

## A. Objectives of the project

Properties of chemical compounds, including these in common use as medicines, materials, dyes, plastics etc., result from the chemical structure of a given molecule. The structure-property relationship is not straightforward, and its study is a core part of many branches of natural sciences. The visible outcomes of such studies are, for example, new materials and medicines designed by molecular modeling. One of successful applications of this approach is Captopril, a vasodilator used in hypertension, heart and kidney disorders. Another example is modeling of complex structures: formation of crystals from single molecules, behavior of molecules on metal surfaces, or the folding of amino acid chain to its final form – a tertiary structure of a protein with a well-defined role in the organism. These successes of science lead us to believe that a combination of the development of computational chemistry, increase in the power of High-Performance Computers (HPC) and creativeness of the scientists will bring us a new, broader view of the processes at the molecular level. The current project is a comprehensive proposal to develop and test a new methodology to describe selected one-, two- and three-ring aromatic compounds with hydrogen bonds. The direct scientific objective of the proposal is development of a methodology to describe influence of nuclear quantum effects on the molecular properties in excited states, and further use of this and other methods to obtain a detailed description of the molecular properties of a coherent set of molecules with two or three fused aromatic rings. The molecules selected for the study comprise: (i) one- and two-ring derivatives with intramolecular hydrogen bonds exhibiting interesting bridge proton dynamics (e.g. hydroxyquinones and N-oxides), (ii) two-ring derivatives with hydrogen bonds, including „proton sponges”, the molecules of exceptionally high proton affinity, „scavenging” the H<sup>+</sup> ions from the environment, (iii) three-ring derivatives mostly, but not only, with hydrogen bond, e.g. phenantrolines and benzo[h]quinolines, including compounds of potential practical use: dyes, luminophores for the OLED diodes etc. If we find it necessary, the study of the core set of the chosen compounds will be extended by further studies on analogous structures, selected so that the additional results will help form most general conclusions, useful in the design of new compounds of potential practical use in materials chemistry and biomedical chemistry. The analogs will be proposed on the basis of the established rules of physical organic chemistry concerning the substituent influence on the molecular properties, e.g. inductive, resonance and steric effects (described quantitatively by special parameters, e.g. Hammett or Taft constants). The studied molecules are aromatic compounds – a class of systems whose main feature is delocalization of the  $\pi$ -type electrons in the ring(s), according to the Hückel's rule. The study of the aromaticity of these systems according to diverse criteria (structural indices – e.g. Harmonic Oscillator Model of Aromaticity (HOMA), electronic indices – e.g. Nucleus Independent Chemical Shift (NICS) or electron delocalization indices of the *Atoms in Molecules* theory) is a partial objective of the project. An important scientific objective is an investigation of the dynamical nature of the systems in a picosecond timescale with the help of *ab initio* molecular dynamics based on quantum mechanics. Trajectories („life stories” of a molecule) will allow us to determine how a given molecule behaves in a ground state as well as in the excited states, resulting from absorption of light (a photon) by the system. Another scientific objective is finding how the state of matter and molecular environment influence the properties of a molecule. Thus, this objective requires us to carry out simulations in the gas phase (isolated molecule), in solution and in the solid state.

## B. Basic research to be carried out

The studies on the core set of molecules described above will be carried out in the electronic ground state and excited states, with the use of established static methods and *ab initio* molecular dynamics – two groups of computational chemistry methods that provide complementary routes to the description of phenomena at the molecular level. The studies will be enriched by an element of development: formulation of a method to describe quantum effects for selected molecular vibrations in the excited electronic state. Further, attention will be paid to the application of already known, but rather new computational methods, such as e.g. metadynamics, quantization of nuclear motions (PIMD, *snapshot-envelope* method), excited state dynamics (*surface hopping* and TDDFT-BOMD), which will provide us with more accurate description of metric, spectroscopic and energetic parameters. The proton transfer phenomenon will be analyzed together with its consequences at the molecular level, especially excited-state induced proton transfer (ESIPT). We will also study photodynamics of the systems – the evolution of metric parameters upon electronic excitation.

The quantum-chemical calculations will be divided into several stages. Stage 1 is devoted to test the computational protocols and develop a method to describe an influence of nuclear quantum effects on the molecular properties in the excited states – an extension of the *snapshot-envelope* method, which was developed by a team including the proposal authors. The development phase of this stage will use several selected molecules, “standards”, simpler in the structure than other systems of the core set – these molecules are known to the authors from the previous studies. Stage 2 is a description of metric and energetic parameters as well as the electronic structure on the basis of static methods. Stage 3 comprises application of the (*ab initio*) molecular dynamics in various formulations. The latter two stages will be based on the whole “core set” of selected molecules.

The static quantum-chemical description of the metric parameters and electronic structure in the ground state will be based on *post-Hartree-Fock* correlation methods, i.e. MP2 and a very accurate, but extremely demanding computationally, CCSD(T) method as a reference; further, we will use the density functional theory (DFT) in its standard version and with dispersion corrections. The excited state calculations will be based on CC2 and TDDFT approaches. The molecular topology and electronic structure will be analyzed in the framework of the *Atoms in Molecules* (AIM) and *Natural Bond Orbitals* (NBO) theories. The *ab initio* molecular dynamics schemes (CPMD, BOMD) will allow for accurate analysis of the metric parameters, electronic structure (Wannier orbitals) and spectroscopic signatures in the ground state. Path integral molecular dynamics (PIMD) will be used for quantization of nuclear motions. The *snapshot-envelope* scheme, based on the *ab initio* molecular dynamics trajectory, will be used to describe quantum effects in a selected vibrational mode and to calculate the potential of mean force (Pmf) corresponding to the free energy, whereas metadynamics will allow us to sample efficiently the phase space of the systems. An exploration of the free energy surface by the *snapshot-envelope* method and metadynamics will allow us to construct two-dimensional energy surfaces (2D Pmf) incorporating the presence of local minima and conformational flexibility of the molecules. The dynamical properties in the excited state will be analyzed by *surface hopping*, TDDFT-BOMD and the *novel method developed in the framework of this project*.

## C. Reasons for choosing the research topic

Our scientific interests have been for several years focused on the molecules that, apart from such prominent features as the

presence of fused rings and intramolecular hydrogen bonds, possess easily modulated proton position in the hydrogen bridge and photoactivity. These features designate the studied systems as basic building blocks of complex systems used as „molecular devices” of potential broad application in medicine as well as materials chemistry. Therefore the results of the current project will form new tools for further computational studies of the photodynamics of complex molecular systems, including dyes, light-activated switches, compounds for the photodynamic therapies. Apart from this reason, the authors are also motivated by scientific curiosity of the topic of unexplored properties of aromatic polycyclic compounds (the very notion of aromaticity is still a matter of scientific debate). On the other hand, hydrogen bonding is a major driving force in formation of most molecular crystals, and only recently has started to be rationally used by scientists to design self-organizing structures. The studied molecules allow us to register the whole gamut of interactions, from strong hydrogen bonds to weak dispersion forces, and all of them influence the stability of the structures (motifs) formed in the molecular crystals. Finally it is worthwhile to mention the „workshop” motivation: testing and broadening the limits of accuracy and credibility of the applied methods and procedures is an indispensable element of the scientist's work, especially when – as in the case of the current project – one of the objectives is a formulation of suitable algorithms constituting a new research methodology (the description of nuclear quantum effects in the electronic excited state of the studied molecule).