole moments of opposite sign, the quadrupole-quadrupole interaction strongly favors a symmetric parallel geometry having C_{2V} symmetry. The carbon dioxide-acetylene complex is an obvious example of such a species. They are three and four atomic linear molecules, which makes their intermolecular potential highly anisotropic. Spectroscopic evidence was presented for the existence of a binary crystalline solid containing carbon dioxide and acetylene.[5] The carbon dioxide and acetylene van der waals dimer had been the subject of many experimental works[6] but to our knowledge, the only theoretical calculation of intermolecular potentials of CO_2–C_2H_2 complex was a work done by De Almeida[7] at HF/4-31G, HF/D95 and HF/6-31G(d,p). He found two stationary points on the potential energy surface: the parallel and linear structures. His method of computations lacks the electron correlation that is essential for the calculation of weak non-bonded interactions in Van der Waalse complexes. In addition, author did not perform a PES scan and only a limited number of configurations had been studied. This promoted us to calculate the interaction energy between these relatively interesting molecules by a more robust method that incorporates effectively the electron correlation and explores more points on the PES hyper surface regarding our computational resource.

Electron correlation contribution to intermolecular interaction has a central role in structures and energetic of van der Waals complexes.[8] Electron correlation can commonly be described adequately when one applies a high-level post Hartree-Fock method in conjunction with a near the saturation basis set. This is a more difficult task in the case of intermolecular correlation effects. The standard basis sets mostly optimized for intramolecular properties then their application to intermolecular problems usually results in a slow convergence to the complete basis set (CBS) limit. To overcome this problem, an alternative approach is the use of bond functions located somewhere between monomers. This approach has been widely employed after the works of Tao et al.[9] However, the application of bond functions causes new difficulties. The major issues are the artificial deformation of charge distributions on the monomers and production of higher-order basis set superposition errors (BSSE) that are uncorrectable via the usual counterpoise procedure.[10] However, application of a large basis set with diffuse functions can diminish considerably the BSSE and basis set incompleteness error (BSIE). There is some alternative BSSE free methods for calculation of potential energy such as local MP2 (LMP2)[11, 12] and symmetry adopted perturbation theory (SAPT).[13,14] However, according to the availability and simplicity of supermolecule method and large basis set used in this work, we intended to apply the supermolecule approach.

In the present study, we have proposed a new four-dimensional ab initio potential for CO_2–C_2H_2 Van der Waalse complex. In this work, the interaction energies have been calculated for two sets of correlation consistent basis sets and finally extrapolate the results to the complete basis set (CBS) limit. The CBS energies have then been fitted to a theoretically based analytical function and details of fitting procedure are described.

2. Method

2. 1. Coordinate System

The complete potential energy surface, including the intra and intermolecular degrees of freedom is a 15-dimensional hypersurface. From these coordinate, 11 of them are the monomers internal degrees of freedom. The structures of monomers in a van der waalse complex can be modified by strong intermolecular interactions; the most affected motion is the low energy bending vibrations. Recently, Makarewicz [15] shown that, at the CCSD(T) level of theory, the deviation of carbon dioxide structure from linearity is negligible in CO_2–H_2O van der waalse complex. Also ab initio potentials using different C–O bond lengths to model vibrational averaging, give phase coexistence properties which are the same within the uncertainties of the simulations [16].So we assume that every molecule is in the ground state vibrational state and mixing with higher energy states or intermolecular degrees of freedom is small.

For two linear molecules, it is often convenient to use a space fixed (or global) axis frame in which center of mass (COM) of one molecule places at the origin and the center of mass of other molecule has located on a point in the positive direction of Z-axis, at a distance R from the COM of the first molecule. The orientation of each molecular axis then has been defined by two polar angles θ and γ. It follows that the relative geometry of two molecules in which the potential energy depends on, is fully described by four independent parameters, namely the distance R between the centers of mass of two monomers, the angles θ_a and θ_b between each molecular axis and global Z-axis, and the difference between their azimuth angles $\gamma = \gamma_a - \gamma_b$.

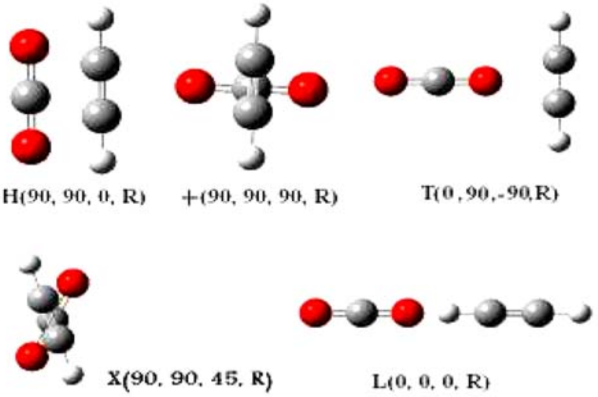

Figure 1. Configurations that studied in this work. Below each configuration the letter abbreviation designated for that configuration with the values of (θ_a,θ_b,γ,R) have been indicated.

By this choice of the coordinate system, each point on the PES will be referred as (θ_a, θ_b, γ, R). In this work we have studied five distinct orientations, as indicated in Figure 1, denoted by four parameters namely: linear (L, $D\infty_h$) (0, 0, 0, R), T shaped (T, $C2_v$) (0, 90, 0, R), parallel (H, $D2_h$) (90, 90, 0, R), plus (+, $D2_d$) (90, 90, 90, R) and X shaped (X, $D2_d$) (90, 90, 45, R). The word in the first parentheses shows an abbreviation used for that orientation; the second one is the point group symmetry of the supermolecule. The PES of CO_2–C_2H_2 complex has been calculated at 5 different configurations and 25 distances for each configuration.

2. 2. Quantum Chemical Calculation Details

The Møller-Plesset perturbation theory[17] up to the second order (MP2) was used for calculations. The ab initio calculations were carried out with GAUSSIAN03 suit of programs.[18] The interaction energy in supermolecule framework is defined as

$$\Delta E\,(\mathbf{R}) = E_{ab}\,(\mathbf{R}) - E_a\,(\mathbf{R}) - E_b\,(\mathbf{R}). \tag{1}$$

Where E_{ab} and E_a (or E_b) are the supermolecule and monomer energies, respectively, and **R** represents a set of radial and angular coordinates. It is favorable to use more accurate methods such as forth order Møller–Plesset perturbation theory (MP4) or coupled cluster CCSD(T) methods in spite of increasing the computational cost. In constructing PES, we are content with the MP2 level of the theory for the following reasons: (i) The MP2 method generally is known to be a good compromise between accuracy and computational cost. In fact, it is believed that the

MP2 method covers a major part of the electron correlation effects (ii) the convergence of MP series is not guaranteed a priori.[19,20] In this work, we used the cc-PVXZ and aug-cc-PVXZ basis set with X = D, T, Q from the Dunning[21] correlation consistent series. Completeness of this standard hierarchy improves systematically, and it is possible to extrapolate their results to the complete basis set (CBS) limit via an empirical estimating scheme.

In the present work, we deal with two major defects of ab initio calculation of PES, namely the basis set incompleteness error (BSIE) and the basis set superposition error (BSSE). Two types of error managements, extrapolation to complete basis set (CBS) limit[21] and counterpoise (CP) procedure[22], respectively can handle these defects. Performance of these error managements might be an important problem, but in our study on the CO_2–C_2H_2 we found that it is crucial to ask about the criterion for the consistency of extrapolation scheme and CP procedure. We have chosen the uniform convergence of PES obtained by different basis sets as the criterion for consistency of the methods being used for removal of BSSE and BSIE.

An exponential scheme has been used for extrapolation of the results of aug-DZ, aug-TZ, and aug-QZ to their CBS limits. The extrapolation formula is

$$\Delta E(x) = \Delta E(\infty) - ae^{bx} \tag{2}$$

Where, x is the cardinal number of the basis set fixed equal to 2, 3 and 4 correspond to DZ, TZ and QZ, respectively. $\Delta E(\infty)$ is the hypothetical CBS value of the interaction energy. Equation (2) is identical to the original formulation of a geometric series by Dunning.[21] Although there is no formal theoretical proof for its accuracy and performance, it can extrapolate not only to the CBS limit of energy, but also to the CBS limit of other molecular properties in many cases successfully. [4]

For removal of BSSE, we have adopted a full counterpoise procedure (FCP) proposed originally by Boys and Bernardi.[22] In the supermolecular approach, when two monomers are brought together the basis functions of each molecule become accessible to the other. This change in functional space results in an unphysical energy lowering for each monomer and for the interaction defined by equation (1). Furthermore, one needs to distinguish between the monomer-centered basis set (MCB) and complex centered basis set (CCB) results by rewriting equation (1) in below form:

$$\Delta E(R) = E_{ab}^{\{ab\}}(R) - E_{a}^{\{ab\}}(R) - E_{b}^{\{ab\}}(R) \tag{3}$$

Where the symbol {. . .} represents the applied basis set in the calculation of each term and ΔE denotes the interaction energy which is free from BSSE. We have defined the magnitude of BSSE as the difference between the CCB and MCB interaction energies.

$$BSSE = E_{a}^{\{a\}}(R) + E_{b}^{\{b\}}(R) - E_{a}^{\{ab\}}(R) - E_{b}^{\{ab\}}(R) \tag{4}$$

This quantity depends on the intermolecular coordinates through the CCB terms. We have calculated the BSSE for all the considered configurations in this work.

2. 3. Analytical Representation of Quantum Calculated PES

To obtain an analytic representation of potential energy surface of CO_2–C_2H_2 Van der Waals complex, the ab initio calculated PES was split into a short range $V_{sh}(R, \theta_a, \theta_b, \gamma)$ and a long range $V_l(R, \theta_a, \theta_b, \gamma)$ parts as

$$V(R,\theta_a,\theta_b,\varphi) = V_{sh}(R,\theta_a,\theta_b,\varphi) + \\ + V_l(R,\theta_a,\theta_b,\varphi), \tag{5}$$

The short-range potential consists of the exponential function:

$$V_{sh}(R,\theta_a,\theta_b,\varphi) = \exp(-B(\theta_a,\theta_b,\varphi) \\ \sum_{k=0}^{k_{\max}} A(\theta_a,\theta_b,\varphi)R^k \tag{6}$$

Where $k_{\max}$ is a proper integer between 2 and 6. The long-range part can be represented by a series of inverse powers of R:

$$V_l(R,\theta_a,\theta_b,\varphi) = \sum_n \frac{C_n(\theta_a,\theta_b,\varphi)}{R^n}, \quad n = 6,8,\ldots \tag{7}$$

These long-range terms were damped by a Tang-Toennies[23] damping function as shown in equation (8):

$$F_n(R,\theta_a,\theta_b,\varphi) = 1 - \left[\sum_{k=0}^{n} \frac{(B(R,\theta_a,\theta_b,\varphi))^k}{k!}\right] \\ \exp\left[-B(R,\theta_a,\theta_b,\varphi)R\right] \tag{8}$$

The limiting behaviors of damping function are:

$$\lim_{R\to\infty} F_n = 1 \tag{9}$$

$$\lim_{R\to 0} F_n = 0 + O(R^{n+1}) \tag{10}$$

Thus, the effect of damping on equation (8) is given by

$$V_l(R,\theta_a,\theta_b,\varphi) = \sum_n F_n(R,\theta_a,\theta_b,\varphi) \\ \frac{C_n(\theta_a,\theta_b,\varphi)}{R^n}, \quad n = 6,8,\ldots \tag{11}$$

We have used a complete orthogonal set of angular functions $\Gamma_{L_aL_aL}(\theta_a, \theta_b, \gamma)$ to represent the angular dependency of coefficients A, B and C_n in the general form

$$Z(\theta_a,\theta_b,\varphi)=\sum_{L_aL_bL} Z_{L_aL_bL}\times\Gamma_{L_aL_bL}(\theta_a,\theta_b,\varphi), \qquad Z=A,B,C_n \tag{12}$$

with L_a, L_b = 0,2,4, and $|L_a - L_b| \le L \le L_a + L_b$. The angular functions are bipolar spherical harmonics[24]

$$\Gamma_{L_aL_bL}(\theta_a,\theta_b,\varphi)=(2L+1)^{1/2}\sum_m(-1)^{L_a-L_b}\times \begin{pmatrix} L_a & L_b & L \\ m & -m & 0 \end{pmatrix} Y^m_{L_a}(\theta_a,\varphi_a)Y^{-m}_{L_b}(\theta_b,\varphi_b) \tag{13}$$

Where Y^m_L is spherical harmonics, $\begin{pmatrix}\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot\end{pmatrix}$ is the Wigner 3J symbol and $-\min(L_a, L_b) \le m \le \min(L_a, L_b)$. The values of parameters $A_{L_aL_bL}$, $B_{L_aL_bL}$ and C_{n,L_aL_bL} will be determined via a fitting procedure.

2. 4. Electrostatic Interaction

The electrostatic interaction energy of a pair of molecules between their permanent charge distributions shown as[24]

$$U_{es}(R,\theta_a,\theta_b,\varphi)=\sum_p\frac{D_p(\theta_a,\theta_b,\varphi)}{R^p} \tag{14}$$

Where U_{es} is the electrostatic interaction between the multiple moments of monomers calculated at the MP2 level of approximation and is a function of the corresponding multiple moments of two molecules, which also controls the anisotropy of electrostatic interaction. A special form for *D* is

$$D_p=\delta_{L_a+L_b,L}(-1)^L\left[\frac{(2L_a+2L_b)}{(2L_a+1)!(2L_b+1)!}\right]^{1/2}\times M_{L_a}M_{L_b}\Gamma_{L_aL_bL}(\theta_a,\theta_b,\varphi) \tag{15}$$

with $L_a + L_b + 1 = p$. M_{La} and M_{Lb} are permanent multiple moments of molecules *a* and b calculated at the MP2 level of theory and have non zero values only for L_a, $L_b \ge 2$.

3. Results

At first, we optimized structures of the isolated monomers. Optimized bond lengths for CO_2 and C_2H_2 for augmented basis sets have been shown in table 1. The aug-cc-PVDZ was unable to reproduce the experimental values. The calculated bond lengths are larger for small basis sets, and it became shorter as the basis sets reach the saturation limit. The aug-cc-PVTZ and aug-cc-PVQZ results are consistent with the experimental values. However; it is obvious that the aug-cc-PVQZ basis set is near the saturation limit for predicting the structures of monomers. In addition, we have examined frequency of vibrational normal modes of both monomers in the prescribed basis sets and find that the agreement with published values[25,26] is excellent, which we have omitted the comparison for brevity.

Table 1. Experimental and calculated bond lengths (Å) of CO_2 and C_2H_2.

	MP2/aug-cc-PVDZ	MP2/aug-cc-PVTZ	MP2/aug-cc-PVQZ	Exp. value[25]
RCH	1.075	1.061	1.061	1.063
RCC	1.229	1.211	1.208	1.203
CO	1.177	1.169	1.166	1.162

In the subsequent calculations of PES, we have used the relevant structures of monomers for each basis set. The first non-vanishing electrostatic multiple moments of the monomers have been calculated for augmented basis sets, and the CBS limits were taken. It is well accepted that the calculated multiple moments are very sensitive to the size of basis set then we take the CBS limit only for the augmented basis sets. The calculated quadruple moments, the CBS limits and experimental values of Kaplan[24] and Gianturco et al.[26] have been shown in Table 2. The agreement between the CBS limits and the experimental values are very good. We have used the CBS limits of calculated quadruple moments for the calculation of electrostatic part of potential energy surface.

Table 2. Quadruple moment of CO_2 and C_2H_2 calculated in different levels of theory in comparison with experimental values. All quantities are in atomic units.

Basis set	CO_2	C_2H_2
aug-DZ	–3.498	5.172
aug-TZ	–3.433	4.957
aug-QZ	–3.463	4.925
CBS	–3.385	4.938
Literature values	–3.309[a]	4.710 ± 0.14[b]

a: have taken from Ref. 24
b: have taken from Ref. 26

The PES of CO_2–C_2H_2 complex has calculated using the cc-PVXZ and aug-cc-PVXZ basis sets at MP2 level of theory. The calculated intermolecular potential energy of CO_2–C_2H_2 for different basis sets for “parallel” configuration shown in Figure 2. It is obvious that the smaller basis sets are unable to provide a satisfactory description of PES at the MP2 level. The results of the standard correlation consistent basis set slowly converged to CBS limit.

Even the results of the largest one, cc-PVQZ, was far from the completeness and leads to a shallow potential.

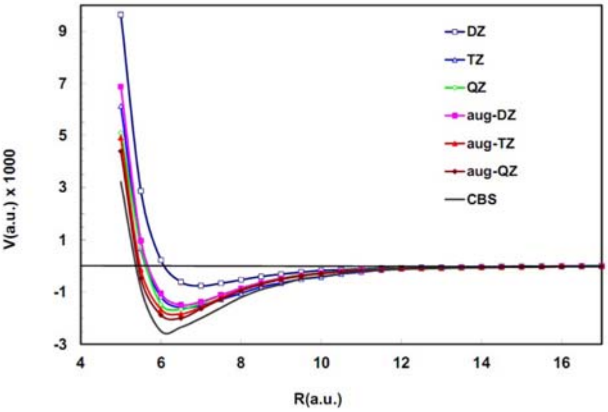

Figure 2. Radial dependence of CO_2–C_2H_2 interaction potential energy for plus parallel (H) configuration at the MP2 level of theory for different basis sets and the CBS limit.

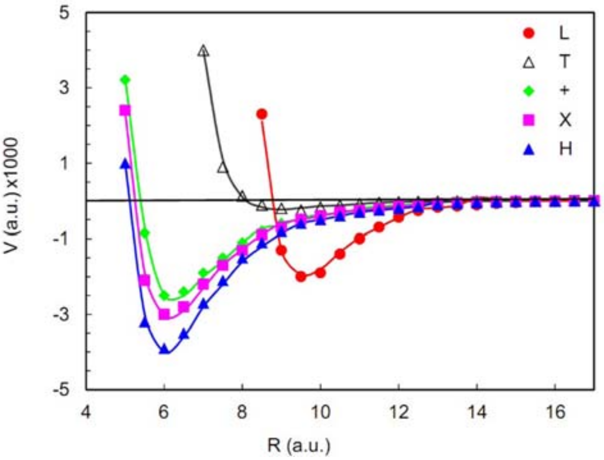

Figure 3. The CBS limit of calculated interaction potential of C_2H_2–CO_2 for different orientations. Symbols denotes the CBS limit of energy points calculated at the MP2/aug-cc-PVXZ (X = 2,3,4). Curves are fitting to the proposed analytical function, equation (5).

Tsuzuki et al.[27] show that the standard correlation consistent basis sets (ccpVXZ) converge slowly to their complete basis set limit when compared with the augmented ones (aug-cc-pVXZ). Unfortunately, due to the huge memory demands when incorporating basis sets like cc-p-V5Z, we were unable to use basis sets larger than aug-cc-PVQZ. So, we take only the CBS limit of aug-cc-PVXZ basis sets and the results of standard basis are shown for completeness.

The calculated potentials are more attractive for larger basis sets combined with the minimum shifts to the shorter distances. However, the calculated potentials for aug-cc-PVQZ and aug-cc-PVTZ are very close to each other. The calculated interaction energies at the augmented basis sets were extrapolated to the complete basis set limits by equation (2). It seems that a fitting of equation (2) with three points is problematic, but as stated before due to the limitation of the current computational resources we cannot go further and do calculations with basis sets larger than aug-cc-PVQZ. However, the rapid convergence of aug-cc-PVXZ results leads to a good fitting statistic. Slow convergence of MP2 points toward the CBS limit can be interpreted as the importance of dispersion part of the interaction energy, which is mainly covered in this level of theory. It must be mentioned that the relative stability of the investigated configurations is the same as those obtained with different basis sets before and after the CP correction. This ordering also does not change after extrapolation to the CBS limit.

The symbols in Figure 3 characterize the CBS limit of calculated interaction energies. The parallel (H) orientation is the most stable configuration, and its well depth is deeper than the other configurations. The crossed (X) and plus (+) orientations are the next after the H configuration, respectively. The distances of the minimum, for three most stable configurations are equal. The T-shaped and linear configurations are characterized by their shallow well depth and larger distance of minimum energy. The interaction energy of T configuration is shallower than the L orientation but its distance of minimum are shorter. The distances and energies at the minimum for all of the studied orientations are shown in table 3. The BSSE has corrected by counterpoise method. At the distance of minimum energy the parallel (H) and cross (X) configurations have the largest BSSE (2.5×10^{-4} a.u.) and the T-shape configuration presents the smallest BSSE (7×10^{-5} a.u.) for aug-cc-PVQZ. Possibly, there are some considerations about the angle dependency of BSSE but the magnitude of BSSE is not of importance as long as the basis set has a reasonable size. In the worst case (T-shaped) the BSSE comprises less than one part in 10^{-5} of interaction energy, so we conclude that the size of aug-cc-PVXZ in this work is reasonable.

Table 3. Distances and energies at the minimum of the interaction energy for different orientations. All quantities are in a.u.

Parametrs	H	X	+	L	T
R_{min}	6.0	6.0	6.0	9.5	9.0
V_{min}	–4.000	–3.030	–2.250	–1.900	–0.150
U_{es}	–2.672	–2.222	–0.891	–0.610	0.340

Figure 3 indicates that the PES between CO_2 and C_2H_2 is highly anisotropic. The studied configurations can be divided into two categories the “slipped“ and “head-on” orientations. The parallel (H), crossed (X) and plus

Table 3. Parameters of the analytic PES obtained from fitting of the MP2/CBS ab initio data to equation (5). All quantities are in a.u.

Short Range				**Long Renge**			
A_{000}	59.409	B_{000}	5843.400	$C_{6,000}$	148.424	$C_{8,000}$	–11541.0
A_{202}	–3.116	B_{202}	4079.700	$C_{6,202}$	106.172	$C_{8,202}$	–8310.5
A_{220}	1.289	B_{220}	359.840	$C_{6,220}$	0.586	$C_{8,220}$	0.341
A_{222}	–0.443	B_{222}	–54.193	$C_{6,222}$	–0.602	$C_{8,222}$	38.099
A_{224}	0.368	B_{224}	–311.480	$C_{6,224}$	3.306	$C_{8,224}$	–171.770

(+) configuration belongs to the “slipped“ type then they have similar shape, nearly identical R_{min} and deep well depth while the “head-on” group, linear (L) and T-shaped (T) configurations, are distinctly have shallower potential well, similar and larger R_{min} than the “slipped” orientations.

The calculated intermolecular potentials at MP2/CBS have been fitted to the equation (5). According to equation (5), the potential has been divided into long and short range parts. The short ranged part decreases rapidly with R, and it became negligible for large R so the long range part constitutes the main part of the potential at large distance and it is zero for short distances. These facts allow us to fit the long range part of equation (5) in an interval $R_{ref} \leq R \leq 17$ a.u. for each configuration. We followed the fitting scheme of Aquilanti et al.,[28] which is a two-step fitting process: (i) knowing the fact that the short range contribution of the interaction energy in equation (6) decays rapidly with R, the long-range coefficients (C_n) in equation (11) are calculated from the ab initio calculated of $V(\theta_a, \theta_b, \gamma)$ at long range. Thus, for separations greater than some reference value, R_{ref}, the contribution by the short-range, is effectively negligible compared to the long-range part of the potential. This fact allows us to obtain the long-range coefficients through fitting of the functional form of equation (11) to the values of $V(\theta_a, \theta_b, \varphi)$ in an interval $R_{ref} \leq R \leq 17$ a.u. We expand the term in equation (11) up to n = 8 and the terms for n > 8 neglected. To determine R_{ref} for each configuration, the fitting procedure was repeated by some test values of R_{ref}. The R_{ref} had been determined for each configuration by repeating the fitting procedure of equation (11) for some test values of R_{ref}. The fitting parameters C_6 and C_8 are independent of the value of R_{ref} beyond a reference value. The values of R_{ref} for different configurations are different a little, but we reach the 13 a.u. as a consistent value for all orientations. The small variation in R_{ref} had a negligible effect on the calculated potential. The parameters of equation (11) for each configuration have been determined by fitting equation (11) to the CBS limit of ab initio calculated potential at the range $R_{ref} \leq R \leq 17$ a.u.. Addition of higher terms C_{10} change negligibly the obtained C_6 and C_8 then do not improve significantly the fitting. The obtained C_6 and C_8 for each configuration held fixed in subsequent calculations. The fitted long-range part has been added to the short rang part of potential and fitting the whole potential versus CBS limits of ab initio PES results in the A and B coefficient of equation (6). The angular dependency of A, B and C_n coefficients have determined by fitting the equation (12) for each coefficient to their values for each configuration. The triple series in equation (12) have expanded for L_a, $L_b = 0,2,4$ and one must note here that the 3-j symbols in series make some of the coefficients zero and some of them equal to each other. The final parameters obtained for the analytical description of PES (equation s (5)–(13)) at the MP2/CBS level of theory are given in Table 3. The solid lines in Figure 4 shows the results of fitting equation (5) to the energies calculated at MP2/CBS for different configurations.

To illustrate the quality of fitting steps individually, we have used two different quantities: the root mean square deviation (rmsd) and the average percent deviation (AD%). Table 4 reports the fitting errors for some configurations in steps (i) and (ii) of fitting procedure. The rmsd and AD% values of step (i) show that the functional form of equation (11) is effectively complete with representation of the long ranged part of potential Vl data in the range $R_{ref} \leq R \leq 17$ a.u. As can be seen from deviation values in Table 4, the errors occurred in step (ii) of fitting procedure is larger than the first step. This might be a result of the use of an exponential form with one parameter. To further criticize the quality of fitting we have chosen a point randomly among the proposed coordinates and calculate the potential energy by the MP2/CBS methodology in this paper and also the fitted analytical potential function. The chosen point was (89, 90, 23, 6.3) and difference of potential energy calculated by the ab initio method and the analytical function was %5. So we concluded that in view of this test and results in table 4 the uncertainty in the calculation of potential energy by the analytical function is no more than %5.

Table 4. Root mean square deviations (Rmsd) and average per cent deviations (AD %) of steps (i) and (ii) of fitting procedure.

	H	X	+	T	L
Step 1					
Rmsd	1.14	1.55	1.73	1.18	1.75
AD%	2.12	2.25	2.52	3.02	3.13
Step 2					
Rmsd	70.09	70.38	64.81	67.35	59.16
AD%	3.47	3.21	3.97	6.77	4.25

We calculate the electrostatic contribution of the interaction potential by means of equations (14) and (15) and obtained multiples. Figure 4 illustrates the electrostatic part of interaction energy for various CO_2–C_2H_2 configurations. It shows that the interaction energy for the T configuration is mainly repulsive because of average effect of vector consequents of molecular charge distributions. For other configurations, the electrostatic interaction contributes mainly in attraction. The large contribution of electrostatic interaction for linear (L) configuration was not unexpected if we note that the polarizability of carbon dioxide and acetylene is maximum in the direction of molecular axes. The electrostatic interaction contributions at the distance of minimum energy for studied orientations are shown in the last row of table 4. The most attractive electrostatic interaction belongs to parallel (H) orientation while the "slipped" orientations characterized by the more attractive electrostatic interaction than the "head-on" orientations (T and L). It is interesting that for the T configuration electrostatic interaction has a repulsion contribution. This can be related to the repulsion between oxygen's electron lone pair of carbon dioxide and bulky π electrons of acetylene. Calculations of cross-sections, thermo physical properties, such as transport properties and virial coefficients would be a crucial test for our PES which is the subject of a subsequent paper.

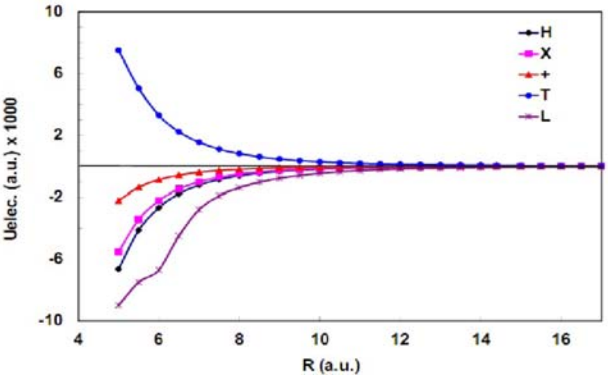

Figure 4. Electrostatic part of interaction potential for different configurations of CO2–C2H2. Points correspond to the multipole interaction calculated from the equation (4) and CBS limits of Quadruple moment of CO_2 and C_2H_2.

4. Conclusion

A new intermolecular potential energy for CO_2–C_2H_2 has been calculated using the Møller– Plesset method up to second order and the standard basis sets from the correlation consistent series. The uniform convergence of PES obtained with different basis sets have been used as a criterion for geometrical consistency of error management. The full counterpoise procedure and the exponential extrapolation to the CBS limit are found to be efficient for the removal of BSSE and BSIE in the present case. To construct an analytical representation for the ab initio data, major physical contributions to the interaction energy are specified, and a functional form are used to represent these contributions. A step-by-step fitting strategy is provided, which helps performing an estimated partitioning of the interaction energy and to examine the performance of each functional form individually. Accordingly, the exponential form of the overlap term for repulsion part of the potential is found to be responsible for much of the error involved in fitting procedures. The MP2 results obtained in the present study show that the most stable configuration of CO_2–C_2H_2 complex is the parallel (H) configurations where the electrostatic energy compromises the most of the total interaction energy in equilibrium distance at 6 a.u.

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6. References

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Povzetek

Z ab-initio računi cc-pVXZ in aug-cc-pVXZ smo določili novo štiri dimenzionalno potencialno energijsko površino (PES) za kompleks CO_2–C_2H_2. Pri računu PES smo sledili supermolekularnemu pristopu na MP2 nivoju. Naši rezultati kažejo, da je paralelna konfiguracija CO_2–C_2H_2 kompleksa najbolj stabilna struktura. Izračunali smo tudi elektrostatiki prispevek k PES in ugotovili, da je le ta izrazito anizotropen.