

Study of the Effect of a Uniform Electric Field on the Bond Lengths and the Electronic Distribution of Diatomic and Polyatomic Molecules

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The study of molecular systems under the experience of an electric field, both theoretically and experimentally consists an important issue in chemistry, physics and biology. Initially, such studies were impelled from the will to gain a deeper insight into the dynamics of chemical reactions through the control of the orientation of the participating molecules. In that framework, recent studies of Shaik et al[1],[2] have revealed that an electric field can affect the energetics of different reaction paths and so to drive a reaction towards the desired products. The authors characteristically mention that an electric field can play the role of a catalyst for a reaction by lowering the activation barriers and in that way control the product formation. Concerning the interest of physics and biology in electric field studies, we report recent investigations on the impact of an electric field on the electronic structure of molecular crystals[3] and the structure of water clusters[4]. For the latter case, it is revealed that an electric field can affect the formation of water assemblies and change their structure from that of a ring to an open water-wire scheme with tremendous biological importance.

Analogous theoretical and experimental efforts from the point of solid state chemistry and physics have opened the way for the design of new materials with potential applications on molecular electronic devices and machines fabrication. Troisi, Ratner, Ho and Donhouser report that the electric field produced by two electrodes can turn the conformation of a molecule which resides between them and by consequence change its molecular conductivity [5]. The understanding of such phenomena holds an important position in the design of molecular junctions and diodes and the rationalization of electron transport processes through them. In the same framework also, it is reported that electric fields can govern the controlled rotation of molecular motors[6].

Furthermore, electric fields are directly related with lasers. Lasers are reported to maintain a substantial role in the attainment of specific molecular excited states[7] with further interesting in the design of quantum computers, an idea which looks becoming reality in the years to come.

Different research groups[8],[9] also bear that strong local electric fields are often present in chemical systems containing ionic and polar entities and as such, it is of great importance to be able to predict their effects on the electronic structure and the geometry of molecular species.

In the present work we examine theoretically the influence of the strength and the direction of a uniform electric field on the bond lengths and the electronic distribution of the molecules HF, HCl, CH₄, SiH₄, H – C ≡ C – H, CH₃Cl, SiH₃Cl, H – C ≡ C – CH₃ and H – C ≡ C – SiH₃. For that reason, we pursue on the geometry optimization of the above molecules (RHF/6-31G*/MP2/6-31G*) in the presence of different strengths and for two different directions of the applied electric field. These optimizations are performed using the GAMESS(US)[10] suit of codes which allows the calculation of molecular wavefunctions under the experience of an electric field.

The electronic distribution of the molecules is expressed by both electrostatic charges of the atoms consisting the molecules and the resonance structures of a chemical bond as they are described in the Valence Bond Theory of Pauling[11]. The weights of the resonance structures of the bonds under study are calculated from the respective molecular orbital (MO) wavefunctions by applying the Polyelectron Population Analysis (PEPA)[12] technique in the basis of the nonorthogonal hybridized natural orbitals (PNHOs)[13]. For the diatomic molecules HF and HCl as well as H – C ≡ C – H, the field is applied along the molecular axis for both directions while for the rest of the molecules the field is applied on the C₃ symmetry axis, again for both directions. From the correlation of the results it is revealed that for a typical simple bond, the application of a Favorable electric field, as it is determined from the main ionic structure of the bond, leads to an increase in the difference of the weights of the two ionic structures of the bond in comparison with the existing difference in the absence of the field and to an increase of the bond length as well. The application of an Unfavorable electric field, in contrast, seems to decrease both the difference between the weights of the two ionic structures and the length of the bond, with a potent existence of a minimum for the later. The only exception in the above generality consists the C_{sp3} – H bond which follows the aforementioned concerning the influence of the field on the weights of the ionic structures but presents a decrease in the bond length until 0.02 a.u. (1 a.u. = 5.1423e11 V/m) strength of a Favorable electric field while an Unfavorable electric field provokes a continuous increase on it. For the triple bonds, it is revealed that the C ≡ C bond of propine seems to follow the behavior of the simple bonds for both its

ionic structures and bond length. The corresponding bonds of acetylene and silyloacetylene are characterized by a continuous increase in both their length and weight-difference of the ionic structures of their π -components under the influence of an electric field. This is predictable for the centrosymmetric bond $C \equiv C$ of acetylene but not for the triple bond of silyloacetylene.

We also pursue in the investigation of the effects of an applied electric field on the hyperconjugation phenomenon, as it emerges in the molecules studied here. As our scope is to examine if and in which extent, the different delocalization effects appearing into the selected molecules can be controlled by an electric field, we estimate, using the NBO program[14], the delocalization energies $E^{(2)}$ and the weights of well selected localized electronic distributions which describe the electron transport from one region of the molecule to another, as they are determined by the corresponding NBOs of the main Lewis structure, under the experience of different strengths and two directions of an electric field. Precisely, the description of the electron delocalization in the frame of resonance theory includes the calculation of the weights of localized wavefunctions – electronic distributions which are represented by localized Slater determinants. Such wavefunctions may be achieved from the usual MO-wavefunctions through Moffitt's theorem[15] and can comprise any type of orbitals which can be written as a linear combination of the basis functions. In our case, we use the NBOs[13b] of the main Lewis structure and the estimation of the weights of this kind of determinants rests on the PEPA methodology which uses both Moffitt's theorem and the second quantization formalism to introduce conditions for electron holes. The results reveal that both the strength and the direction of the applied field can be used in the control of the electronic delocalization from one region of a molecule to another. Important is also the fact that while for the silyloacetylene molecule in the absence of a field, there is not any type of delocalization involving the Si – H bonds and the π -system of the triple bond, the application of a field can activate that hyperconjugation phenomenon in both directions.

Finally, in the framework of the new branch of Molecular Electronics and based on our conclusions concerning the impact of a field on the hyperconjugation phenomenon, we propose two molecular systems which, under the influence of an electric field can act as molecular logic gates.

- [1] Sason Shaik, Sam P. de Visser and Devesh Kumar, *J. Am. Chem. Soc.* 2004, 126, 11746 - 11479
- [2] Hajime Hirao, Hui Chen, Maria Angels Carvajal, Yong Wang and Sason Shaik, *J. Am. Chem. Soc.* 2008, 130, 3319 – 3327
- [3] Jaroslav Tóbkik, Andrea Dal Corso, Sandro Scandolo, Erio Tosatti, *Surface Science* 566 – 568 (2004) 644 - 649
- [4] Young Cheol Choi, Chaeho Pak and Kwang S. Kim, *J. Chem. Phys.* 124 094308 (2006)
- [5] Alessandro Troisi and Mark A. Ratner, *J. Am. Chem. Soc.* 2002, 124, 14528 – 14529 and references cited therein
- [6] a) Gwénaél Rapenne, *Org. Biomol. Chem.*, 2005, 3, 1165 – 1169; b) Alexandre Carella, Gwénaél Rapenne and Jean-Pierre Launay, *New J. Chem.*, 2005, 29, 288 – 290
- [7] Sitansh Sharma, Purshotam Sharma and Harjinder Singh, *J. Chem. Sci.* 119, 2007, 433 – 440 and references cited therein
- [8] Kersti Hermansson and Harald Tepper, *Mol. Phys.* 1996, 89, 1291 – 1299
- [9] a) Hiroshi Nakatsuji, Toshiaki Hayakawa and Teiji Yonezawa, *J. Am. Chem. Soc.* 1981, 103, 7426 – 7432; b) Yasushi Honda, Hiroshi Nakatsuji, *Chemical Physics Letters* 293 (1998) 230 – 238
- [10] Michael W. Schmidt, Kim K. Baldridge, Jerry A. Boatz, Steven T. Elbert, Mark S. Gordon, Jan H. Jensen, Shiro Koseki, Nikita Matsunaga, Kiet A. Nguyen, Shyjun Su, Theresa L. Windus, Michel Dupuis and John A. Montgomery, Jr., *J. Comput. Chem.* 14, 1347 – 1363, 1993
- [11] a) Philippe Hiberty, Sason Shaik, *J. Comput. Chem.* 28, 137 – 151, 2007; b) Gjergji Sini, Philippe Maitre, Philippe Hiberty and Sason Shaik, *J. Mol. Struct. (THEOCHEM)*, 229, 163 – 188 (1991)
- [12] Ramón M. Parrondo, Padeleimon Karafiloglou, Enrique Sánchez Marcos, *Int. J. Quantum Chem.* 52, 1127–1144 (1994)
- [13] a) J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.* 1980, 102, 7211 – 7218; b) Alan E. Reed, Larry A. Curtiss, Frank Weinhold, *Chem. Rev.* 1988, 88, 899 – 926
- [14] NBO 5.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales and F. Weinhold, *Theoretical Chemistry, Institute, University of Wisconsin, Madison* (2001)
- [15] a) Moffitt, W. *Proc R Soc* 1953, A218, 486; b) Karafiloglou P., Ohanessian, G. *J Chem Ed* 1991, 68, 583