POTENTIAL ENERGY SURFACES FOR INTERACTIONS OF H_2...HX AND H_2...X_2 SYSTEMS, USING A (HYPER)SPHERICAL HARMONICS REPRESENTATION

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1. Introduction

The characterization of the intermolecular potential energy surfaces (PES's) of pairs of simple molecular systems and their compact representation through suitable analytic functions is an essential requirement for applications of classical, semiclassical, and quantum-mechanical approaches to molecular spectroscopy and dynamics. We report (i) the results of quantum-chemical *ab initio* calculations on a series of interactions between diatomic molecules, specifically, H_2…X_2 and H_2…HX, where X = H, F, Cl, Br; (ii) their use to assemble full dimensional intermolecular PES's in the framework of a spherical-harmonics expansion, and (iii) the optimized global minimum configuration.

2. Theory

The construction of the global intermolecular potential energy surface based on *ab initio* calculations of potential energy profiles for a series of leading configurations for H_2…X_2 and H_2…HX systems, with X = H, F, Cl and Br atoms, are defined by a spherical-harmonics expansion of the neutral-neutral molecular interaction [1, 2]. These *ab initio* calculations were performed at CCSD(T)/aug-cc-pVQZ level with counterpoise-corrected interaction energies, using the MOLPRO code [3]. The functional form depends on a radial coordinate R between centers-of-mass of the two molecules and the polar and dihedral angles (θ_1, θ_2, ϕ) and the moments of the spherical-harmonics expansion are determined by choosing a certain number of representative configurations (leading configurations) based on geometrical and symmetry considerations, which allow the solution of a system of linear equations. Figure 1 define the coordinate system used in this case, see reference 1 and 2 (and reference cited in this papers) for more details about the leading configurations and potential development. Then, we adjust the points found with Pirani potential function [4, 5] and, also, the generalized Rydberg function [6], which allows us to explore important parameters contained in the molecular interaction, generating efficient and simplified models for both the isotropic term and the additional anisotropic terms derived from electrostatic contributions or charge-transfer. The PES was minimized in order to find the global minimum representing the least energy point. After that, we select the most stable principal configuration and calculate the energy considering floppy diatoms where the length of their chemical bonds could vary and we compare the results obtained.
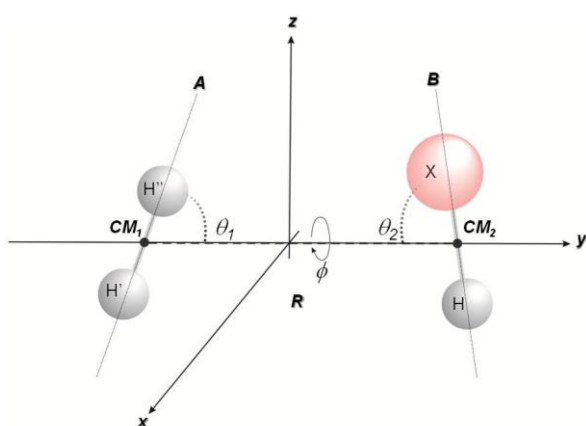

Fig.1: *The mutual position of the H_2 and X_2 or HX molecules is expressed by four coordinates in the Cartesian coordinate framework x,y,z. The radial coordinate $\boldsymbol{R}$ is defined as the distance between the center of mass of H_2, CM_1, and the center of mass of X_2 or HX, CM_2, θ_1 and θ_2 are the angles between the HH bound and y axes and XX or XH bound and y axes, respectively, and they vary between 0 and π, φ is the dihedral angle, and its value varies between 0 and π.*

3. Results and Discussions

Accurate results for this system have a high computational cost. Here, we show that the calculation of a small number of selected geometry allows the precise construction of the PES. We can verify that the rotor-rigid methodology can be considered in these cases of non-reactive systems with van der Waals type bonds, since the presented results differ minimally from one another. Nevertheless, it must be rethought when the system has a reactive character, since it presents values with considerable differences.

Table 1 compared the global minimum of the PES with the minimization calculation. It can be seen that the center of mass distance of H_2…X_2 systems decreases by 99.63%, while for the H_2…HX systems this

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distance increases by 82.43%, on average. The energy increases by 99.72 and 99.31% for the $H_2…X_2$ and $H_2…HX$ systems, respectively.

Table 1: *Minimum distance and energy among the $H_2…X_2$ and $H_2…HX$ systems when compared the PES and the minimized calculation*

System	T_b for $H_2…X_2$ and T_c for $H_2…HX$		Minimized	
$H_2…H_2$	3.380	-35.258	3.366	-35.526
$H_2…F_2$	3.497	-99.587	3.484	-99.615
$H_2…Cl_2$	4.019	-191.877	4.004	-191.801
$H_2…Br_2$	4.229	-226.098	4.215	-226.975
$H_2…HF$	2.477	-359.349	3.576	-361.299
$H_2…HCl$	2.983	-201.380	3.400	-202.538
$H_2…HBr$	3.160	-168.674	3.500	-170.271

Figure 2 and Figure 3 show the minimum configuration of the $H_2…X_2$ and $H_2…HX$ systems. One can see that the T configuration are the minimum configuration for all the systems.
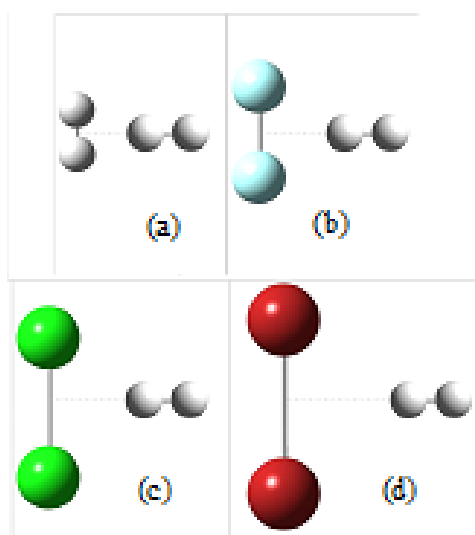

Fig. 2. *T_b configuration of $H_2…X_2$ system, where (a) X=H (b) X=F (c) X=Cl and (d) X=Br.*
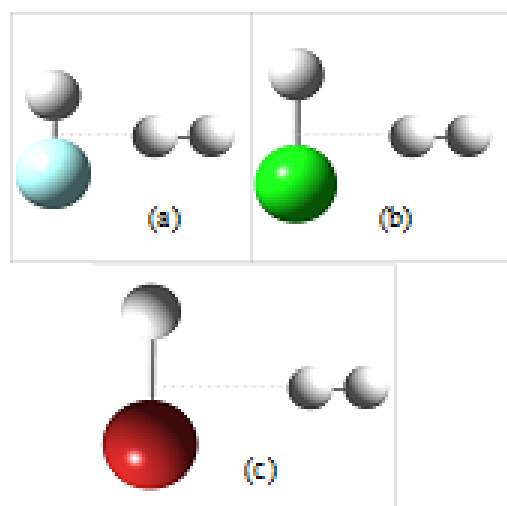

Fig. 3. *T_c configuration of $H_2…HX$ system, where (a) X=F (b) X=Cl and (c) X=Br.*

4. References

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