

The spherical-harmonics representation for the interaction between H₂O-HX molecules, with X = H, F, Cl and Br atoms.

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Abstract: The explicit representation of the potential energy surfaces (PES) for interactions of H₂O-HX systems, with X representing the atoms H, F, Cl and Br, based on orthogonal vectors, via harmonic expansion functional depending on the distance between the centers of mass of the two molecules and on four angles, assuming that the two molecules are rigid[1-3]. In this way, account for two contributions: an external one depending on the three angle variables which define the mutual orientation of the two molecules and an internal one expressed by the angle which describes the position of the oxygen atom in H₂O with respect to the H₂O -HX system, as can be seen in the figure 1.

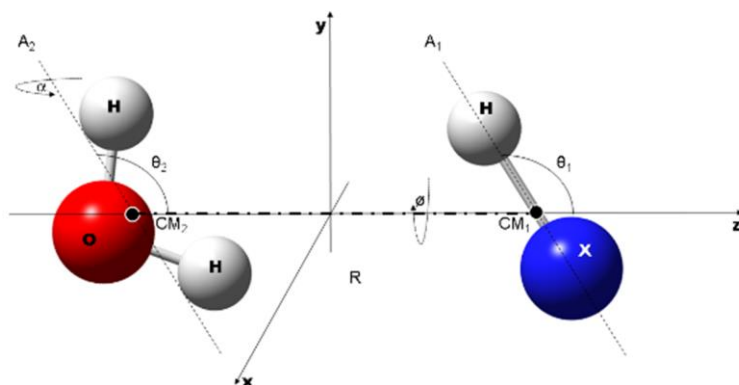


Figure 1. The mutual position of the H₂O and HX molecules is expressed by five coordinates in the Cartesian coordinate framework *xyz*.

The potential energy surface (PES) was generated in the framework of the supermolecular approach, using the counterpoise-corrected interaction energies at the CCSD(T), auc-cc-pVQZ level with the Molpro code. Comparisons with the atoms involved are presented and their features are discussed. The analytical form of the potential energy surfaces, for each of the leading configurations, is constructed by fitting the energies to a fifth degree generalized Rydberg function [4,5] and Improved Lennard Jones [6] respectively into the *ab initio* points, taking the advantage of the parameters also obtained as source of comparisons. The PES was computed for about one hundred points for each of the 27 leading configurations, whose number reduces to 23 because of symmetry properties. In the figure 2, we report the isotropic components of the interaction potential of H₂O -HX system, which can be measured experimentally, allowing the comparison and evaluation of the capacity of the theoretical method used.

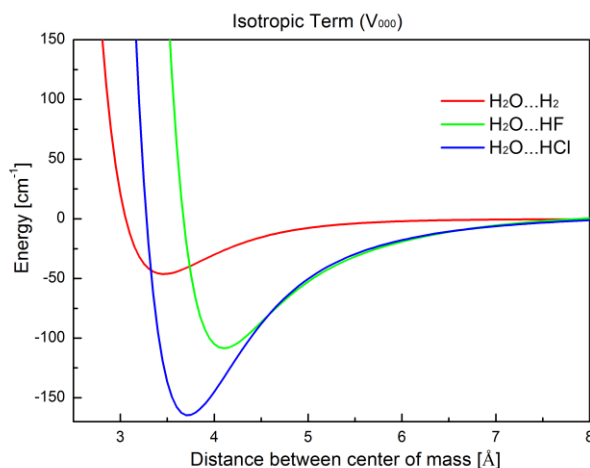


Figura 2. Isotropic Term for the H₂O -HX System, with X = H, F and Cl atoms.

The results for the system reduced the number of degree of freedom, reducing the computational cost simplifying the fitting and representation of the potential energy surface for other applications also to classical and quantum molecular dynamics simulations.

Key-words: Potential Energy Surfaces, van der Waals interactions, Rydberg function, Improved Lennard Jones function, Spherical Harmonics.

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