

Potential Energy Surface for H₂O ... CO₂

Patrícia Regina Pereira Barreto(PQ)¹, Alessandra Ferreira. Albernaz (PQ)², Eberth Correa³

prpbarreto@gmail.com, albernazalessandra@gmail.com, eberthcorrea@gmail.com

¹Laboratório Associado de Plasma, Instituto Nacional de Pesquisas Espaciais, CP515, São José dos Campos, SP CEP 12247-970, Brazil, ²Instituto de Física, Universidade Brasília, CP04455, Brasília, DF CEP 70919-970, Brazil, ³Ciências Naturais Aplicadas, Universidade de Brasília, Campus do Gama, Gama, DF CEP 72444-240, Brazil

Keywords: Potential Energy Surface, H₂O-CO₂, second virial calculation

INTRODUCTION

We have been working in the development of potential energy surface (PES) for several years. Basically, for system as AB-CD¹, where A, B, C and D are atoms, that can equals or not, and H₂O-X₂, where X can be any atom². Now, we propose a new surface, based in the H₂O-X₂ PES for H₂O ... CO₂, 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, where the geometries of H₂O and CO₂ are kept frozen in their equilibrium. Fig. 1 shows the coordinate system used.

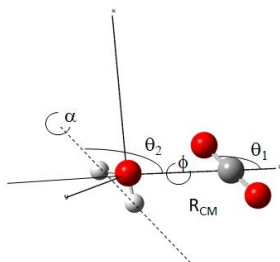


Fig 1: Coordinate system, where R_{CM} is the distance between the centers of mass (CM) of H₂O and CO₂, θ_1 is the angle of CO bond with the Z axis, θ_2 is the angle formed by the imaginary axis that pass through the CM of H₂O and parallel to the line connecting the H atoms of H₂O and the Z axis, ϕ is the dihedral angle and α is the angle that describes the rotation of H₂O around the the line connecting the H atoms.

The angular function is written as:

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

Where $\omega_i(\alpha)$ is a cosine expansion in α angle, $Y_{L_a L_b}^{L, 0}(\theta_1, \theta_2, \phi)$ 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 leading configurations whose choice is due to physical and geometric considerations. These configurations are divided in three groups, each group for three different α angle, as 0, $\pi/2$ and π . In each group we have six configurations, as H($\pi/2, \pi/2, 0$), L(0,0,0), T_a($\pi/2, 0, 0$), T_b(0, $\pi/2, 0$), Z($\pi/4, \pi/4, 0$) and X($\pi/2, \pi/2, \pi/2$).

RESULTS

The H₂O and CO₂ are optimized using the Gaussian code³ 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 H₂O and CO₂ calculated at aug-cc-pVDZ (aDZ), aug-cc-pVTZ (aTZ), aug-cc-pVQZ (aQZ), in comparison with experimental data.

	aDZ	aTZ	aQZ	Ref.
H ₂ O				
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, while Fig. 2(b) compares the SAPT and Molpro energies for Ta LC with $\alpha=\pi$, and Fig. 2(c) shows the SAPT contribution.

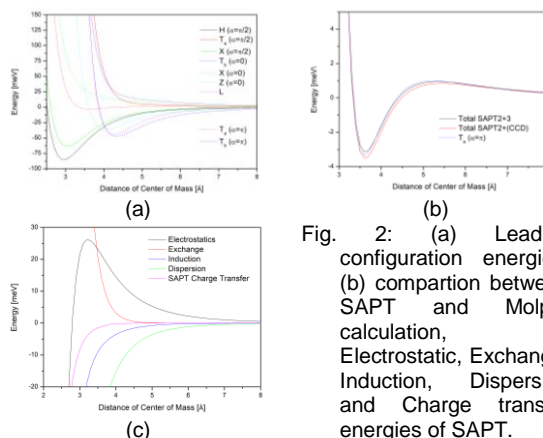


Fig. 2: (a) Leading configuration energies, (b) comparison between SAPT and Molpro calculation, (c) Electrostatic, Exchange, Induction, Dispersion and Charge transfer energies of SAPT.

ACKNOWLEDGEMENTS

I thank FAPESP and FADF.