Potential Energy Surface for H_2O … CO_2

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INTRODUCTION

We have been working in the development of potential energy surface (PES) for several years. Basically, for system as AB-CD[1], were A, B, C and D are atoms, that can equals or not, and H_2O-X_2, where X can be any atom[2]. Now, we propose a new surface, based in the H_2O-X_2 PES for H_2O … CO_2, according to:

$$V(R_{CM}, \alpha, \theta_1, \theta_2, \phi) = \sum_m F_m(\Omega) v_m(R_{CM})$$

Where R_{CM} is the distance between the centers of mass, $F_m(\Omega)$ is an angular function and $v_m(R)$ are the moments.

METHODS

The system are treated as rigid motor, were the geometries of H_2O and CO_2 are kept frozen in theirs equilibrium. Fig. 1 shows the coordinate system used.

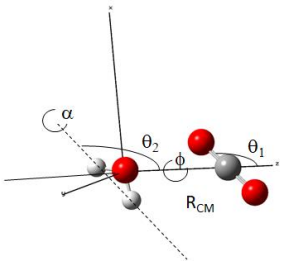


Fig 1: Coordinate system, where R_{CM} is the distance between the centers of mass (CM) of H_2O and CO_2, θ_1 is the angle of CO bond with the Z axis, θ_2 is the angle formed by the imaginary axis that pass through the CM of H_2O and parallel to the line connecting the H atoms of H_2O and the Z axis, ϕ is the dihedral angle and α is the angle that describes the rotation of H_2O around the the line connectiong the H atoms.

The angular function is written as:

$$F(\Omega) = \sum_i \omega_i(\alpha) \sum_{L_1,L_2,L} \Upsilon^{L,0}_{L_1L_2}(\theta_1, \theta_2, \phi)$$

Where $\omega_i(\alpha)$ is a cosine expansion in α angle, $Y^{L0}_{L_aL_b}(\theta_1, \theta_2, \phi)$ represents the bipolar spherical harmonics. The angles $(\alpha, \theta_1, \theta_2, \phi)$ are given in Fig. 1.

To determine the moments $v_m(R_{CM})$, we choose 18 18 leading configurations whose choice is due to physical and geometric considerations. Theses configuration are divided in three groups, each group for three different α angle, as 0, π/2 and π. In each group we have six configuration, as H(π/2,π/2,0), L(0,0,0), T_a(π/2,0,0), T_b(0,π/2,0), Z(π/4,π/4,0) and X(π/2,π/2, π/2).

RESULTS

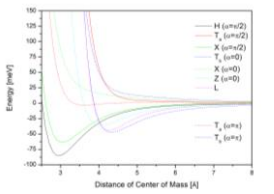
The H_2O and CO_2 are optimized using the Gaussian code[3] for different basis set and the geometric and electrical properties were determined, the results as shown in Tab.1.

Table 1: Geometric and electrical properties of H_2O and CO_2 calculated at aug-cc-pVDZ (aDZ), aug-cc-pVTZ (aTZ), aug-cc-pVQZ (aQZ),in comparison with experimental data.

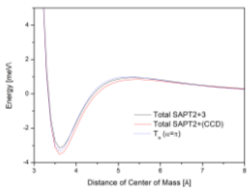
	aDZ	aTZ	aQZ	Ref.
	H_2O			
r_{OH}	0.967	0.962	0.959	0.958
A_{HOH}	103.9	104.2	104.4	104.5
E_{ZEP}	13.34	13.40	13.47	12.88
μ	1.995	1.970	1.963	1.857
α	9.239	9.493	9.538	10.128
Θ	12.553	12.509	12.488	13.184
IP	12.33	12.49	12.55	12.62
EA	0.69	0.56	0.51	1.20
PA	162.24	163.46	163.63	165.00
	CO_2			
r_{CO}	1.177	1.167	1.163	1.162
A_{OCO}	180	180	180	180
E_{ZEP}	7.11	7.21	7.26	7.17
μ	0	0	0	0
α	17.466	17.514	17.473	16.916
Θ	41.288	39.722	39.129	27.452
IP	9.72	12.52	13.77	13.78
EA	3.70	3.81	4.23	-0.60
PA	122.79	151.35	0.00	129.20

As one can see the aQZ basis set are in good agreement with experimental data, and this base will set for future calculation.

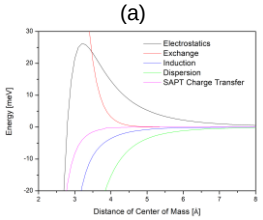
Molpro and SAPT determined the Leading Configuration energies at aug-cc-pVQZ. Fig. 2(a) shows the results for few LC, whle Fig. 2(b) compares the SAPT and Molpro energies for Ta LC with α=π, and Fig. 2(c) shows the SAPT contribution.



(a)



(b)



(c)

Fig. 2: (a) Leading configuration energies, (b) compartion between SAPT and Molpro calculation, (c) Electrostatic, Exchange, Induction, Dispersion and Charge transfer energies of SAPT.

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