

Editorial

Special Issue on Proton Transfer Processes

Henryk Chojnacki

Institute of Physical and Theoretical Chemistry, Laboratory of Quantum Chemistry, I-30, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland
E-mail: chojnacki@kchf.ch.pwr.wroc.pl

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It is well established that the hydrogen bond plays crucial role in many areas of physical, chemical and biological phenomena. The relevant proton transfer reactions are the simplest but very important in many chemical problems as well as in some biological processes. It appears that the low-barrier hydrogen bond (LBHB) for this displacement may play fundamental role in stabilizing intermediates in enzymatic reactions and in energy lowering of transition states (Cleland, D.; Kreevoy M.W. *Science* **1994**, *264*, 1887-1890). There is considerable evidence that a LBHB may be important in the reaction catalyzed by Δ^5 -3-ketosteroid isomerase (Warshel, A.; Papazyan, A. *Science* **1995**, *269*, 102-103). Recent computational and gas phase experimental studies (Garcia-Viloca, M.; Gonzales-Lafont, M.; Lluch, J.M. *J. Am. Chem. Soc.* **1997**, *119*, 1081-1086) have shown that LBHB can exist in the gas phase systems as well. The implications of isotope effects have also been studied for structures containing low-barrier hydrogen bonds (Huskey, W.P. *J. Am. Chem. Soc.* **1996**, *118*, 1663-1668). On the other hand, the multiple proton transfer seems to play an important role in quantum chemical interpretation at molecular level of some biological processes like heredity, mutations, aging and cancerogenic action (Löwdin, P.O. *Adv. Quantum Chem.* **1965**, *2*, 213-360, T. Bountis (Ed.), Proton Transfer in Hydrogen-Bonded Systems, NATO ASI Series B, Physics, Vol. 291, Plenum Press, New York and London, 1992). Closely related to these problems is the contribution of high-level quantum-chemical and quantum dynamics calculations of the tautomerization equilibria and rate constants of isolated and monohydrated cytosine and guanine molecules (Y. Podolyan, L. Gorb and J. Leszczynski).

The potential barrier for the double proton transfer has been evaluated and discussed for the benzoic acid dimer (M.J. Wójcik, K. Szczeponek, M. Boczar). It was found that the energy barrier for the proton tunneling amounts to 6.5 kcal/mole. The normal mode frequencies have been computed

including modes coupled to the proton tunneling mode. The two-dimensional model PES predicts monotonic increase of the tunneling splitting with the excitation of the planar modes.

The specific features of the intramolecular proton transfer reactions have been considered in the case of Schiff bases (A. Koll). It was pointed out that the tautomeric forms being in equilibrium in Mannich and Schiff bases are essentially different. Despite of the opinion that the proton transfer forms in systems with internal π -electron coupling are mainly keto forms it was shown that in Schiff bases the content of keto structures is slightly less than zwitterionic one.

The importance of the proton transfer within the quantum-mechanical tunneling model has been pointed out within the model first-principle calculations of ammonia dissociation on the Si (100) surface (K. Z. Smedarchina and M.Z. Zgierski). This process was investigated by means of the density functional and approximate instanton methods. It was demonstrated that, even at room temperatures, the dissociation process of ammonia is dominated by tunneling mechanism.

Some aspects of the excited state proton transfer have been studied for carbazole (N. Chattopadhyay) giving rise to the dual fluorescence from the two prototropic species. It was found that the relative intensity of the two emissions is sensitive not only to the pH of the medium but also to the microenvironment around the probe.

It seems that the electron density distribution within the hydrogen bond atoms is of essential importance for considerations of the proton transfer reactions. However, the systematic studies of this property are rather scarce in the present literature. Although theoretical studies are numerous, most of them are concentrated on the ground state properties. On the other hand, mainly Mulliken population analysis is usually performed and no comparison with other methods was done so far. It seems that at least in some cases, in excited states the hydrogen atom transfer within the hydrogen bond might be responsible for the tautomeric interconversion reactions (H. Chojnacki).

In general the problem of the proton transfer is as important as complicated and far from the solution and completion. Our papers only touch this problem and point out on its importance in various fields of contemporary science. On the other hand, recent important progress in the development of new theoretical methods and the advent of larger and more powerful computers should enable its application to more complicated systems and the resulting errors for theoretical results should be essentially reduced (Del Bene, J.E.; and Jordan M.J.T. *Theochem* **2001**, 573, 11-23).