Quantum Chemistry Calculations for interaction between H_2O-HX and H_2O-X_2 systems, with X=H, F, Cl, Br atoms using SAPT Method

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Resume. *The characterization of the intermolecular potential energy surfaces (PES) 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 optimized most stable leading configuration on a series of interactions between H_2O-HX and H_2O-X_2 systems, where X = H, F, Cl, Br atoms, and (ii) and the analyze of these interactions energies, via SAPT methodology.*

Keywords: Potential Energy Surfaces; van der Waals interactions; geometry optimization; SAPT.

1. Introduction

The characterization of the potential energy surface of molecular interactions of pairs of simple molecules and their compact representation through analytical functions is an essential requirement for viable uses. [Albernaz et al. 2016] The nature of intermolecular interactions of water molecules with atoms has been the subject of a wide series of works, both theoretical and experimental. [Belpassi et al. 2010, Cappelletti et al. 2010, Candori et al. 2008, Cappelletti et al. 2005, Barreto et al. 2012]. Theoretical works were mainly focused on the development of potential energy surface (PES) while a few articles discuss the origin of the interaction. This work shows the complete analysis of the isolated components that contribute in the energetic interaction for H_2O-HX and H_2O-X_2 systems. The structure of this paper is as follows: Below we present details of the metodology used. The results and discussion was in Section 3. This paper ends with the conclusion in Section 4.

2. Metodology

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 these systems study was defined by a spherical-harmonics expansion of the neutral-neutral molecular interaction [Cruz and Barreto], where several local minima were found for all the complexes considered, but we will limit our discussion to the global minimum configurations. Then, we

selected the most stable main configuration, optimized its geometry using the Gaussian code [Frisch et al. 2016] at the MP2/cc-pVDZ level, and the results were interpreted using PSI4 Open Source Quantum Chemistry [Smith et al. 2018] via SAPT (Symmetry Adapted Perturbation Theory)[Jeziorski et al. 1994], expressed as a sum of perturbative corrections, where each correction results from different physical effects, providing the energetic profile of the interaction, such as the contributions Electrostatic, Exchange, Induction and Dispersion, where each of them exists a series of corrections of second and third order. The interaction energy, E_{int}, at second perturbative order used here is

$$E_{int} = E_{elst} + E_{exch} + E_{ind} + E_{(exch-ind)} + E_{disp} + E_{(exch-disp)} + \Delta E_{int} \qquad (1)$$

where ΔE_{int} takes into account the corrections due to third and higher perturbative orders in Potential, E_{elst} is the electrostatic energy, E_{exch} is the exchange energy, E_{ind} and $E_{(exch-ind)}$ are the induction (dispersion) energy and its exchange counterpart, respectively.

3. Results and Discussion

We can verify the optimized geometries of the most stable leading configuration for the H_2O-HX and H_2O-X_2 systems, in Figure 1, and theirs small variations in the values of angles. The total energy, in $[cm^{-1}]$, and the energetic profile for each system, considering the main energy contributions, is shown in the Table 1.

The greatest contribution in the composition of the total interaction energy comes from the electrostatic energy that varies from 60 to 67% in the H_2O-HX systems and from 56 to 57% in the H_2O-X_2 systems, except for the H_2O-H_2 which is 46%. The induction energy contributes from 22 to 25% in the total energy, except for the H_2O-F_2 system that is 16%. The dispersion energy shows a variation of 10 to 17% in the H_2O-HX systems and 20 to 29% in the H_2O-X_2 systems, only H_2O-Br_2 system with 18% of the total energy.

Table 1. The energy profile in $[cm^{-1}]$ for H_2O-HX and H_2O-X_2 systems.

System	Electrostatic	Exchanged	Induction	Dispersion	Total
H_2O-H_2	-211.0242	277.0914	-112.7565	-131.8045	-455.5852
H_2O-HF	-3856.2633	3210.9084	-1303.5965	-612.5943	-5772.4541
H_2O-HCl	-2862.2939	2935.3040	-1019.6831	-689.5836	-4571.5607
H_2O-HBr	-2456.3540	2713.9205	-927.7000	-673.8422	-4057.8963
H_2O-F_2	-526.3606	595.0071	-145.8463	-259.0347	-931.2416
H_2O-Cl_2	-1722.4008	2188.2186	-663.6561	-625.9638	-3012.0206
H_2O-Br_2	-2431.5084	3157.4888	-1065.2892	-751.2772	-4248.0748

4. Conclusion

We know that electrostatic energy is originated from the interaction between the permanent multipole moments, up to quadrupoles, of the two molecules. The induction energy comes from the interaction between permanent multipole moments of a molecule and the induced multipole moments. It is related with the polarizability of each monomers. The dispersion energy is related to the interaction between the instantaneous multipole moments, prompted in the two molecules, instead of the classical description of it. It is related with the ionization potential of each monomers. The systems H_2O-X_2 are expected to have a smaller electrostatic energy than the H_2O-HX, because, as being a apolar-polar molecules only the quadrupole-quadrupole contribution are counted for, while the apolar systems have the dipole-dipole, dipole-quadrupole
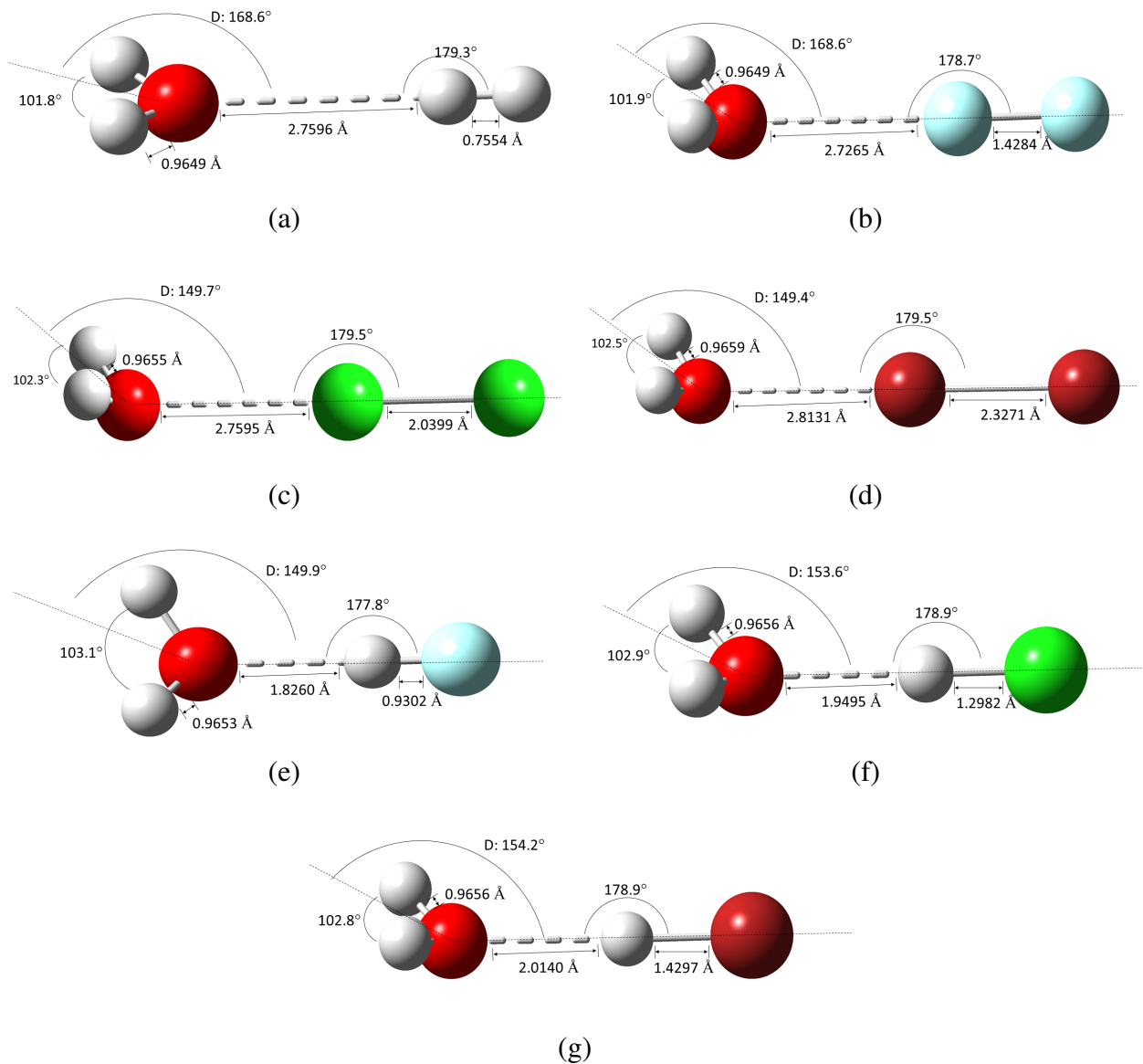
(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 1. The optimized (MP2/cc-pVDZ) most stable leading configuration for the H$_2$O-X$_2$ and H$_2$-HX systems: (a) H$_2$O-H$_2$, (b) H$_2$O-F$_2$, (c) H$_2$O-Cl$_2$, (d) H$_2$O-Br$_2$, (e) H$_2$O-HF, (f) H$_2$O-HCl and (g) H$_2$O-HBr

and quadrupole-quadrupole contribution. The induction energy has a sum polarizability $\times$ multipole ($\alpha_B \times \mu_A$). For the apolar-polar system, only once it is computed, while for the apolar-apolar systems it is counted twice, so the induction energy for the H_2O-HX are higher than for the H_2O-X_2 system. The dispersion energy is related with the ionization potential $\times$ polarizability, as the polarizability of X_2 monomers are higher than the HX monomers, it was found higher dispersion energy for the H_2O-X_2 system.

References

Albernaz, A. F., Aquilanti, V., Barreto, P. R. P., Caglioti, C., Cruz, A. C. P. S., Grossi, G., Lombardi, A., and Palazzetti, F. (2016). *J. Phys. Chem. A*, 120:5315–5324.

Barreto, P. R. P., Albernaz, A. F., Capobianco, A., Palazzetti, F., Lombardi, A., Grossi, G., and Aquilanti, V. (2012). *Comput. Theoret. Chem.*, 990:53–61.

Belpassi, L., Reca, M. L., Tarantelli, F., Roncaratti, L. F., Pirani, F., Cappelletti, D., Faure, A., and Scribano, Y. (2010). *J. Am. Chem. Soc.*, 132:13046.

Candori, P., Cappelletti, D., Falcinelli, S., Pirani, F., Roncaratti, L. F., Tarantelli, F., and Vecchiocattivi, F. (2008). *Phys. Scrr.*, 78:038102.

Cappelletti, D., Aquilanti, V., Cornicchi, E., Teixidor, M., and Pirani, F. (2005). *J. Chem. Phys*, 123:024302.

Cappelletti, D., Candori, P., Roncaratti, L. F., and Pirani, F. (2010). *Mol. Phys.*, 108(10):2179.

Cruz, A. C. P. and Barreto, P. R. P. *Unpublished*.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Jr., J. A. M., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B., and Fox, D. J. (2016). Gaussian 09, revision a.02. In CT, W., editor, *New Trends in Animation and Visualization*.

Jeziorski, B., Moszynski, R., and Szalewicz, K. (1994). *Chem. Rev.*, 94:1887.

Smith, D. G. A., Burns, L. A., Sirianni, D. A., Nascimento, D. R., Kumar, A., James, A. M., Schriber, J. B., Zhang, T., Zhang, B., Abbott, A. S., Berquist, E. J., Lechner, M. H., Cunha, L. A., Heide, A. G., Waldrop, J. M., Takeshita, T. Y., Alenaizan, A., Neuhauser, D., King, R. A., Simmonett, A. C., Turney, J. M., Schaefer, H. F., Evangelista, F. A., III, A. E. D., Crawford, T. D., Patkowski, K., and Sherrill, C. D. (2018). Psi4numpy: An interactive quantum chemistry programming environment for reference implementations and rapid development. *J. Chem. Theory and Comp.*, 14(7):3504–3511.